Cranfield University

Professor Simon J. T. Pollard

PhD, FRSC CChem, FCIWEM CWEM, FHEA, MCIWM, SiLC

CONTRIBUTIONS TO RESOURCE AND ENVIRONMENTAL RISK MANAGEMENT

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ABSTRACT

This thesis charts a research journey through the disciplines of waste chemistry, environmental risk assessment, policy analysis and corporate risk governance since award of the candidate's PhD in 1990. The insights gained present a distinctive perspective on resource and environmental risk management - assessments of risk must reflect our understanding of the science and evidence that supports them; and the protection of public and environmental health, as an overarching motive, requires greater prominence if the confidence of citizens in the Government and industry handling of risk is to be secured.

Waste management *is* risk management and without an understanding of the fundamental science and engineering of wastes and how they behave in the environment, process technologies for their treatment can not be optimised, nor regulatory oversight designed properly to protect public health and the environment. The candidate's research on the chemical characterisation of complex wastes and their interaction with soils, waters and air, offers a more optimistic assessment of these risks, at least within developed nations. This said, technical assessments of risk are insufficient, in isolation, to secure the confidence of communities, investors, or the wider citizenry. The motives and values of process operators and regulators that oversee operations are as critical as technical demonstrations of environmental safety. The recent contributions in this thesis examine organisational competencies in *preventative* risk management, specifically within the water sector as it responds to international calls for improved risk governance.

In concert, the candidate's contributions and practical achievements in resource and environmental risk management reported here represent a unique and substantive body of problem-oriented research, directed at reconciling societal unease about waste with our responsibilities for its safe management. Significant insights are made on the reuse of hazardous and carbonaceous wastes, on the characterisation, fate and transport of hydrocarbons in the environment, on the practice of environmental risk assessment and the organisational competencies required to manage risk to the levels of stakeholder confidence expected in the 21st century.

DECLARATION

No part of the published or unpublished work has been presented, or is being submitted, for any other degree or other academic or professional distinction by the candidate at Cranfield or any other University. This thesis has been prepared in accordance with Regulations of Cranfield University (40.1 – 40.9 and 35.4, as amended). The general approach within the body of research presented is that the candidate was the originator of the contribution; identifying the research problem and designing the investigations, with the detailed analysis, modelling and experimental work being performed with co-investigators. Synthesis and interpretation of the research results was undertaken jointly. In the large majority of cases, these publications were edited and communicated by the candidate to the research journals.



Prof. Simon Pollard, Head of Department, Sustainable Systems
School of Applied Sciences, Cranfield University, UK
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Most of the papers presented here are jointly authored, being the result of close collaborations in a multidiscipline field. I wish to express my sincere gratitude to my various co-authors over the years, including the postgraduate students, postdoctoral fellows and colleagues who I have worked with since 1991. My thanks go to (in alphabetical order):

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SUMMARY

This thesis comprises an examinable selection of eighty academic papers and eighteen additional scientific contributions from the candidate's career, conducted since completion of his PhD in 1990. The research presented has been performed by the candidate and various co-workers in the field of applied environmental science, with an emphasis on resource and environmental risk management. The publications are presented in six main sections. For each, a discussion of the distinctive contribution, its context and significance is offered. Further, in accord with University Regulations, section 7 includes an additional selection of scientific reports, guidance documents and expert judgement providing evidence of further practical achievements over and above the academic core of the thesis.

This body of papers and achievements addresses two research ambitions: one, an attempt to bring a scientific robustness to the waste and resource management agenda, through the examination and exploitation of waste chemistry; the other, a critique of environmental risk management, risk policy and risk governance. The latter, has particular significance in light of the current desire to compare risks across the environmental policy agenda to inform policy priorities and the proportionate expenditure of public funds on managing environmental risks. The themes are exemplified through a body of contributions on the assessment and management of hydrocarbon-contaminated soils. Here, the desire has been to improve analytical techniques, modelling approaches and waste characterisation to allow a more representative and evaluation of exposures to hazardous constituents in these wastes.

The regulation of risks from contaminated land and other environmental hazards leads to latter contributions on environmental decision-making in general, better regulation and risk policy. Finally, the recent work considers the organisational governance of risk within the water utility sector, reflecting one sector's attempts to embed a preventative risk management culture under a modern regulatory philosophy of risk-based regulation.

GLOSSARY

AD	Anaerobic digestion
APC	Air pollution control
ASTM	American Society for testing and materials
BNFL	British Nuclear Fuels Limited
BBSRC	Biotechnology and Biological Sciences Research Council
BSE	Bovine spongiform encephalopathy
Defra	Department for Environment, Food and Rural Affairs
DTi	Department of Trade and Industry, that was
EC	European Commission
EPSRC	Engineering and Physical Sciences Research Council
FMD	Foot and mouth disease
IWA	International Water Association
NERC	Natural Environment Research Council
ODA	Overseas Development Agency, that was
OECD	Organisation for Economic Co-operation and Development
OPC	Ordinary Portland cement
PAH	Polynuclear aromatic hydrocarbons
PFA	Pulverised fuel ash
PROMISE	Optimising biopile processes for weathered hydrocarbons within a risk management framework, project acronym
QRA	Quantitative risk assessment
REACH	Registration, evaluation, authorisation and restriction of chemicals
RBCA	Risk-based corrective action
SNIFFER	Scotland and Northern Ireland Forum for Environmental Research
S/S	Solidification/stabilisation
TIE	Toxicity identification and evaluation
TPH	Total petroleum hydrocarbons
UNECE	United Nations Economic Commission for Europe
WEEE	Waste electrical and electronic equipment
WRAP	Waste and resources action programme

PUBLISHED WORK AND PRACTICAL ACHIEVEMENTS

This chapter provides an exposition of the candidate's published work and practical achievements, and a discussion of their value and significance. Copies of the examinable papers and contributions are presented in tagged sections behind this chapter, which offers a synthesis of the contribution. Throughout, superscripts in the text refer to contributions from the candidate's published research, including the examinable material listed in the References section starting on p 27. The full listing of career communications (1990-2009[1-342]) is presented in the Appendix, forming the bibliography to which the superscripts refer.

Section 1 Overall value and significance of contribution

Four papers[38, 43, 74, 77] are presented here. They represent significant contributions to the development of an environmental risk assessment capability within Government in the UK from 1998 onwards, in which the candidate was instrumental, and subsequent development of a comparative risk assessment methodology for diverse environmental risks. The *Environmental Science and Technology* paper[38] was the first (2002) academic exposition of the development and direction of environmental risk assessment in UK Government, and describes the Environment Agency's response to its new powers under the Environmental Act, 1995, and subsequent developments in risk-based regulation, specifically on role of operator pollution risk appraisal (OPRA).

The *Risk Analysis* paper[43] describes a methodology, developed between 1999 and 2004, that has informed State of the Environment Reporting (2000) in England and Wales[90, 95, 98, 180, 186, 202] and since been the basis of the Environment Agency's forward research on comparative risk assessment. Adapted versions of the approach are expected to see use in strategic risk appraisals of Defra's policy priorities through the work programme of the newly-established Research Councils/Defra collaborative centre of excellence in understanding and managing natural and environmental risks at Cranfield University for which the candidate is the Centre Director.

The *Chemosphere* paper[74] adopts, uniquely, a fugacity approach to estimating exposures from biopiled hydrocarbons, and infers a very low availability for risk-critical compounds released during the bioremediation of hydrocarbon-contaminated soils. The research illustrates the critical role of oil-phase partitioning within

contaminated soil systems, a role to date ignored by regulatory exposure assessment methodologies and conventional contaminated land risk assessments.

The *Environment International* paper[77] by MacGillivray and Pollard (2008) presents the conclusions of the candidate's benchmarking of risk management capabilities in the international water utility sector[123, 129, 130, 140, 314, 318, 335, 339]. Building on related papers[42, 52, 58, 59], it identifies where future attention should be paid within the water utility sector on issues of risk governance; here especially for those water suppliers at low levels of risk management maturity (Pollard, S.J.T., Bradshaw R.A. *et al.*, 2009, *in press*). The paper modifies a previously published benchmarking tool[67, 123], and is now seeing application in the context of an international study on advocacy for safe drinking water among water utility leaders, funded by the International Water Association (IWA) at Cranfield University and directed by the applicant.

Section 2 Waste minimisation and resource management

The earlier research (1987-1990) performed by the candidate[1-3, 142, 166, 256] deals with a well-recognised problem of the time - the management of a self-combusting 'special waste' from the edible oil industry; spent bleaching earth. Looking forward to the eventual ban of such hazardous wastes from landfill, the first three papers in this section[5, 6, 11] build on the candidate's PhD[142] and consider the reuse of spent bleaching earth as a low-cost adsorbent; prepared through the controlled pyrolysis and activation of residual oil on the interlamellar montmorillonite surface of spent Fuller's earth. The metrology and characterisation of micropore size distributions and pore volumes in these low-cost carbons[6] is supported by evaluations of surface-specific adsorptive capacities for different reuse applications; in water and wastewater treatment (phenol removal) and the cleansing of edible oils (PAH removal from coconut oil[11]).

Building on an exhaustive review of low cost carbons for water and wastewater treatment in middle income and less-developed counties[5], the next five contributions[20, 21, 27, 30, 31] stem from Overseas Development Administration (ODA, now the Department for International Development) funded research on low-cost carbons prepared from the waste seed husks of *Moringa oleifera*, a decorative plant used widely in Africa and India, the seed extract from which has water coagulant properties. Evaluations of micropore volumes for *Moringa* carbons[31] and comparisons with

commercial analogues proved them highly competitive and capable of, for example, the uptake of considerable quantities of *Microcystin*-LR toxin from algal blooms[30], a common feature of Lake Victoria, Milawi. Working closely with the local water supplier in Blantyre, Milawi[87-88], the candidate developed a single stage steam pyrolysis activation procedure[21] for these carbons that could be implemented with ease using locally-sourced activation process plant[88].

Mixed inorganic-organic wastes from electroplating processes, for example, continue to be problematic for waste producers and demand specialist treatment. One technology, cement-based solidification/stabilisation (S/S) has seen wide application in the US for nuclear and inorganic waste streams with small (2-5 $\%^{w}/_{w}$) contributions of organic contaminant (oil, solvent) load. The technology has had a controversial operating history in the UK, but a number of high profile process failures involving incomplete set of the ordinary Portland cement (OPC) in the process mix resulted in low regulatory confidence in this technology for 20 years. In these three papers[4, 16, 24], the candidate and co-authors review the process science of S/S waste technology, the microstructural interference effects of organic contaminants on cement set, and illustrate successful S/S application for flue gas desulphurisation wastes, processed using ordinary Portland cement (OPC) and pulverised fuel ash (PFA). The papers provide S/S operating thresholds for the organic content of mixed wastes, and demonstrate a valid application of this technology for a problematic high volume waste produced from coal-fired power stations[16]. Notwithstanding a substantive research effort into these wastes over the last 20 years, the technology remains controversial in the UK. Latter attempts to present the technology as a risk management solution for problematic wastes[284, 291] have proved difficult, on account of the increased volume of the stabilised matrix and the dramatically reduced availability of hazardous waste landfill capacity in the UK.

The remaining nine papers in this section[13, 40, 46, 54, 62, 63, 68, 70, 71] represent similar examinations of the process science and technology that underpin a suite of waste treatment technologies. The waste sector has not always been forthcoming in researching the chemical, biological and engineering basis for its chosen technologies, many of which have emerged from mining and agricultural engineering practices rather than the research pilot hall (Velis *et al.*, 2009a, b, *in press*). These contributions

include a critical review of constraints on the efficiency of bioremediation[13], published at a time (mid 1990s) when unsubstantiated claims were being made among technology vendors of the capabilities of low cost bioremediation to treat hydrocarbon-contaminated soils. A further two manuscripts describe the progression toward sustainable landfill in a post Landfill Directive (1999/31/EC) policy environment[62-63].

The later contributions in this section develop a 'new waste technology' theme, being concerned with bioaersosol exposures from green waste composting sites[70], the effectiveness of the Waste Electrical and Electronic Equipment (WEEE) Directives (2002/96/EC and 2003/108/EC) to influence sustainable product design[54], market stimulation for household waste segregation[68] and resource flows within the UK economy[71]. Collectively, the candidate has been concerned here with policy appraisal, regulatory effectiveness and the market response to the new waste agenda[163]. In a policy environment aspiring to be less reliant on landfill, new hazards are generated from technologies process biological waste that require regulatory oversight if community and investor confidence in these technologies is to be secured. A particularly fruitful research thread in this regard has been the evaluation of bioaerosol exposures released from green waste composting facilities[70]. Providing a characterisation of the source term for bioaerosol hazards has proven central to their effective and proportionate regulation in the face of a rapidly expanding market for compost technology, in line with the ambitions of the Government's and devolved administrations' waste strategies. Research performed under this theme[69-70, 111, 117, 122, 127, 132, 134, 208, 221] has led to the drafting of guidance to waste operators on bioaerosol risk assessment requirements (currently underway).

Section 3 Analysis of complex environmental media

A consistent feature of environmental regulation in the 1990s was the promotion of risk-based 'Superfund' clean-ups in the United States, and the growing application of environmental risk assessments to guide contaminated site assessment and remediation. Notwithstanding the advances in analytical, and especially chromatographic science since the late 1960s, for petroleum- and creosote-contaminated sites which featured highly among cleanups in North America, the wide use of the surrogate 'oil and grease' parameter to infer contaminant load was a fundamental constraint on meaningful site evaluation. This series of papers[7, 14, 41, 28,

[15, 19, 23, 12, 8, 22, 26, 37, 50, 47, 69, 55, 76, 78] develops improved analytical methods, protocols and strategies for heavy oil and creosote residues, initially for contaminated sites in Alberta, Canada[7, 14, 41], and then more broadly[15, 19, 23]. Seeking to reveal the complexities of the weathered contaminated oil-soil matrix and improve remediation strategies, the research describes chromatographic[7, 15], mass spectroscopic[41, 12] and isotopic[23] analyses to characterise the extent of weathering, range of substituted polynuclear aromatic hydrocarbons, and the varying polarity and toxicity of components in these complex matrices. Funded by the provincial regulator, Alberta Environment[169-171], this research informed the prioritisation of Alberta's contaminated sites programme and the identification of candidate sites for detailed investigation, full risk assessment and ultimately remediation.

The fugacity approach to environmental fate and transport has had a marked influence on the development of these papers and those in the section that follow. The fundamental physicochemical properties of chemicals determine, in large part, where one can expect to find them in the multimedia environment, which analytical techniques are appropriate for their analysis, which exposure pathways will be significant for human and ecological receptors, and which media – waste[74], soil residues[22], leachate[45], off-gas[56] – should be a priority for treatment to reduce exposures and thus risk[60]. Central to these assessments is the characterisation of the waste, or 'source (of the hazard) term'. Research presented in these papers was directed towards understanding the complex composition of hydrocarbon waste residues isolated from wood-preserving waste sites and former petroleum battery sites in urban and rural Alberta, Canada[7,14, 41]. As for those papers above, without an informed analysis of the composition and fate of oils and their constituents at these sites, regulators may be drawn to cost-inefficient solutions. This work assisted directly in the prioritisation of Alberta's bioremediation programme[169].

Using a range of automated thin-layer chromatography[7, 82] and nitrous oxide chemical ionisation (soft) mass spectroscopy[41], the candidate and co-workers developed a toxicity identification and evaluation (TIE) protocol[28] for component classes in these oils, and revealed their substituted polyaromatic and polyalicyclic composition of these residues[41, 170]. The insights gained through detailed chemical examination prove to be at odds with the rudimentary chemical data used in the risk

assessments of environmental consultants at the time, which adopted single target species within coal tar creosote and petroleum, or worse, inferred their concentration from estimates of 'oil and grease' load[19]. A critical failing in the quantitative risk assessments was an absence of any recognition of where indicator (risk-critical) compounds resided at these sites – that is, within the oil matrix (the source term). In Superfund risk assessments, the assumption of human exposure to individual labile polynuclear aromatic hydrocarbon (PAH) molecules and with complete bioavailability was the norm. In contrast, the candidate's original research[41, 170] demonstrates a family of PAH and substituted analogues *comprising* the waste oil matrix, and ultimately co-solved in one another; the waste oil acting as a powerful partition medium for hydrophobic risk-critical contaminants[74], much more so even than soil organic matter. This proves pivotal to assessments of exposure because it means contaminants in these matrices are not free to transport within the environment unless accompanied by the source term itself and far from bioavailable. Revised analytical protocols using a tiered suite of analytical tools[14, 83], were recommended and the above rationale on the limited availability of PAH in waste oils applied to limit the remediation of Albertan contaminated sites to those posing greater risks.

The middle series of papers in this section[15, 19, 22, 26], co-authored with Dr Martin Whittaker, extend these studies back in the UK using North Sea crude oils. Researchers (*e.g.* Westlake and others working at the University of Alberta) in the mid 1970s demonstrated the changing chemical composition of crude oils subject to biotic and abiotic weathering and described an increasingly condensed polyaromatic structure that develops as the oil becomes more asphaltenic over time. With most hydrocarbon residues having been subject to decades of biotransformation and physical weathering at industrial sites since their original deposition to site soils, the residual oil at these sites offers an even stronger partition medium for risk critical compounds than that for freshly deposited oil. The candidate's evaluations of so-called 'refractory' (resistant to biotransformation) oils in hydrocarbon-contaminated soils[15, 23, 56, 223, 237, 238, 264] provide novel insights into the extent and nature of weathering and allowed the development of new indices[26] capable of distinguishing between oils that have experienced biotransformation and those that have not. Ultimately, this collective body of work reported in this section led to the candidate drafting the national

consultation[109, 193] and regulatory guidance[200] on the assessment of risks from hydrocarbon-contaminated soils for the Environment Agency of England and Wales, and it set the theoretical groundwork for a £1m industrial research consortium 'PROMISE'[115, 139, 313, 324] (Bioremediation-LINK funded project BIOREM_35 on optimising the biopiling of petroleum hydrocarbons within a risk management framework) addressing the risk-based bioremediation of weathered hydrocarbon wastes (2004-2008). Analytical techniques developed under this programme[78] are now set for inclusion in the UK Standing Committee of Analysts' 'blue book' of accredited analytical methods, here for petroleum hydrocarbons.

In the same way that the uptake of bioremediation technology in the US led to a wide range of new entrant technology providers during the 1990s, the rapid expansion of large scale composting in the UK has generated a concern over operator competencies and the proportionate regulation of on-farm and industrial scale compost technology. Specifically, the generation of peak releases of bioaerosols during waste shredding and windrow turning has stimulated community concerns about the environmental safety of these processes. Seeking to reassure the public, the Environment Agency (2002) issued guidance on the health risks from composting and established a 250m 'cordon' between compost plants and sensitive receptors (largely housing). Facilities planned, or operating closer than this to sensitive receptors, are subject to a quantitative assessment of bioaerosol exposure. Though effective in promoting a culture of operational risk assessment within a growing sector, this policy was, at the time, without any underpinning understanding of source term releases of actinomycetes and *Aspergillus fumigatus*, two of the key bioaerosol constituents of concern (Drew *et al.*, 2009, *in press*). The papers in this section[50, 47, 69] with Dr Mohamad Pauze Taha and Dr Gillian Drew, including the invited submission[47] to *Waste Management*, provide original contributions for a reappraisal of the 250m-rule in light of new insights into bioaerosol loads generated during compost processing. They quantify, for the first time, the relative contributions to total site load of waste shredding, windrow turning and fugitive releases at authentic compost facilities, and they have allowed revised regulatory advice to compost operators on the management of on-site exposures to workers and off-site publics[208, 221, 288, 315]. This research resulted in a collaborative NERC grant between the candidate and Cranfield

researchers with colleagues at the University of the West of England exploring bioaerosol fate and transport, post-release, with a view to generating reliable exposures and risk estimates.

Section 4 Fate and behaviour of hydrocarbons in the multimedia environment

Six submissions[25, 33, 34, 148. 161, 56] appear in this section, including two invited papers[148, 161]. Coincident with the analytical investigations above, is a stream of research on the environmental fate and partitioning of risk critical compounds[25, 56] within hydrocarbon waste matrices. The papers here represent attempts to quantify the multiphase partitioning of compounds in hydrocarbon-contaminated soil environments, together with a similar study on vinyl chloride[56], a known human carcinogen by inhalation, present in landfill gas. Related to these is the *Chemosphere* paper[74] included in Section 1.

The significance of these contributions is apparent when one considers that risk assessments supporting regulatory decisions at the time, and still, take no account of the relative availability of individual chemical species within a weathered hydrophobic matrix, as noted above. Hence the likelihood is, over and above the gross approximations that risk estimates infer because of necessary extrapolations from the baseline toxicology, that an additional overestimate of risk is incorporated because of very low contaminant availability. The practical impact of these overestimates is remediation disproportionate to the significance of the risk and potentially, the inefficient use of public and private funds. In a broader sense, this type of error reflects an over confidence in the application of quantified risk analysis to environmental issues; arguably one overly concerned with the generation of numerical risk estimates rather than the targeted application of interventions that minimise exposures[60, 107, 125, 136, 155, 157]. The candidate holds the view that the focus of these assessments should rather be in identifying opportunities for risk management and improved decision-making[80, 91].

Section 5 Environmental risk management

Environmental protection should be risk-informed, and interventions should focus on those hazards, pathways of exposure and receptors that contribute most to the risk. The development of risk-informed regulation[18, 35, 92, 177, 276] and the desire to

promote proportionate, effective environmental protection by reference to an analysis of risk led to an increasingly integrated environmental risk management capability within the UK Government and its agencies from 1995 onward[273]. With explicit requirements for environmental risk assessment within the statute, and new general powers introduced in the Environment Act of 1995, regulation of environmental risk assumed growing importance for operators and their professional advisors[17, 18] – environmental consultants and lawyers, not least because effective environmental protection (inferring a wise and proportionate use of resources) has been asserted as a central tenet of successive UK sustainable development strategies. The papers in this section[9, 10, 17, 18, 29, 32, 44, 42, 45, 48, 49, 57, 58, 52, 59, 60, 53, 65, 73, 75], including five invited submissions[42, 48, 49, 59, 60], provide a distinctive narrative on the developments in environmental risk management practice occurring at the time. They provide the link between the theoretical work above, albeit in a highly practical scientific context, and the operations of business and regulation directed towards risk management[18, 32, 42, 57, 146, 153, 155, 157, 158, 159, 162]. Increasingly, these contributions address the theme of environmental decision-making in the round[80] and lead on, in the next section, to an original evaluation of the organisational competencies for good risk governance (Pollard, S.J.T., Bradshaw, R.A. *et al.,* 2009, *in press*; Pollard, S.J.T., Lemon, M. *et al.,* 2009, *in press*; Bradshaw, R.A., and Pollard, S.J.T., 2009, *in press*) where much of the candidate's current research efforts are focused.

The UK has a successful convention of pragmatic risk assessment and management[273, 274, 278]. Nationally, we have resisted the desire to quantify risks that are not fully understood, and have relied instead on the codification of expert evidence, experience and practice, and the use of informed expert judgement as the basis for robust decision-making. However, internationalisation of the global consulting market in the mid 1990s saw the introduction of US-style quantitative risk assessments (QRAs) to environmental protection problems. The contributions here[9, 18, 29, 44, 57, 58, 59] represent a body of action-oriented research (collaborative research with practitioners) and research commentaries with the broad aim of holding dear to this UK convention that has served policy makers well. A particular concern of the candidate has been the computation of quantified risk estimates (probabilities) presented in increasingly precise terms with integers and negative exponents (10^{-7}, 10^{-15}), for which

a poor scientific basis often exists. The papers here have been made alongside the theoretical contributions in the sections above and relate to risk management for contaminated sites, as a decision tool to inform regulation and its application within the water utility sector.

The first three papers in this section address QRA and the uncertainties it embodies. Calling for a more robust, well-founded evidence base for the assessment of risks at contaminated sites and incinerators[9, 10, 17], the earlier papers pave the way for the mid-series contributions on environmental risk management practice. Here, the contributions promote a tiered approach to risk analysis, a strong focus on problem definition and risk prioritisation, and the incorporation of economic appraisal, technology assessment, social issues and management accountability to decisions on risk management.

Examples of the proportionate and targeted application of quantitative exposure assessment are provided in the incineration[17, 32], spray irrigation[45] and air pollution control (APC) residue papers[53], together in each case with discussion of uncertainty. The section then includes a series of commentaries[9, 18, 29, 44, 49, 57, 59, 65] for practitioners on the appropriate use of risk analysis in environmental protection. A recurrent theme is the application of risk tools, not in their own right, but to *inform* the management of risk which, though seemingly obvious, is a common oversight by practitioners with a strong focus on securing regulatory approvals for new developments, process modifications and the reauthorisation of long-established operations. Of note and influence in this regard is the candidate's contribution to the safety case review of the British Nuclear Fuels Limited (BNFL) low-level radioactive repository at Drigg, Cumbria, regulatory discussions on which embodied the tensions between QRA, risk-informed regulation and stakeholder confidence in risk governance[93, 175, 176, 183, 187, 190]. The insights gained from research undertaken by the candidate whilst at the Environment Agency (1998-2002) are published with his co-workers elsewhere in the open literature, and discussed in Section 7 of this thesis.

The final paper[75] in this section represents recent insights into the disposal of animal carcases and associated risks to public health, animal health and the wider environment[205]. A multidimensional problem, policy and regulatory officials must manage rapidly escalating pressures on the waste management infrastructure of

countries during animal disease outbreaks. A critical feature of these events is the safe, responsible and efficient disposal of animal carcases, which must be performed with risk reduction in the forefront of the minds of veterinary and environmental specialists. Historical disposals during the foot and mouth, bovine spongiform encephalopathy (BSE) and avian flu outbreaks tended to rely on a structured hierarchy of waste technologies (Pollard, S.J.T., 2009, *in press*). However, the need for operational agility during these crises and the practical necessity of needing to access a wider range of waste technologies prompted Defra-funded research[205] into a risk-based appraisal of disposal options. The distinctive insights gained from an exposure assessment of 28 waste process chains, communicated in the *Environmental Science and Technology* paper[75], led to a revision of the Government's contingency plan for exotic animal disease outbreaks in the UK. The methodology adopted has since informed the development of end use protocols for anaerobic digestion and compost products going to land in the UK[211] and is underpinning stakeholder confidence in the reuse of these waste residues, as 'products' within the Government's revised waste strategies.

Section 6 Environmental policy, regulation and governance

Following the promotion of explicit environmental risk assessment tools and techniques within Government from 1995 onwards, attention has turned to the development of organisational capabilities for risk management, a reappraisal of UK risk policy following the BSE and for and mouth disease (FMD) crises, and to the response of the regulated communities to risk-based regulation. In part, these developments were driven by introduction of renewed codes of corporate governance, their implementation across Government, following severe criticism of the handling of risk, and a growing recognition within organisations of the necessity to manage risks well in order to secure their 'licence to operate'.

Eleven papers[35, 36, 39, 51, 158, 160, 61, 64, 72, 66, 67] and two invited submissions[158, 160] are included in this section. The first three papers largely reflect the contributions of the candidate to the development and implementation of regulatory risk assessment, whilst within the Science function of the Environment Agency[35, 36, 39, 99, 155, 157, 177, 178, 181, 182, 184, 188], . The most recent contributions[66, 67] explore this theme within the water utility sector and return to an earlier theme (Section 2), the provision of safe drinking

water, a risk worth prioritising given its essentiality to human life and the dependence of economic growth on its continued provision.

The original insights developed here[66, 67], secured through research funded by the American Waterworks Association Research Foundation (AwwaRF) and a consortium of international water utilities[52, 61, 66, 67, 77, 112, 113, 114, 123, 129, 130, 160, 206] consider the organisational competencies required to manage risks well. Drawing on theories of high reliability organisations, mindfulness and safety culture, this body of research represents a natural progression from earlier work on risk assessment, and considers the pre-requisites for a *preventative* risk management culture within the environmental goods and service sector, specifically within water utilities. Water suppliers have become complex businesses with ageing infrastructures, outsourced functions and skills shortages. In this operating environment, managing corporate and environmental risk is a huge practical challenge but one increasingly under regulatory, investor and community scrutiny. The candidate and co-workers have explored inter- and intra-organisational competencies in risk management in the context of supplying safe drinking water. Modern water utilities have become expert at managing water quality incidents through the use of advanced control rooms and targeted workforce planning, but struggle to embed a preventative approach to managing risk. One chief risk officer interviewed in this research explained the paradox: water suppliers operate unit processes and, in effect, put these assets at risk in order to protect public health. The candidate's observations suggest that the asset management mindset and the increasing adoption of a lean management philosophy that potentially erodes inherent margins of safety (whilst maximising returns on investment for shareholders) may be contributing to latent errors in the operation of utility infrastructures– potentially building a future of increased incidents, service outages and impacts on customers. The papers co-authored with Dr Brian MacGillivray[66, 67] illustrate where improvements can be made. Investments in managing risks within a water utility's outsourced businesses, in training and educating their staff in risk management and in managing in-house on knowledge risk are singled out. Actions here are likely to reduce business exposures, improve vigilance and competencies on the front line of water and wastewater treatment, and help build a lasting legacy of organisational learning on preventative risk management (Pollard, S.J.T., Bradshaw, R.A. *et al.*, 2009, *in press*). These

insights were instrumental in establishing the Defra/Research council funded collaborative centre of excellence in understanding and managing natural and environmental risks at Cranfield University in 2008 under a £1.25m Engineering and Physical Sciences Research Council (EPSRC) awarded to the candidate.

Section 7 Additional evidence of practical achievements

The University regulations provide for the submission of further practical evidence of achievement, over an above significant academic achievement, in considering the candidacy of a DSc applicant. The contributions in this section represent additional evidence in support of ten practical achievements made over the course of a 20 year research career in academia, environmental consultancy and environmental regulation. In each case, the candidate was a central contributor to the work, the research and policy significance of which is discussed. As a whole, they represent attempts to transfer many of the research insights discussed in the papers above into practical knowledge for end user communities. They offer a mixture of practitioner guidance, expert judgement, regulatory science and research in support of new regulatory initiatives on resource and environmental risk management. The discussion of each is supported by a shortlist of publications available in the open literature, cross-referenced from the candidate's career publications in the Appendix.

7.1 GUIDANCE ON RISK COMMUNICATION FOR CONTAMINATED LAND

The SNIFFER publication[145] (1999) presented in this section, co-authored with colleagues from Dames and Moore consultants and the environment agencies in Scotland, England and Wales represents early attempts in the UK to transfer the state-of-the-art on risk communication to the developing policy context of contaminated land legislation[239,270]. The guidance presented saw very wide application in the sector among contaminated land practitioners and an update has recently (2008) been commissioned. This and the contributions below on participatory risk assessment[96, 194] (section 7.5) resulted in the candidate being asked to draft guidelines on community consultation for contaminated sites in Australia, research currently underway[120, 131], in collaboration with the University of South Australia.

7.2 GUIDANCE ON RISKS FROM TOTAL PETROLEUM HYDROCARBONS

The development of soil guideline values (SGVs) for the assessment of land contamination in the UK has been long and drawn out. One of the most common site contaminants and source of known pollution incidents has been hydrocarbon-contaminated soils. Efforts in the US to adopt risk-based corrective action (RBCA) for petroleum contaminated soils (1996-) led to the development of guidance and later recommendations for assessing exposures from total petroleum hydrocarbons, under the auspices of the US-led Total Petroleum Hydrocarbon (TPH) Criteria Working Group. These two contributions[193, 200], authored principally by the candidate, represent the national consultation[193] on the approach to assessing risks from TPH at contaminated sites in the UK, and the development of a subsequent risk management framework[200] for TPH. Drawing heavily on the research insights described in sections 3 and 4 of this thesis, the consultation uniquely sets out guidance on the assessment of weathered hydrocarbons at these sites. Ongoing research discussions with the Environment Agency on the exposure assessment model used to generate soil guideline values is informing the development of SGVs for TPH[74]. The fugacity paper referred to in section 1 of this thesis[74] will be an important input to these discussions, so that the values generated are not unnecessarily conservative.

7.3 REVIEWING THE POST-CLOSURE SAFETY CASE FOR DRIGG

The UK has a single strategic facility for the disposal of low-level radioactive waste – the repository at Drigg, in Cumbria. From 1998 onward the candidate assumed responsibility for overseeing the technical review of the then operator's (BNFL) post-closure safety case[187, 190]; that is, BNFL's assessment of the radiological risks to public health and the environment following future closure of the facility once the site's radiological capacity is met (*ca.* 2050). Working closely with front line regulatory colleagues[190], radioactive waste risk analysts within the Agency[187], policy specialists and a group of external experts[93, 175, 176, 187], the candidate provided a technical review role to the Agency on the requirements of the post-closure risk assessment and on the reasonable requirements of this assessment to inform the decision on reauthorizing disposal at Drigg[190]. These contributions reflect the intellectual inputs to this process, and in particular, the candidate's desire to move away from a single, quantitative, deterministic risk curve with time (forward in time,

from closure, 100 000 years) to a more diagnostic risk assessment illustrating key risk drivers and, therefore, engineering features and operational practices that were candidates for regulatory control in the immediate term so to protect long term safety. The 2003 document here[190] has national significance because it represents the Environment Agency's qualified approval of the post-closure safety case and risk assessment, and thus informed the reauthorisation, with permit conditions, of the Drigg facility.

7.4 RISK ASSESSMENT REQUIREMENTS FOR UNDERGROUND WASTE STORAGE

This guidance[188] and expert evidence[185] represents original thought on the regulation of underground disposal facilities for hazardous wastes in the context of the European Council Landfill Directive (1999/31/EC). The 'Minosus' development[189] is the UK's only underground, as opposed to near-surface, hazardous waste facility. Unique regulatory guidance[188] for the developer of this facility was required during the planning process and drafted by the candidate and co-authors. Expert witness evidence to the planning inquiry for this facility was provided by the candidate[185], describing in technical detail the risk assessment requirements the Environment Agency would have on the operator during the future permitting of the facility. As development of the facility progressed through the planning stage and the various appeals that ensued, these contributions required substantive innovation in regulatory process, and the application of safety case methodologies for risk assessment, previously only applied to radioactive waste repositories in the UK. The candidate drafted these requirements for the Environment Agency and subsequently reviewed the operator's submissions[189]. Potentially controversial, because of the risk of a precedent for all hazardous waste facilities, the safety case approach[189] adopted proved instrumental to the environmental permitting of this national facility and to the avoidance of judicial review by opponents of its construction. In brief, the level of rigour required of the facility developer in assessing operational and future risks built confidence within the broader community in its robust regulatory oversight. This was the first time that a safety case approach had been applied to a hazardous waste facility in the UK.

Following this evidence, the candidate incorporated the interests of the local community within Agency-funded research on participatory risk assessment[194-196];

research devised and directed by the candidate and co-authored with researchers at the University of Birmingham (7.5 below).

7.5 ON THE PRACTICE OF PARTICIPATORY RISK ASSESSMENT

The shortcomings of a technocratic approach to risk analysis, in isolation of contributions from the broader social science agenda of environmental justice, equity and trust, has long been paraded in the risk literature. Despite the pragmatism referred to earlier in this thesis, the UK has been slow to adopt the deliberative-analytic approach to risk management developed, for example under the auspices of the US Presidential Commission on Risk Management (1997). Seeking to incorporate these aspects and building on the contribution in 7.1 above, the candidate directed research on participatory risk assessment collaboratively with the University of Birmingham and consultants Pat Delbridge Associates[96, 100, 194-196,]. The contributions developed build on the sentiments of Frank Fischer's 'greening of risk assessment' (1995). Using the qualitative research methods of structured interviews with triangulation of elicited data, this research[194] sought to understand where publics would wish to be involved in the risk assessment process (problem definition – framing, and risk characterisation), and to offer guidance to regulatory staff on involving others in risk assessment. Trials of similar approaches in the Environment Agency's flood risk and waste management functions indicated the practical challenges of eliciting engagement in this sort of technically complex and often inaccessible regulatory science[196]. Nevertheless, this research was able to recruit the community objectors from the Minosus waste facility above and, with them, explore in focus groups what engagement processes might work in practice. The co-authored literature review[194] and project reports represent the first attempts in the UK to respond to this agenda by environmental regulators. Though controversial at the time because of the inferred resource requirements, the UK has since ratified the United Nations Economic Commission for Europe (UNECE) convention on access to information, public participation in decision-making and access to justice in environmental matters (the Aarhus Convention), becoming a full party to the convention in May 2005. The Convention is an important step towards environmental democracy throughout the UNECE and tools like those developed under this project are in growing demand.

7.6 TOOLS FOR STRATEGIC RISK APPRAISAL

A recurrent theme for Government and environmental regulators over the last 10 years has been a requirement in the statute to report on the state of the environment, a necessity to compare a suite of diverse risks, and an operational need to advise on the proportionate use of resources to address environmental concerns. The contributions offered here[90, 95, 186, 202] represent the Environment Agency's development and application of strategic risk assessment tools. Nationally, the techniques[43, 80, 90, 95, 98, 178, 180, 186, 197, 202] saw use in the 2000 'State of The Environment' report for England and Wales and they have since influenced thinking in Defra. Intellectually, they extend the work of the German Advisory Council on Global Change (1999), seeking to defensibly incorporate an assessment of non-monetisable values within the strategic appraisal of environmental risk, and improve the visualisation of strategic risk issues on various probability-consequence axes[43]. Their application has not been straightforward, because end users need to climb a substantive learning curve on risk characteristics before they can rank strategic risk issues[197]. Nevertheless, the original thinking developed during their design and implementation has informed comparative risk assessment in the Environment Agency and revealed some hitherto ignored aspects of environmental risk, especially latent effects, the reversibility of environmental change and the spatial heterogeneity of impacts. Research directed and co-authored by the candidate in this theme produced one of the key publications discussed in Section 1 of this thesis, and strategic risk appraisal is a key research theme of the Defra/Research councils collaborative Centre of Excellence in understanding and managing natural and environmental risks, under the direction of the candidate at Cranfield University.

7.7 EXPOSURE ASSESSMENT METHODOLOGY FOR CARCASE DISPOSAL

The research contributions to this theme are discussed in section 5 above. The candidate has made significant practical contributions to the development of risk assessments for animal disease outbreaks. These include his membership of the core intergovernmental team drafting the Department of Health's qualitative risk assessment of health effects during the 2001 foot and mouth disease (FMD) outbreak and subsequent attendance at the Government's spongiform encephalopathy advisory committee (SEAC), to advise on risks to groundwater from carcase disposal during the

2001 FMD crisis. A single report is presented in this section[205]. It describes research advice to Defra on exposures to pathogenic and chemical agents across 28 disposal options for animal carcases. The research, currently being further developed, resulted in a shift of emphasis within Animal Health (Defra), away from a focus on suitable waste management technologies and towards one concerned with the significance of exposures along various points in a process chain. This has delivered greater flexibility for Defra in its use of waste treatment options and sharpened the focus on fast, effective management of exposures at source when exotic disease outbreaks occur.

7.8 UNDERPINNING THE QUALITY PROTOCOLS FOR WASTE-DERIVED PRODUCTS

A growing dissatisfaction with the capacity of conventional regulation to provide sufficient certainty and signals to the market has spawned new approaches to encouraging the uptake of waste-derived products. Under the theme of 'wastes as resources', the contribution offered here[211] adopts the generalised exposure assessment methodology developed in 7.7 above for anaerobic digestion (AD) residues being put to end use on land. This research is now underpinning the Environment Agency/WRAP specification for AD product end use, by providing stakeholder confidence in the safe and responsible use of AD residues on land. Pivotal to the exposure assessment has been (i) the prioritisation of risks by reference to hazard potency, environmental persistence and exposure pathway availability, and (ii) the visualisation of process risks so to identify critical control points. The exposure assessment methodology and output developed by the candidate has been used in the drafting of the quality protocols for AD producers, such that specification-compliant products can be brought to market with confidence. Success with this methodology has resulted in similar research on the use of compost products funded by WRAP.

7.9 RISK GOVERNANCE IN ANIMAL HEALTH LABORATORIES

The Institute for Animal Health (IAH) is a national strategic research facility for the study into exotic animal disease transmission. The laboratories at Pirbright, Surrey were subject to a series of Government reviews in 2007 following the release of FMD virus from the multiuser site at which the laboratories are situated. This section includes one of these reviews[164]: the 'Beringer report' to BBSRC council, of which the

candidate was a co-author and key contributor. Among the terms of reference for Sir John Beringer's review of IAH was the requirement to advise on issues of risk governance. The candidate was the key advisor to the review panel on these issues, offering recommendations to the panel on corporate risk management and its relationship with issues of biosecurity, the preserve of the related review led by Dr Martin Jeggo. The Beringer panel's recommendations have had national strategic implications for IAH and the retention of a national capability in exotic animal disease prevention. The specific recommendations on risk governance are of wide application across all research facilities and point to a need for a single 'line of sight' by the executive on issues of risk management, the need for clear accountabilities on issues of risk, and the maintenance of a risk management culture among all staff. In making these recommendations, the candidate was able to draw heavily on AwwaRF-funded research referred to in section 6 of this thesis.

7.10 REGULATING ENGINEERED NANOMATERIALS

One research report is presented here[220]. Manufactured nanomaterials are now widely used in a range of industrial and consumer products. However, they remain largely unregulated at present other than through voluntary disclosure agreements with the sector. This research report co-authored with Dr Sophie Rocks and others represents guidance to Defra of the risk assessment requirements for engineered nanomaterials. The research was commissioned by Defra, via international competition and prepared for the Organisation for Economic Co-operation and Development's (OECD) working party of manufactured nanomaterials (Rocks, S.A., *et. al.*, 2009, *in press*). A key recommendation of the work, directed by the candidate, has been the need for a formal weight of evidence framework for engineered and manufactured nanomaterials that can be integrated within the European chemicals (REACH - registration, evaluation, authorisation and restriction of chemicals) legislation, thus guiding manufacturers on the regulatory requirements of nano risk assessments in support of the societal use of these materials. This work has led directly to the development of a Cranfield responsible care (nanocode) initiative for the sector now established at the University.

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Other work presented for examination - evidence of practical achievements

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APPENDIX

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Current Directions in the Practice of Environmental Risk Assessment in the United Kingdom

SIMON J. POLLARD,* ROGER YEARSLEY, NICK REYNARD, IAN C. MEADOWCROFT, RAQUEL DUARTE-DAVIDSON, AND SUSAN L. DUERDEN

National Centre for Risk Analysis and Options Appraisal, Environment Agency, Kings Meadow House, Kings Meadow Road, Reading, RG1 8DQ, United Kingdom

The manner in which regulators apply environmental risk assessment to their decisions on managing risk is changing. Expectations of risk assessment work are becoming clearer, the social issues agenda is having an impact on risk assessment practice, and there is a trend toward harmonizing approaches to the treatment of environmental risk. For risk analysts, the multiplicity of environmental problems is providing opportunities for the transfer of expertise between the different contexts of applying environmental risk assessment. With the latter as a focus, we summarize recent policy developments in the United Kingdom and illustrate how Government guidance on environmental risk assessment and management is being implemented. We emphasize the need for proportionality in risk analysis, the targeting of regulatory effort to risk, and the explicit treatment of uncertainty. These developments are contributing toward better "risk-informed" environmental decisions in which risk analysis plays an important part alongside other considerations. The forward agenda is likely to see further practical integration between technical risk issues and economic and social concerns, and the positioning of environmental risk assessment within a broader landscape of decision-making tools.

Introduction

The use of environmental risk assessment has received growing prominence in the United Kingdom (UK) since the early 1990s, in part, as a response to the explicit requirements of recent environmental legislation. For practitioners, one result has been the emergence of a set of common themes that cut across the technical contexts in which environmental risk assessment is applied, from ecological risk to process plant failure. For example, assessing the risks associated with the performance of radioactive waste repositories, the environmental safety of process plants, the impacts of climate change on water resources, chemical exposures from historically contaminated land, and flood defense schemes involves the treatment of uncertainties. Environmental risk assessment, where applied to these situations, must be able to inform and improve regulatory and business decisions on how best to manage risks from environmental hazards. Arguably, however, the treatment of environmental risk by nuclear, chemical, and civil engineers, and by climatologists and environmental scientists has developed along parallel lines without an obvious impetus for the transfer of expertise between specialists. This is changing. Government interest in the consistent handling of risk in Europe and the UK is drawing professional communities of experts closer. No more so is this evident than in the field of environmental risk. This "convergence" has been given increased impetus by recent risk episodes in the UK and by legitimate calls for greater participation in environmental decision-making (*1*–*4*).

Rechard (*5*) provides an exhaustive review of international developments in environmental risk assessment. Historically, there have been philosophical differences between environmental risk assessment practice in United States (US) and in the UK. In the US, risk assessment developed out of the requirements of food, drug, and pesticide legislation, while in the UK, early drivers were the setting of occupational exposure limits, the safety case requirements of the offshore oil industry, and their subsequent adoption to on-shore process facilities (*6*). As practice developed, the US approach retained an emphasis on quantified risk estimation, particularly for cancer risk, while the UK, in general, adopted a more cautious approach to quantification, promoting qualitative approaches as a prerequisite. These generalized philosophies are now also converging, driven by a need for targeted, streamlined, and inclusive approaches (*7*) and a desire to position risk assessment within the range of support tools available to decision-makers (*8*) (Figure 1).

Our aim here is to reflect on recent developments in environmental risk assessment by reference to regulatory practice in the UK and to highlight the opportunities that exist to transfer expertise between applications. We address (i) the use of tiered approaches to risk assessment; (ii) the application of risk rating systems for risk management resource-planning; (iii) the treatment of uncertainty for complex risks; and (iv) the use of risk scenarios. The implications of these issues on regulatory decision-making are discussed.

Policy Context. The handling of "risk" by governments and their agencies has moved up the political agenda in the last 10 years. In the UK, a commitment to improve public policy in the handling of risk was made in the 1999 White Paper "Modernising Government" (*9*). UK government departments and agencies are preparing risk management frameworks, explaining how they assess, manage, and communicate the risks for which they have responsibilities (*9*, *10*). The Department for Environment, Food and Rural Affairs (DEFRA) and the Environment Agency of England and Wales have responded (*11*) by (i) presenting recent developments in the policy and practice of environmental risk assessment; (ii) setting out their own approach; and (iii) communicating to practitioners and others their expectations of risk assessment work undertaken in support of environmental permitting. Revised DEFRA and Environment Agency guidance (*11*), updating previous advice (*12*), reflects the current debates in risk assessment practice and adopts many internationally accepted principles. Good problem definition, proportionality and consistency of approach, the explicit treatment of uncertainty, and presentational transparency are common themes (*6*, *10*, *13*). The guidance offers a generic, over-arching risk assessment-risk management framework (Figure 2) to which specific risk guidance, such as that for waste management regulation, historically contaminated land, flooding, and coastal defense, can refer (*14*).

Recent developments in risk policy (*9*, *10*) are benefiting from the emphasis on the social aspects of decision-making

* Corresponding author phone: +44 (0)1189 535 249; fax +44 (0)1189 535 265; e-mail: simon.pollard@environment-agency.gov.uk.

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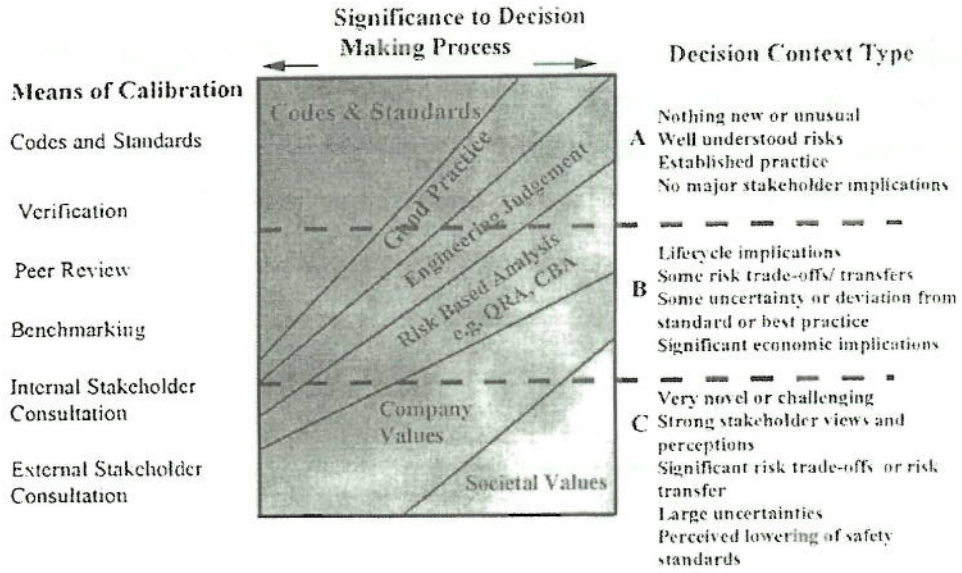


FIGURE 1. A decision support framework for major accident hazard safety developed for the offshore oil industry (after ref *8*, with permission). This has wide application beyond the process sector. The framework takes the form of a spectrum of decision contexts and accompanying tools ranging from those for conventional engineering decisions to those where corporate and societal values are seen as dominant factors. Groups of characteristics A–C are used to describe the decision context for the user and the balance of tools shown adjacent within the box. The means of checking these types of decisions are provided on the left-hand side of the box.

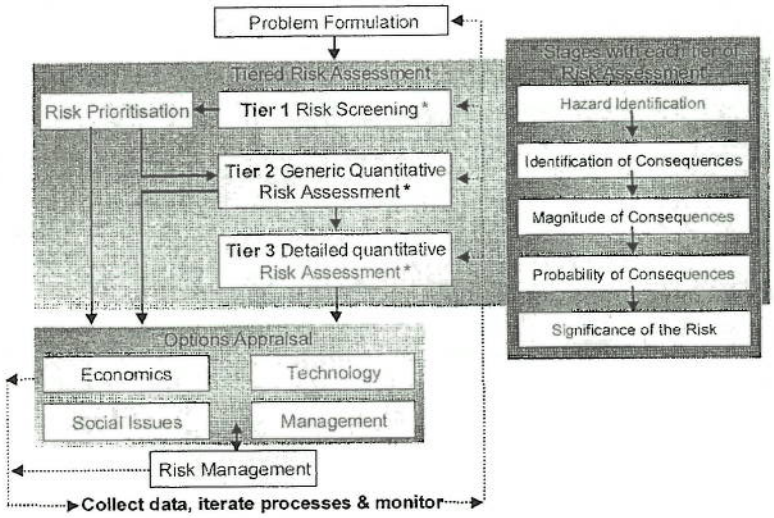


FIGURE 2. A framework for environmental risk assessment – risk management in the UK (*11*). The schematic provides an overarching framework to which approaches for specific hazards from flooding, waste disposal, and historically contaminated land can refer.

(*1, 2, 11–13*), and, while not detailed here, this is having a growing influence on risk assessment practice. Calls for increased stakeholder and public involvement (*1, 3, 4*) are requiring greater access to risk assessments, and both national (UK) and international legislation is emphasizing consultation as a duty among public and governmental organizations. Following developments in the US, there is need in the UK for risk assessments to become more accessible to nonexpert audiences and available for critical evaluation and constructive challenge. How risk assessment practice responds to this agenda, while retaining its analytical power for decision-support, is developing into an important debate among practitioners and stakeholders.

Tiered Approaches: From Project to Strategic Risk. Central to the UK approach to environmental risk assessment is the concept of proportionality (Figure 2) (*11, 15*). The "tiering" of assessment effort allows the degree of sophistication in the analysis to be matched to the complexity of the problem and our understanding of the supporting science, so avoiding redundancy or misplaced precision. This applies whether one is concerned with individual risk problems at the project (*16*) or the strategic level (*17, 18*). For strategic analysis, where comparisons between risks quite different in character may preclude numerical analysis, qualitative screening and prioritization techniques (tier 1, Figure 2) are more appropriate (*19*). For high priority risks from well-defined hazards at the project scale, such as those arising from the disposal of radioactive waste in containment facilities, tailored quantitative risk assessment techniques may be more applicable (tier 3, Figure 2). Complex risks that involve well-described and/or less well understood aspects require a range of approaches and the means for meaningfully synthesizing qualitative and quantitative data.

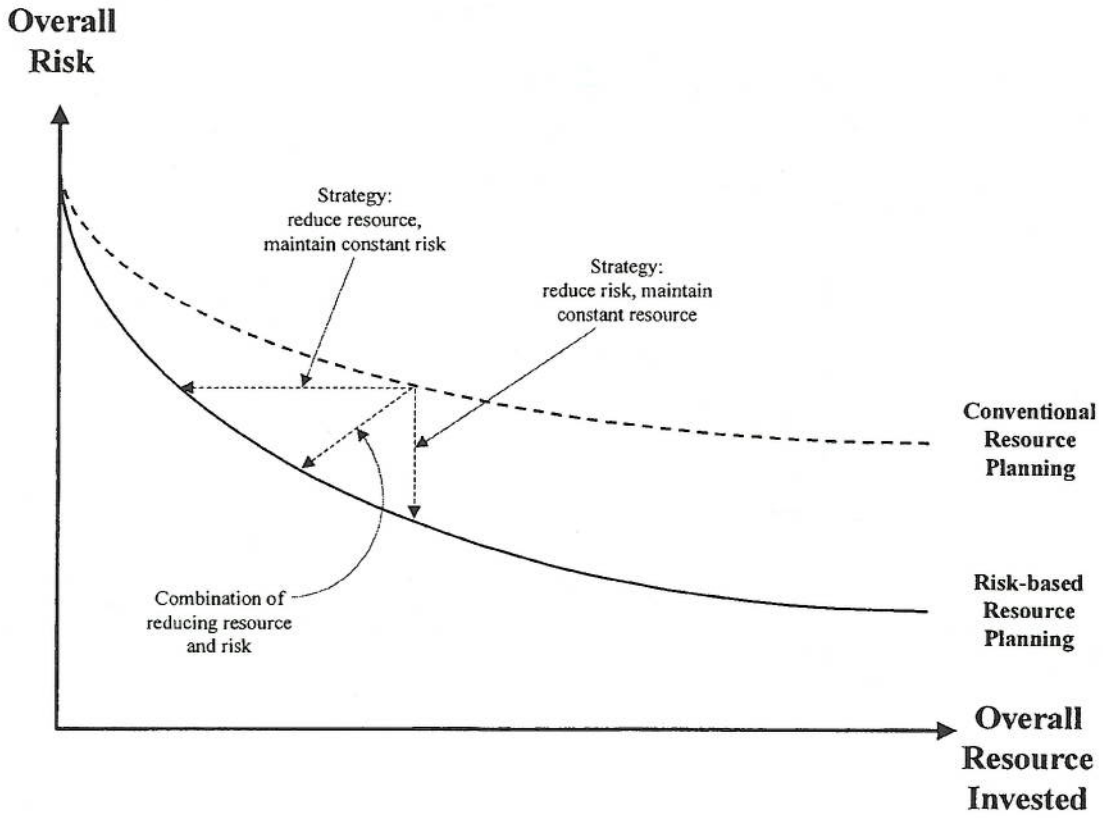


FIGURE 3. Risk-based regulation attempts to optimize the cost of regulatory effort with risk, by shifting resources from low risk toward high risk activities, setting the level of inspection according to how the risk varies as a function of inspection (*23–25*). In targeting the inspection effort, and without losing sight of the performance of individual sites, the aim is to set inspection frequencies for all sites so that *overall* reductions in risk outweigh any individual increases in risk.

One illustration of the above discussion lies in the development of waste management installations. Environmental risk assessment is fundamental to all phases of the development from the strategic planning level, where site screening and selection are progressed, through development planning and on to permitting where quantitative risk assessment helps identify risk management options required to mitigate risks from the installation. Risk management measures become stipulated as risk-based license conditions, for example, with respect to gas and leachate control. Following permitting, the routine inspection, monitoring, and review of such installations can be prioritized according to the degree of risk posed, so as to best utilize the regulatory resource for maximum risk reduction.

Prioritizing Risk and Resourcing Risk Management. The UK strategy for sustainable development (*20*) emphasizes the need for *effective* environmental protection. Among the means of achieving this is the targeting of regulatory resources (time, human resources) through risk-based, or risk-informed, regulation (Figure 3).

The use of risk ranking systems for informing risk management, particularly regulatory inspection, is well established (*21, 22*). For a set of common activities, this approach represents a "tradeoff" whereby regulatory attention on low risk activities is released for focusing on ones of higher risk. Risk ranking systems have their critics (*22*), but designed well, they can improve regulatory efficiency and offer incentives for better risk management (*23–25*). Targeting regulatory resources in this fashion requires a risk assessment for the subject under study, using a range of critical factors that contribute to the overall risk. For flood defense inspection, these factors might include the design standard, the physical condition of the defense, and the type of land-use protected. The selection and grouping of the individual risk factors is conducted according to the needs of the individual scheme (*21*). The Environment Agency's operator pollution risk appraisal (OPRA) system (*23*), applied to the resourcing of regulatory inspections within the process sector, has risk factors grouped by the inherent pollution hazard posed by a facility and those dependent on the operator's performance in managing the hazard. Identifying those factors within the control of the developer, operator, or regulator, and those factors less easy to control reflects the sensitivity of any factor to intervention and can help influence regulatory priorities and individual site responses to risk reduction.

The design of risk ranking systems can be contentious because the scale of risk represented by scores is arbitrary—only the relative risk between facilities has meaning. One benefit of "scoring" over a qualitative descriptor of risk, however, is in distinguishing between probability and consequence contributions to risk, for example, in distinguishing between a hazardous process (consequence) and the performance of an operator in managing the potential risks posed by its operation (probability). A disadvantage is the potential abuse of the scores for purposes other than that for which they were designed. Experience in the US and UK demonstrates that these systems need to be simple, clear, piloted prior to wider use, and made reproducible.

Having assessed the risk, resource allocation can be achieved, allowing for other considerations, by apportioning the available resource according to the grand sum of overall risks, or by assessing the grand sum and constructing a case for resources accordingly. A combination of resource "sup-

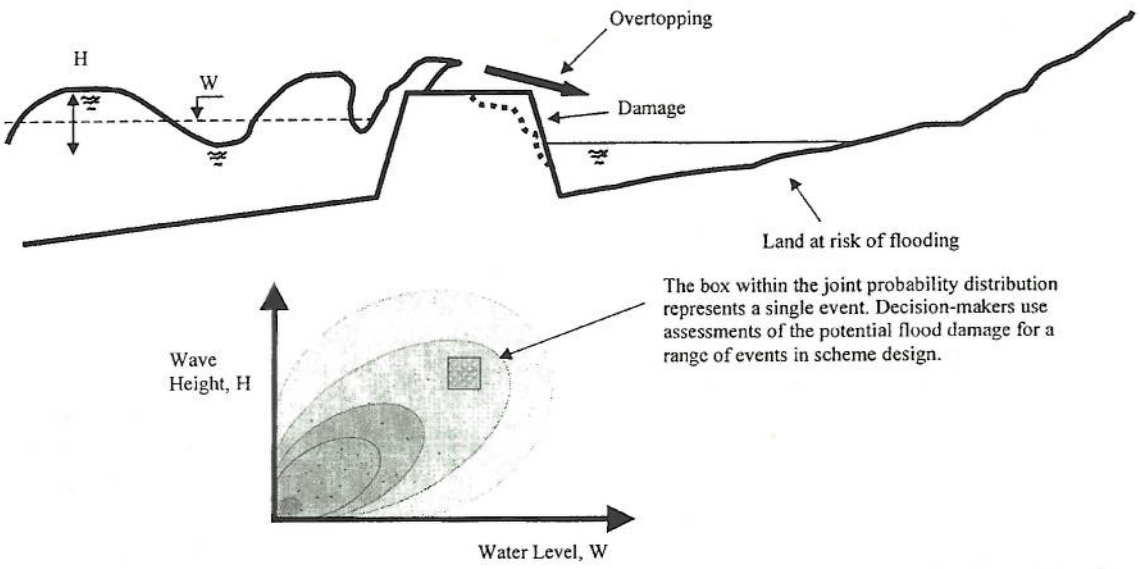


FIGURE 4. For many flood and coastal defenses in exposed locations, overtopping depends on both water level and wave height. Damage to a defense and the possibility of breaching is also related to the combination of loads. Joint probability (JP) approaches are used to estimate the probability of combinations of high water level (W) and wave height (H), shown simplistically as p(W,H) for a given combination. When combined with suitable "structure functions" such as formulas for overtopping or damage, JP analysis can be used to assess risks of flooding taking a wide range of load combinations into account. Similar principles apply to other cases such as combined tidal/fluvial effects.

ply"- and "demand"-led approaches usually applies. Progressing to a demand-led approach raises important policy issues of comparative cost-benefit tradeoffs and equity in the relative allocation of resources for the management of quite different risks, such as, for example, flooding, historically contaminated land and local air pollution control. Initially, resources can be allocated in proportion to the risk levels assessed using the scoring scheme. With experience, as risks are reduced over time, the regulator can assess where resources are having greatest effect and where a resource surplus exists. Resource planning can then adopt a further aspect of targeting by turning attention on risk critical factors where reductions are most readily achieved.

Dealing with Uncertainty. A principal outcome of recent risk episodes in the UK has been recognition of the need to be explicit about uncertainties (*1*, *26*). Environmental risk assessments account for a range of uncertainties, and, for numerical risk estimates, the types of uncertainty addressed will influence the risk distribution. A number of classifications of uncertainty have been developed. One distinguishes between "epistemic" and "aleatory" uncertainties. Epistemic uncertainties are those associated with a lack of knowledge or of observational data and can be reduced through additional experiment or by provision of a greater data record. Aleatory uncertainties relate to those events for which there cannot be observational data, for example, future human actions. In this case, probabilities can only be defined through expert judgment, and there is no way of reducing the uncertainty at the time of assessment. One approach to the epistemic uncertainties associated with extremes within a data record is the joint probability method. The method also addresses a common, often erroneous presumption, which is that events, or the conditions that initiate a hazardous event, act independently.

Joint Probability Studies. Many environmental risks are characterized by the consequences of rare or extreme events or by some combination of events. The Environment Agency and DEFRA have put significant investment into understanding environmental extremes. Extreme value (EV) analysis, which assumes that random processes drive a hazard, has been the basis of engineering design to resist environmental loads, such as the extremes of wave height or water volume, for decades (*27*, *28*). EV methods involve fitting a probability distribution to data on the variable of interest, and then extrapolating to a low probability, high consequence (extreme) event to help set design criteria, such as the crest height of flood defense structure or reservoir. However, often (i) the adverse consequences following an extreme event depend on a combination of loads, rather than on a single load; (ii) consequences other than those which the "design" mitigates against may be important; and (iii) there may be several different failure mechanisms to which the design is susceptible.

Increasing pressure to understand the risks faced by society from natural hazards and extreme events has led to increased flexibility in methods for analysis and design. Consider coastal flood defense design. In England and Wales, some two million homes and businesses are located in areas at risk from flooding and coastal erosion. Many are dependent on defenses for protection without which the total potential annual average damages would be approximately £3 billion, with about 50% in sea or tidal risk areas. Here, defense structures must withstand combinations of high waves (surge) and high water (tidal highs). While they are unable to predict the precise combination of loadings that will occur, risk analysts and design engineers must account for the effects of different combinations of wave height and water level and their probabilities of occurrence.

A key parameter for a coastal defense structure is the overtopping flow rate, expressed as a volumetric flow rate per meter run of a defense. This parameter has a direct effect on flood volume and area and is a good indicator of the likelihood and magnitude of structural damage to the crest and landward slope of the defense structure (Figure 4). Formulas can predict overtopping flow rates for a range of sea defense geometries. The combined influence of wave and water levels can be addressed in two ways. In the structure variable approach (SVA), the overtopping rate is calculated for each independent record of wave and water level conditions. Providing these variables are recorded concurrently, the sequence of overtopping can be ordered and extrapolated to the required extreme value. In the joint

probability approach (JPA), extrapolation is performed on the loads such as wave height and water level rather than the response parameters. This requires a complex, multivariate, distribution to be fitted, with extrapolation to obtain joint exceedence probabilities: the likelihood that the wave height *and* the water level exceed the height of the defense structure simultaneously, over a given time period. The value of the JPA approach is that it accounts for the dependence *between* variables. This can have a major impact on risk in some cases. A practical advantage is that it needs to be carried out only once at a particular site, although the multivariate distribution fitting is potentially more complex. Multiple failures can also be explored using Monte Carlo sampling to produce a long sequence of synthetic load conditions that matches the extremes of all the individual variables, and which incorporates their interdependence. A synthetic data set forms the ideal basis for the risk analysis of a defense structure having a number of possible failure mechanisms (*29*). At its simplest, a record-by-record check can then assess whether a failure condition is met for one or more of the prescribed mechanisms. The proportion of records registering a "failure" can then be converted to a probability of failure on an annual basis and compared with a risk acceptability criterion.

This type of analysis is being increasingly favored as strategic approaches to the management of flood and erosion risk gain acceptance. These view flood and erosion systems at a larger scale, such as whole catchment or coastal cell. The first generation of catchment flood management plans are currently being produced in England and Wales. Decision-makers managing risk in an integrated way will need better information on the spatial pattern of risk as well as on the contributions from different causes and processes: what is the combined probability of simultaneous flooding in neighboring catchments? What is the relative likelihood of extensive compared with localized flooding? and What is the probability of flooding due to long-term increases in groundwater levels combined with short-term heavy rainfall? The joint probability method is one way to examine these issues and has an important role in the integrated analysis of flooding problems and their solution.

Presenting Risk Distributions. Presenting and communicating risk distributions is difficult, particularly where extreme values must be considered. This is especially the case where complex risks are being assessed, at least in part, by reference to a single numerical criterion. One UK example is in the licensing of land disposal facilities for low and intermediate level radioactive waste. A risk assessment is central to the post-closure safety cases for such facilities (*30*). Briefly, the known features of the disposal facility, together with the processes and events that are reasonably certain to occur, can be used to predict its normal or expected behavior over time. The overall consequences of the interactions between these high-probability processes and events, with the associated uncertainties, determine whether the expected behavior of the facility is tolerable in terms of risk. The system can also be affected by further events, faults, or accidents that have lower probabilities of occurrence and where the associated uncertainties are aleatory, such as inadvertent human intrusion into the facility at some point in the future. These events can result in adverse consequences greater than would be expected under normal behavior, and their contribution to the overall radiological risk over time is dependent on expert, but subjective judgments of their probability (*30–32*).

Current regulatory guidance (*33*) for applications to dispose of low and intermediate level radioactive waste to land adopts an upper bound individual risk target of 10^{-6} per year (above background, annual increase in the likelihood of a radiological-induced health effect) in the period after closure of the facility. This represents the radiological risk

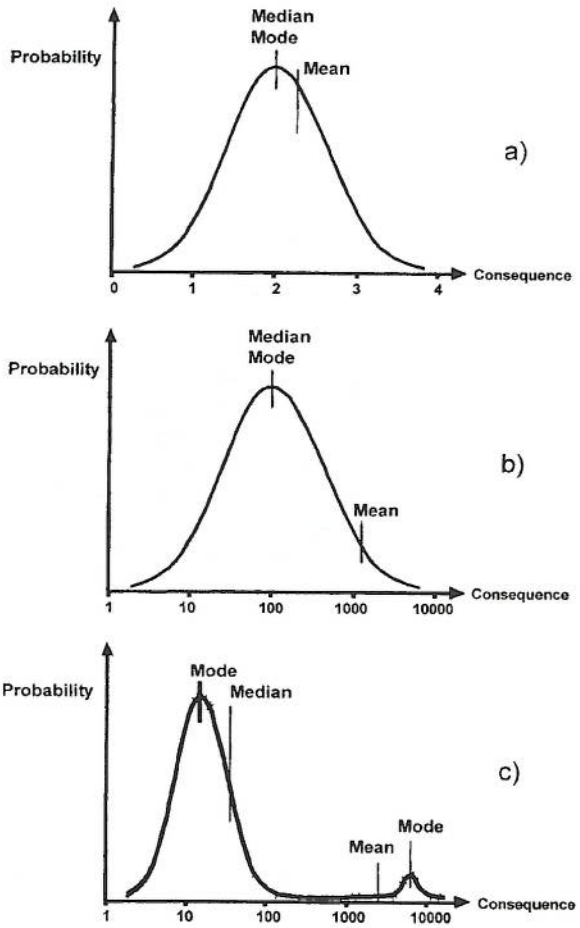


FIGURE 5. Schematic illustration of how the mean and other measures of central tendency vary with the form of the distribution. In decision-making, the mean estimate can be significantly affected by extremes within a distribution. This can particularly be the case when considering very long timecales when future events may be speculative.

from the facility to a representative member of the potentially exposed group at greatest risk. Typically, safety cases for disposal facilities express *distributions* of dose or risk, and this presents the problem of collapsing the distribution to a single value for comparison with the regulatory risk target. One approach is to present the arithmetic mean, or "expectation value" of the risk. Others include presentation of the median (50th percentile), the 90th or 95th percentiles, or the mode (Figure 5). The expectation value is sensitive to changes at the high-end of the distribution, and requires an arbitrary integration limit for distributions that cannot be integrated analytically. In the context of risks relating to long-term safety over hundreds of thousands of years, the expectation value has disadvantages in that the risk is calculated as a function of time for each of many sets of events (futures). Each future may involve different exposed groups, in which case, averaging across futures becomes inappropriate. Even for similar groups, estimated risks may be "diluted" if different futures give rise to peak risks at slightly different times (*32*).

Loss of information on the shape of a distribution when collapsed is especially important for highly skewed distributions (Figure 5b,c) where low probability, high consequence (extreme) events dominate the mean. These situations might arise from, say, the impact of extreme climate events. In Figure 5c, the distribution might represent the impact arising

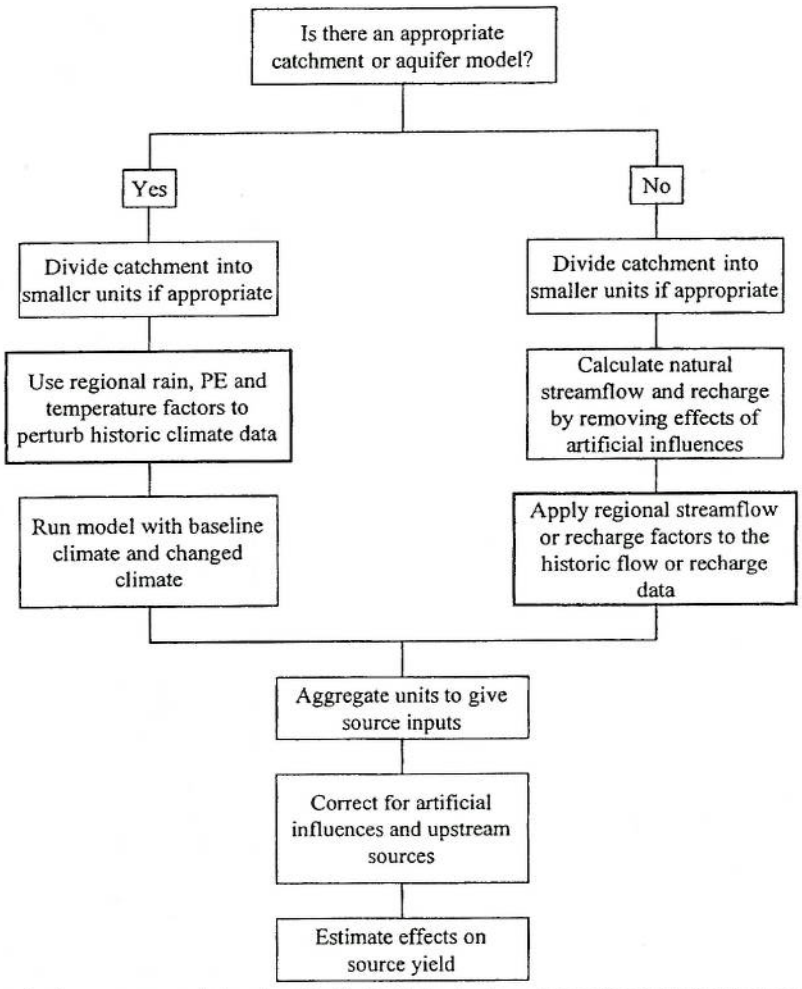


FIGURE 6. Methodology for the assessment of the potential effects of climate change on source yield. The figure summarizes for decision-makers the sequential methodological steps for estimating future water resource yields under the influence of climate change.

from normal behavior of a waste repository with high consequence events arising from, for example, possible future human intrusion. In such cases, use of the expectation value could be misleading unless information on the form of the distribution is presented, together with a discussion of the level of confidence attached to the risk estimates. Presentation of conditional risks and the separation of different types of uncertainty aid regulatory decision-making and may assist stakeholder dialogue (*34*) where "what-if" calculations are presented for different risk scenarios and futures.

Scenario-Based Approach to Management Decisions. The scenario approach is now in wide use for assessing the possible impacts of climate change, generally using the output of global climate models (GCMs) (*35*). While scenario-based analyses can be scientifically satisfying, their application to management decisions can sometimes be limited. The spatial and temporal resolution of the scenarios is often inappropriate for modeling impacts and arguably for the decision-process itself. Most business planning horizons are far shorter than the single time horizon used for climate change scenarios, which conventionally look to the 2020s or 2050s. Further, the current data from GCMs provide little information on changes in the frequency and magnitude of extremes, and it is often changes in the nature of this type of event that have the greatest impact. These uncertainties create problems where long-term financial investment is required, or where there is an aspect of irreversibility about a management decision. The lack of information on the probability of the scenarios, or the ability to provide a "best guess", compounds these problems. Use of a single scenario, be it the central estimate or the "worst case", may make good business sense but may not provide a basis for sound investment decisions because of the inherent model uncertainty (*36*).

One example of a scenario-based approach to asset management is the management of investments by the UK water industry. In 1996, the then Department of the Environment required the water industry to take account of climate change in its future asset management plans (*37*). Water resource managers required a rapid, strategic-level assessment of climate sensitivity, so that a range of climate futures could be applied to the water resource base, and impacts on regional supply compared (*38, 39*). Despite the uncertainties associated with climate change scenarios, a core set was used as a consistent basis for water resource planning to inform estimates of future investment, the potential need for water abstraction schemes and reservoirs, for example. The methodology developed (Figure 6) presents the user with a series of tasks selected according to the available modeling capability. Ideally, the water resource manager works with an appropriate hydrological model (catchment or aquifer) to assess resource yield. In these cases, the standard Intergovernmental Panel on Climate Change (IPCC)-recommended impact analysis could be carried out as in the left-hand trunk of Figure 6. The driving variables are rainfall, temperature, and potential evaporation. These are perturbed to represent future conditions, estimated

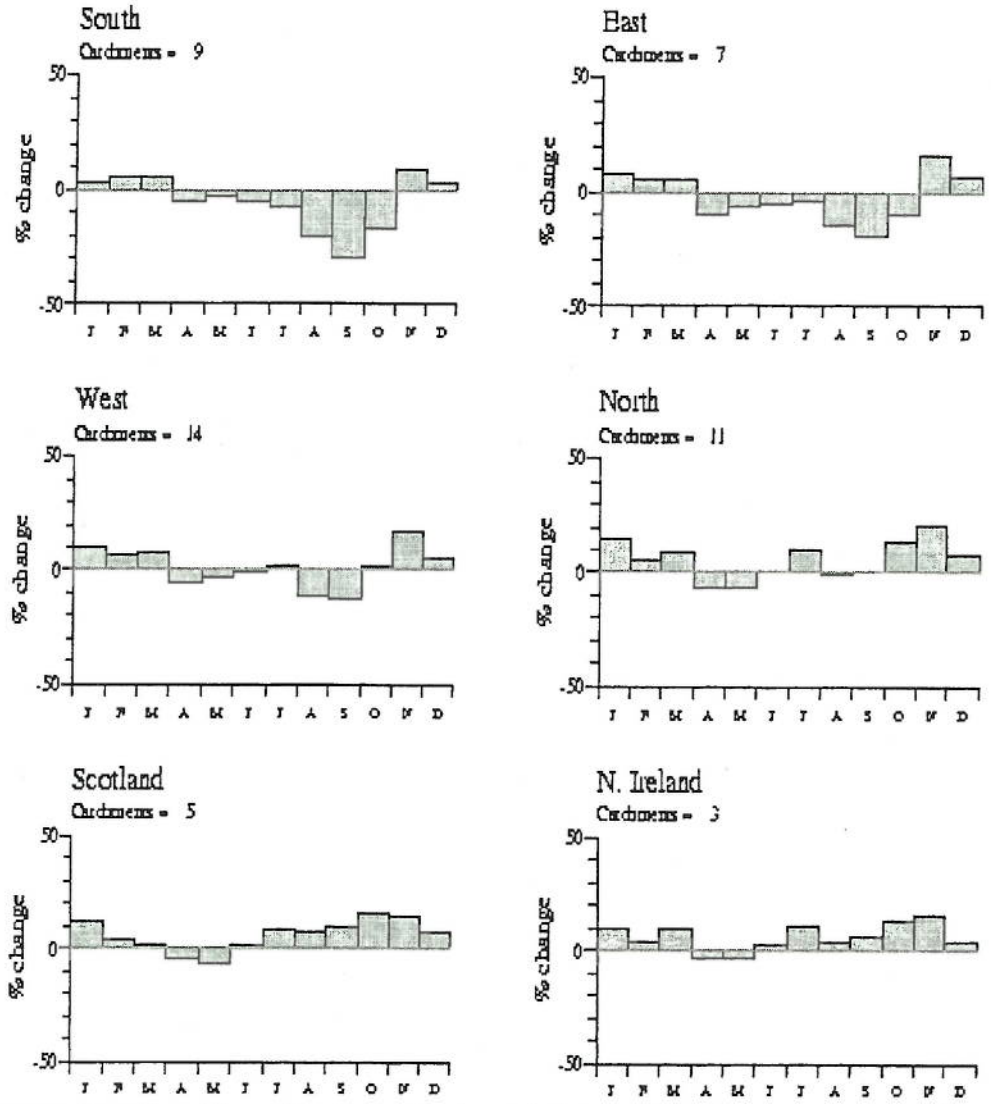


FIGURE 7. Average change in monthly runoff for the six UK regions under just one climate change scenario for the 2020s as compared to the 1961−1990 conditions. The schematics provide a visual impression of the potential impact of climate change in regional catchments. Decision-makers can apply these factors to historic data in determining the impacts of climate change on source yield (as in Figure 6).

monthly averages by the 2020s, according to the core set of scenarios. The model is run under perturbed conditions, and the resulting yield is compared with that under the current climate.

In practice, models exist for only a small proportion of supply sources, and considerable effort would be required to develop, calibrate, and apply them for all sources. Therefore, a fast-track, screening approach provided a broad indication of the vulnerability of source yields to climate change (*39*). This involved application of regional factors for changes in yield, from groundwater recharge and streamflow, to observed recharge and flow data. The UK was divided into six regions, broadly based on the boundaries of the UK Hadley Centre global climate model (*40*). For each region, flows were simulated in a number of catchments under current, and a range of possible, future climate conditions. The regional factors were then determined as the average changes in monthly flow. The regional factors in groundwater recharge were determined from the results of an aquifer recharge model run for a small number of groundwater-dominated catchments.

The result of this analysis was a set of perturbed flow series indicative of conditions under the changed climate of the 2020s. The results for one of the climate change scenarios, for the six regions, are presented in Figure 7, showing the average change in monthly runoff for the 2020s. The potential reduction in late summer/autumn runoff is clear in the South, as is the possible increase in flows throughout the year in northern England, Scotland, and Northern Ireland. What is not clear is the degree of variability between the scenarios. In some regions, runoff increased under some scenarios and decreased under others. Further, at present, it is not possible to highlight the "best-guess" scenario.

This approach provided water managers in the UK with a pragmatic tool for undertaking a rapid screening of the potential risks from climate change on water resources in the light of significant uncertainty. As with all scenario-based approaches, the methodology carries with it a number of assumptions and caveats, of which the decision-maker, water managers in this case, should be aware. Importantly, the regionally averaged factors hide a substantial amount of within-region variability but in this case, it was felt that to

further subdivide into smaller regions would considerably compromise practical application of the method.

Discussion

Risk assessment is one tool among many used to support decisions about managing the environment, within a broader framework of cost-benefit analysis. Others include environmental appraisal, multi-criteria analysis and game theoretical approaches (*41*, *42*). Further, the development of environmental risk frameworks is not new. Their value is in showing the relationships between different stages and components of the decision, and so they have an important role in improving the transparency of decisions. What is new is the increasing attempts made by risk analysts to cross-fertilize between different contexts of application. We have provided some examples of where such transfer of expertise is taking place. Others include (i) in the use of "risk registers" during hazard identification, initially developed for hazard and operability (HAZOP) studies in the chemical industries (*43*); (ii) the increasing use of formal expert elicitation techniques in environmental exposure assessment, adopted widely for the performance assessment of radioactive waste repositories (*44*); and (iii) the use of failure mode and effect analysis (FEMA) developed within the process industries, for the microbiological risk assessment of pathogens in the environment (*45*). Risk analysts increasingly work in multidiscipline teams to address risk problems, the characteristics of which often extend beyond the technical characterization of the hazard under study. The Environment Agency's National Centre for Risk Analysis and Options Appraisal is making important strides forward in this regard by developing more integrated approaches. Among the interdisciplinary "transfers" being addressed here are (i) the role of uncertainty in climate change impact assessment and in environmental appraisal, which have historically been impact- rather than truly risk-led; (ii) developments in our understanding of environmental harm, considering damage characteristics such as latency, reversibility, and heterogeneity that are often disregarded in risk analysis; and (iii) the importance of "framing" during the problem definition stage of risk assessment and, in particular, the influence of stakeholder agendas in setting the context for environmental risk assessment.

The emergence of the social issues agenda as a key driver for sustainable development in the UK is having a real impact on environmental decision-making. Along with the US and the rest of Europe, the UK is witnessing a move toward integrated decision-making, taking jointly into account the social, environmental, natural resource, and economic aspects of environmental management problems. Flood and coastal defense provides an excellent illustration of where these considerations collide. For those designing to a particular standard, or appraising the risks, costs, and benefits of alternative options for defense structures, the type of joint probability analysis described above provides a comprehensive description of loads and failure mechanisms leading to improved solutions. The benefits are economically robust solutions more closely matched to an improved risk analysis of the imposed loads. The approach is being widely applied, particularly for design of structures along the coast and in estuaries.

This move toward integration is forcing a re-appraisal of the capabilities and limitations of individual decision tools (*46*). The practical nuances and differing emphases of individual tools in terms of the level of detail at which they are optimally applied, the extent to which they address the various aspects of environmental decisions, and the degree to which they address uncertainty and wider societal values are all under debate. In response, decision-makers are developing a "palette" of decision analysis tools for dealing with individual risk problems (*47*). There are also signs that the concerns of nongovernmental organizations with respect to environmental risk assessment are being addressed in part by greater stakeholder participation in risk assessment processes (*48*–*50*). It is clear that the integration being experienced between risk analysts now needs to progress with practitioners of other appraisal tools in the broader context of sustainable development. One challenge for risk analysis as a discipline is how to respond to this policy agenda while maintaining and developing an analytical rigor that can address environmental issues of deep uncertainty.

Environmental regulators have a range of responses at their disposal for managing pressures from, or on, the environment. Modern approaches to environmental regulation attempt to match the regulatory response to an operator's performance and attitude, using influence and education to deliver outcomes, wherever possible underpinned by regulation. In practice, this means using a minimum of administration and bureaucracy to greatest effect, retaining firm and proportionate prosecution and enforcement policies and standardizing and simplifying decisions where possible. The move toward "risk-informed" regulation that allows the targeting of inspection and monitoring effort has been welcomed by government and industry (*21*, *23*, *51*) and, in principle, allows for resources to be released for other influencing activities. The Environment Agency's experience in applying risk-ranking systems for individual business sectors is now being extended to the recently introduced integrated pollution prevention and control (IPPC) regime that offer an opportunity to apply risk appraisals within and between business sectors. Notwithstanding the considerable challenge of comparing between quite disparate risks, the application of these systems may ultimately offer a "bottom-up" approach to setting to regulatory priorities that can complement the "top-down" assessments informed by state of the environment reporting.

Finally, the need to be explicit about uncertainty in risk analysis (*52*) has long been recognized and is a recurrent theme for policy analysts and risk practitioners. Being clear about those uncertainties that can be addressed through more observation and experiment and those that cannot is a start, but clearly the debate needs to deliver us to a point where we can be more comfortable about decision-making under circumstances of complexity and extreme uncertainty. Gradually, this is happening. Developments in risk analysis are influencing policy directions, informed by the analysis described above for water resource planning, the Environment Agency's new water resources strategy assumes no change in the national water supply over the next 20 years, there being sufficient current or planned capacity. Instead, the Agency has chosen to emphasize the demand side of the water balance, both in terms of changes in demand due to climate but also other socio-economic factors. Practical, accessible tools for decision-makers (*53*) like those described that can be integrated alongside accepted business and planning processes are required if we are to make genuine progress.

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Characterizing Environmental Harm: Developments in an Approach to Strategic Risk Assessment and Risk Management

Simon J. T. Pollard,[1]* Ray V. Kemp,[2] Mark Crawford,[2] Raquel Duarte-Davidson,[1] James G. Irwin,[1] and Roger Yearsley[1]

Environmental policymakers and regulators are often in the position of having to prioritize their actions across a diverse range of environmental pressures to secure environmental protection and improvements. Information on environmental issues to inform this type of strategic analysis can be disparate; it may be too voluminous or even absent. Data on a range of issues are rarely presented in a common format that allows easy analysis and comparison. Nevertheless, judgments are required on the significance of various environmental pressures and on the inherent uncertainties to inform strategic assessments such as "state of the environment" reports. How can decisionmakers go about this type of strategic and comparative risk analysis? In an attempt to provide practical tools for the analysis of environmental risks at a strategic level, the Environment Agency of England and Wales has conducted a program of developmental research on strategic risk assessment since 1996. The tools developed under this program use the concept of "environmental harm" as a common metric, viewed from technical, social, and economic perspectives, to analyze impacts from a range of environmental pressures. Critical to an informed debate on the relative importance of these perspectives is an understanding and analysis of the various characteristics of harm (spatial and temporal extent, reversibility, latency, etc.) and of the social response to actual or potential environmental harm from a range of hazards. Recent developments in our approach, described herein, allow a presentation of the analysis in a structured fashion so as to better inform risk-management decisions.

KEY WORDS: Environmental harm; options appraisal; strategic risk assessment

1. INTRODUCTION

Conventionally, harm to the environment is assessed by reference to the magnitude of the impact, usually by reference to the exceedence, or otherwise, of environmental quality standards.(1) The use of standards in isolation has recognized limitations.(2) They may not take into account other important characteristics of the damage such as its delayed onset, its irreversibility, or the uniqueness of the environmental resource being damaged. Nor do they necessarily take account of the values society places on different components of the environment. The use of standards as surrogates for environmental harm has, arguably, led to an implicit assumption that any exceedence of the standard will result in a detriment. This is rarely, if ever, the case because derivation of

[1] Environment Agency, Environmental Policy—Centre for Risk and Forecasting, King's Meadow House, Reading, UK.
[2] Galson Sciences Limited, Oakham, Rutland, UK.
* Address correspondence to Simon J. T. Pollard, Integrated Waste Management Centre, School of Industrial and Manufacturing Science, Cranfield University, Building 61, Cranfield, Bedfordshire, UK; s.pollard@cranfield.ac.uk.

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the standard involves margins of safety in the form of uncertainty factors intended to act in a precautionary fashion.[2,3]

Two situations illustrate the limitations of a standard-based approach: (1) managing harm from low probability, high consequence events often requires an understanding of the characteristics of harm beyond its potential magnitude so that good contingency measures can be set in place, should the consequences be realized; and (2) at a strategic level, the comparison of risks is problematic because there is no accepted way of comparing the harm from, say, flood damage to that from the historic contamination of soils, or that from stratospheric ozone depletion to the long-term harm to an important aquifer from historic landfilling. In these circumstances, a purely technical approach proves too restrictive, and, with respect to valuing the damage, monetization in isolation fails to capture the societal aspects of harm beyond an economic estimate of the stock at risk.

The Environment Agency of England and Wales has long recognized the need for a framework for the multidisciplinary analysis of environmental risks at a strategic level. Our initial work in this area[4,5] focused on the development and illustration of a semi-quantitative risk tool. While this proved useful for assessing technical risk issues at the regional scale where detailed supporting information was available, the Agency recognized a need to develop this further and incorporate a consideration of social and economic damage alongside the physical harm to the environment—aspects more challenging to quantify. This broader appreciation of the characteristics of environmental risk becomes critical to strategic decision making and particularly important for policymakers prioritizing risk issues.[6–11] The key methodological difficulty is the apparent incommensurability of environmental risks—that is, the practical challenge of "comparing apples with oranges."

Policymakers, regulators, and agencies face this challenge directly in their work on sustainable development, environmental strategy development, and "state of the environment" reporting.[7,8,12–14] Typically, strategic assessments apply the Organisation for Economic Cooperation and Development[15] pressure-state-response (P-S-R) model or the derived drivers-pressures-state-impacts-response (DPSIR)[16] framework to describe the interactions between society and the environment (Fig. 1). For risk practitioners, attempting to assess and prioritize the risks, rather than impacts (consequences), from a large set of diverse environmental threats, the methodological challenge comes in characterizing the actual or potential harm meaningfully in order to design well-reasoned and defensible policy and regulatory responses.

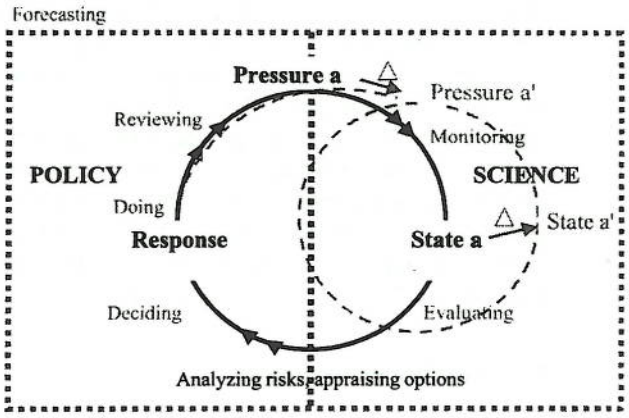


Fig. 1. The pressure-state-response model for "state of the environment" reporting. Environmental management involves environmental monitoring, evaluating data, making decisions on how to act, and reviewing those decisions. Monitoring and evaluating data (assessing the state of the environment) results in an understanding of environmental pressures and the identification of a set of risks from which options for risk management can be identified. Strategic risk-assessment tools can help prioritize these risks. Following on round, the selection of policy options (responses) may result in the reduction of pressures (pressure a to pressure a′) on the environment and an improvement in the state of environmental quality (state a to state a′).

2. STRATEGIC RISK-ASSESSMENT METHODOLOGY

2.1. Overview

We have reported developments in our approach to strategic risk assessment previously.[3–5,14,17,18] In the second phase of this research described here, we focus on identifying technical and social characteristics of environmental harm (e.g., severity, reversibility, dread, equity) using key "attributes" of the harm, informed, in part, by the approach to risk management described by the German Advisory Council on Global Change[9] and discussed recently in this journal.[11] Harm is conventionally assessed by reference to its magnitude, but clearly has wider dimensions. In terms of the relationship between exposure to a hazard and the harm caused (the dose-response relationship) we recognize the attributes of harm per unit exposure (potency), the lag between exposure and response

(latency), and the reversibility of harm. These multidimensional aspects of harm can be equally applied to social and economic impacts (e.g., economic recovery) and are important risk characteristics that inform decisions on how to manage risk. Practitioners applying these broader aspects of harm to environmental decision making seek to balance a sophistication of approach, so as to incorporate the multidimensional aspects of risk with a simplification of the method so that their risk tools can be widely used.

2.2. Recent Developments

In this article, we describe developments in the characterization of environmental harm. For the purpose of informing which harm characteristics drive the risk from a range of environmental hazards, harm attributes are "scored" on a semiquantitative 1–5 scale and displayed schematically. The approach is informed by an elicited rather than a formal analytical assessment of risk using an expert group. At this developmental stage in the strategic risk-assessment tool design, we have not directly engaged broader stakeholder involvement. Societal concerns are surrogated for using the representative views of environmental policy experts who day-to-day manage a wide range of communications on individual environmental issues from stakeholder and special interest groups. The analyses generated do not substitute for more detailed studies that will be required for individual issues, but they offer the advantages of a clearer depiction and communication of risk characteristics and a clearer basis for the selection of risk-management strategies for complex risks within a systematic and comparative framework.

In practice, the initial identification of the risk issues to be assessed and the risk characterization and ranking of the harm attributes requires an informed understanding of the attributes of harm, their meaning, and a familiarity with the risk issues. Eliciting scores for individual harm attributes requires a group with expertise across the physical, social, and economic aspects of the harm being assessed, supported by a facilitator with experience of the tool and its application. The group needs to consider the accepted heuristic biases and errors in eliciting subjective estimates.[19] The tool can be used to assist in two key areas in the Environment Agency's approach to risk assessment and management.[20,21] (1) In *risk screening and prioritization*, harm attribute scores can be examined in isolation and in combination using schematics to help identify and prioritize key risk issues from various perspectives. Different presentational styles can be adopted to help inform decisions for a range of audiences (e.g., senior managers, affected communities, technical groups). (2) In *options appraisal and risk management*, the attribute scores and schematics help identify key contributors to the risk and which risk-management actions might be most effective.

Application of the tool is summarized in Fig. 2. Subsequent figures provide the detail. The selection of risk issues to be assessed, the identification of key receptors, and the basis for assigning scores to each risk issue are recorded using a predefined format.[18] Users record and justify a scoring of the attributes, promoting compatibility between multiple applications of the framework. Risks to be assessed are described in terms of: (1) the hazard (a property or situation that could lead to harm), e.g., flooding, radon; (2) the pressures that result in the hazard, e.g., increased traffic, diffuse pollution in agriculture; and (3) the key receptors that can potentially be harmed by the hazard and the consequences of the harm, to allow the characterization of the risk issue.

2.3. Harm Attributes and Their Ranking

An initial classification of harm attributes and scoring scales has been reported.[3,5,17] Each attribute represents a distinct characteristic of harm relevant to the assessment. Grouping harm characteristics into classes assists in presentation and in use of the tool for risk prioritization and options appraisal. A refined list of attributes is presented in (Table I for the physical properties of the harm (attributes classed A1–A11), and the social response to the harm (B1–B6). Within these two classes, attributes are further subcategorized.

The value of the physical damage associated with each risk issue is assessed assuming the harm from the hazard is realized (the scoring of Attribute A1—"stock at risk"). Because of a lack of comparative data and widely varying estimates of the costs of environmental damage, only an estimate of the value is possible. The probability of damage being realized and the assessed value of physical damage (A1) are presented on a risk characterization (probability-value) schematic similar to that described by Klinke and Renn[11] (Fig. 2). Different types of "stock at risk" (A1) information can be used, such as the economic cost of the consequences of each risk, the number of receptors affected, budgetary provisions per year to manage the risk. A scoring report encourages this information to be recorded, offering the potential for

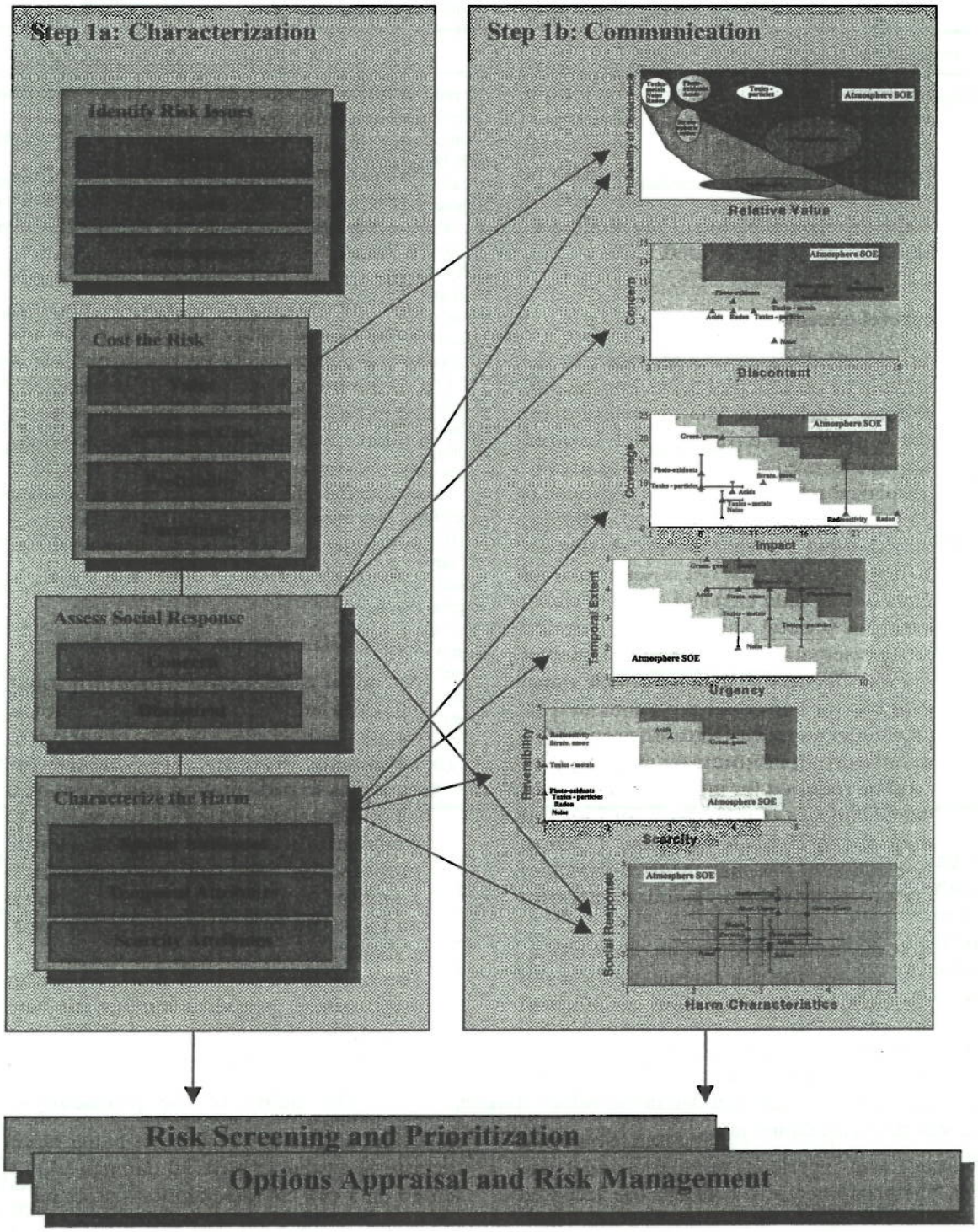


Fig. 2. Summary of the strategic risk-assessment tool. The risk screening and prioritization stages are depicted. Individual schematics are expanded upon below. The process focuses on risk characterization (Step 1a) using a set of harm attributes (Table I) and risk communication. During risk characterization, attributes are ranked and depicted using a series of schematic formats (Step 1b). While there remains uncertainty in the rankings, the overall risk characterization (probability of occurrence vs. relative value) allows prioritization of issues and the design of risk-management strategies. Communication issues associated with these schematics are discussed below.

Table I. Classification of Harm Attributes Used in the Strategic Risk-Assessment Tool

Attribute Class	Subcategory	Attribute Name, Code, and Description
Physical	Value characteristics	"Stock at risk" (A1): a valuation (either physical numbers of receptors or economic valuation) of the overall harm.
		"Knock-on (indirect) effects" (A2): reflects that harm to one receptor may affect the well-being (physical, social, or economic) of another.
	Impact characteristics	"Spatial extent" (A3): the overall area over which harm is experienced.
		"Heterogeneity" (A4): reflects that within the overall area denoted by the "spatial extent," there may be heterogeneity in terms of the harm experienced (a "patchiness" of harm).
		"Sensitivity of receptor" (A5): reflects the proportion of receptors exposed that are likely to exhibit harm.
		"Severity of effect" (A6): the general (rather than worst-case) physical effect on an individual sensitive receptor only.
	Temporal characteristics	"Temporal extent" (A7): the duration over which the harm will be experienced.
		"Latency" (A8): considers the period of time between exposure and environmental harm being realized (delayed onset of harm).
		"Accumulation" (A9): reflects changes in the rate at which the harm is realized.
	Scarcity characteristics	"Reversibility" (A10): whether the effects of the harm are reversible and, if so, over what timescale.
		"Scarcity" (A11): reflects the abundance of the receptor, and is used to consider the loss of cultural resources, as well as physical environments.
Social	Concern characteristics	"Dread" (B1): reflects that society can have an aversion to, or fear of, a harm that may be largely unrelated to its physical nature.
		"Unfamiliarity" (B3): provides an assessment of concern that may arise out of a low degree of knowledge and understanding of the harm.
		"Notoriety" (B6): reflects the potential for raised awareness of, and anxiety about, the harm via the media and other channels of information.
	Discontent characteristics	"Unfairness" (B2): reflects the discontent that may arise from the inequity or unfairness of a harm's distribution.
		"Imposition" (B4): reflects the social value afforded by the degree of personal control over the harm.
		"Distrust" (B5): captures the consequences of a lack of trust in the characterization of the harm or in those responsible for its management.

a database of applications and improved consistency with time. It is necessary to specify: (1) the probability of each risk issue, taking into account the probability of the initiating event(s), of the receptors being exposed to the hazard and the harm being realized from the exposure, on a scale of high, medium, and low; (2) the uncertainty associated with each value estimate, in terms of high, medium, and low levels of confidence; and (3) whether any knock-on (indirect) effects of the harm are included in the value estimate, or whether a multiplier needs to be identified and applied where such indirect effects are substantial (the scoring of Attribute A2—"knock-on effects").

For each risk issue, each of the remaining attributes is given a semiquantitative score using a simple 1–5 Likert scale,[22] where 1 represents a low score for that attribute and 5 a high score. Descriptive guidance on the scoring scale for each attribute has been developed as a means for promoting consistency between applications.[18] Schematic presentation of the risk characterization assists in the communication and application of the results to decisionmakers. A number of configurations summarized in Fig. 2 are now discussed.

2.4. Presentation

2.4.1. Probability-Value-Response Schematic

The utility of the probability-value-response schematic is in communicating risk prioritization to senior decisionmakers.[9,11] Strategic risk issues are presented in terms of the likely probability of the occurrence of harm, the relative value of the resultant damage, the associated uncertainty, and the social response to the risk (Fig. 3). The x-axis presents relative value, calculated from (A1 × A2). The y-axis presents the probability of occurrence of the risk, on a scale of high, medium, or low. Risks are presented as representative areas on the schematic to reflect the

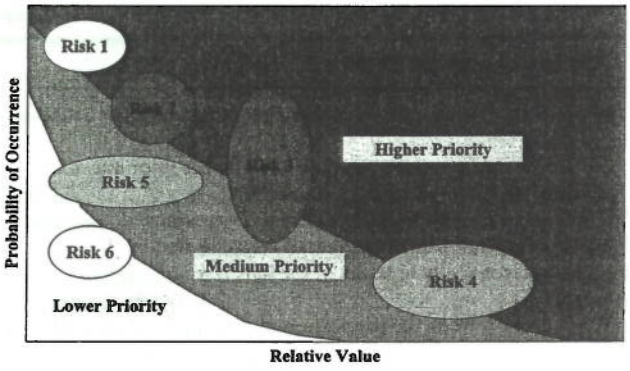


Fig. 3. Probability-value-response schematic. This schematic places emphasis (i.e., priority) on high probability-high value risk issues, with the distinction between issues with similar value and probability being provided by social responses to the risk. Ellipse shapes indicate the relative uncertainty in probability or value assignments.

uncertainty in the scoring and here in dark, medium, and light shading to reflect the social response to the issue.

2.4.2. *Physical Harm—Social Response Schematic*

A useful method of showing the social and physical valuation of the harm associated with each risk issue is to present "B" attributes (social response) against mean "A" attribute (physical harm) scores, each presented with their standard deviations of the elicited scores.

The results of applying the approach to a range of air pollution issues and averaging the A and B scores are illustrated in Fig. 4.[3] Subsequent pilot applications of the tool will be published separately. The risk issues in Fig. 4 vary in terms of their positions relative to each other for both the A and B attributes. Radioactive releases scored most highly in terms of societal concern, followed by stratospheric ozone depletion and climate change resulting from greenhouse gas emissions. The lowest B attribute scores were for nuisance pollutants such as noise and radon, the latter influenced by low scores for imposition and distrust. Consideration of the physical attributes scored greenhouse gases most highly, followed by stratospheric ozone depletion and radioactivity. Not surprisingly, the lowest A score was for nuisance pollutants such as noise. Considering the elicited scores that generate the schematic, the physical harm scores show greater variability. For example, A3 heterogeneity is low because, although low-level radioactive deposition may be widespread, only localized farming areas may be affected, as in the case of Chernobyl. Similarly, affected ecosystems are not necessarily unique and A7

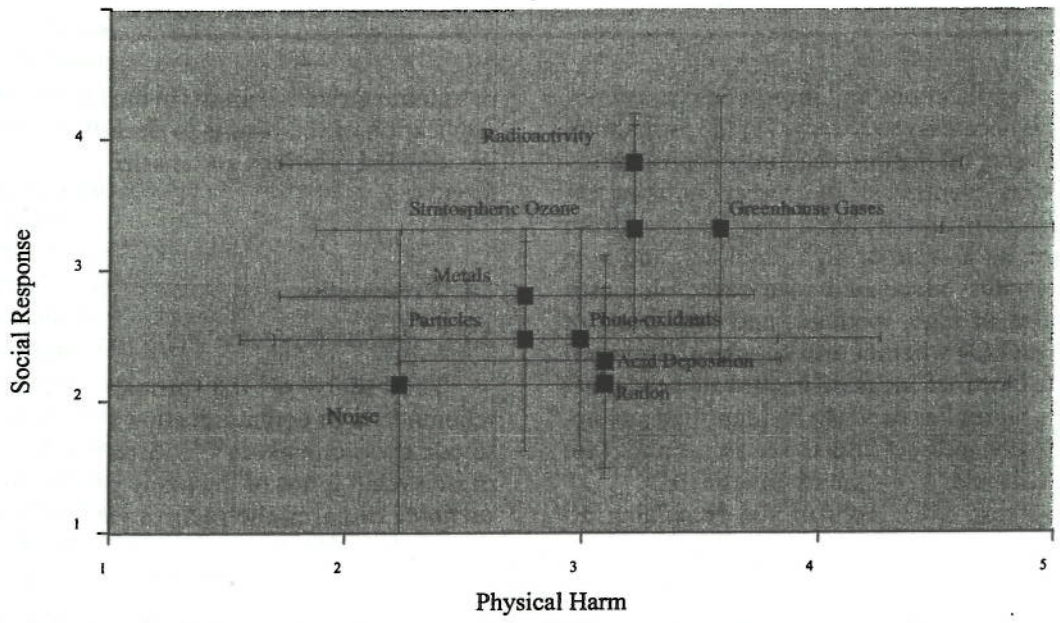


Fig. 4. Character-response schematic for atmospheric pollutants. Error bars represent the standard deviation around the mean score and reflect the variability between all of the attribute scores. The characterization is for illustrative purposes only, and does not necessarily reflect an Environment Agency position.

therefore attracts a low score. In contrast, because of the latency of the onset of cancer, the A4, temporal extent, score is high as is A6 for irreversibility.

2.4.3. *Social Response Schematic*

Similarly, a social response schematic can be generated (Fig. 2) to help users identify risk-management techniques appropriate to social priorities. The B attributes are grouped to reflect the potential level of personal concern ("dread," "unfamiliarity," and "notoriety" [B1 + (add) B3 + B6]), and the potential level of discontent ("unfairness," "imposition," and "distrust" [B2 + (add) B4 + B5]). These two groups are plotted on the *y*- and *x*-axes, respectively. The schematic is divided into areas of low (light), medium (medium), and high (dark shading) response. The area that an issue occupies on this schematic can be transposed to the probability-value schematic for comparison with other risk issues (Fig. 3).

2.4.4. *Harm Characteristics Schematic*

If required, the remaining attributes (A3–A11) can be presented on three harm characteristics schematics (not shown), allowing a more in-depth analysis of various subcategories of harm and reflecting the three main groups of characteristics: (1) the *impact characteristics schematic* represents the coverage of the harm ("spatial extent" × "heterogeneity" [A3 × A4]) against the impact of the harm ("sensitivity of receptor" × "severity of impact" [A5 × A6]); (2) the *temporal characteristics schematic* represents the temporal extent of the harm ("temporal extent" [A7]) against the urgency of the harm ("latency" + "rate of accumulation" [A8 + A9]); and (3) the *scarcity characteristics schematic* represents "reversibility" (A10) against "scarcity" (A11).

3. DISCUSSION

Two practical principles for all risk tools[23] are to ensure the problem drives the analysis (avoiding a paralysis by analysis) and to make the analysis as simple as it needs to be (avoiding misplaced confidence in oversophisticated techniques). The key benefit of this strategic tool is in its characterization of risk: What kind of risk is this? What drives it as a risk issue? A characterization of a diverse set of strategic risk issues using this approach can inform the consideration of risk-management options and help identify risk-management strategies. By illustration, we consider below various strategies for managing the risks of environmental harm, categorized in Table II. Risk-management strategies appropriate to reducing certain risks from high to low priority on the schematics shown above have also been developed through this work.[18]

Table II. Categories of Risk-Management Techniques

Management Category	Examples
Communication	Stakeholder dialogue
	Information reporting
	Stakeholder involvement in decisions
Education	School and adult education
	Training
	Technical assistance
Technological intervention	Research into basic processes
	Development of technology to reduce or counter harm
	Development of alternative technology
	Monitoring
Environmental management	Management systems (ISO 14001, EMAS)
	Environmental auditing
Market incentives	Pollution levies and charges
	Tradable emissions
	Subsidies
Regulation	Environmental standards
	Technology-forcing regulations
	Product bans
	Permitting
	Emergency procedures
Enforcement	Liability
	Compulsory insurance
Cooperation	International collaboration
	Interorganizational action
	Regulator-polluter dialogue

In addition to the risk-management strategies set out in Table II, it is helpful to focus on conventional policy tools for risk reduction to which certain types of risk are amenable. A typology of four key policy tools for environmental risk management is identified here that applies across the range of potential environmental harm issues. The approaches are not mutually exclusive, but we can broadly characterize the types of risk issue that these approaches commonly applied to in terms of position on the probability-value schematic (Fig. 3), which is itself composed from a synthesis of the attribute scores elicited using the tool. The four policy tools (Fig. 5) are:

1. *The precautionary approach*—often applied to low-to-medium probability risks with potentially severe, often uncertain, and irreversible consequences, usually with high latency. Often considered for issues of high

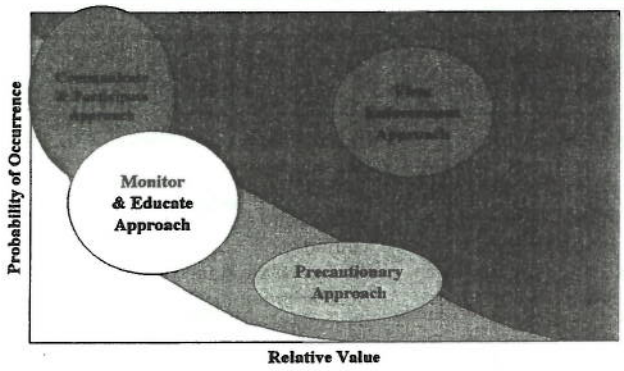


Fig. 5. Policy tools for risk management mapped onto the probability—relative value—social response schematic.[9,18]

social concern, such as nuclear energy and endocrine disruptors.[9,11]

2. *Firm enforcement*—applied to well-understood, high-probability, high-consequence risks. Usually also of high social concern—for example, the control of processes involving hazardous substances.
3. *Risk communication and participatory decision making*—where there is demonstrable high social concern, although the physical consequences may be low with low to high probability.
4. *Environmental monitoring and education*—where uncertainty over the probability and consequence are coupled with low-to-moderate social concern.

To further assist regulatory decision making, these policy tools (Fig. 5) can themselves be considered alongside the suite of regulatory approaches available for environmental risk management[24] (Fig. 6). By linking strategic risk-assessment output with the available policy options and accepted regulatory processes, risk-management programs can be developed that respond to the technical, social, and economic dimensions of environmental harm.

Attempts to map and categorize decision uncertainty along the lines of the approach described here[9,11] borrow fundamentally from the work of Funtowicz and Ravetz on decision stakes, uncertainty, and the inclusion of trust, liability, and consent.[25] The application of these holistic approaches to the comparative analysis of apparently "incommensurate" strategic risk issues within science and policy debates, in state-of-the-environment reporting, for example, brings additional complexity, as do attempts to "score" (rank) and aggregate risk attributes in a defensible manner.[26,27] The contribution of this work has been to offer refined descriptions of environmental harm. Through a series of case studies, we intend to develop our presentation of incertitude in these analyses and consider how broader stakeholder input might be better incorporated into these analyses. Other workers[28,29] are making valuable contributions in this regard. Summarizing the New Jersey Comparative Risk Project, an analytic-deliberative project evaluating and attempting to prioritize 88 environmental risk problems, Andrews *et al.*[28] describes the results of applying a range of scoring systems within the context of a resource limited risk ranking exercise. Their findings, specifically with respect to the tracking and presentation of types of uncertainty within these exercises, offer further practical developments and advances for the approach described in our work.

4. CONCLUSIONS

The strategic risk-assessment tool provides a basis for comparing disparate risk issues by identifying common attributes of the environmental harm associated with the risk issues and scoring these attributes on a common scale. It helps to formalize a strategic analysis and provide traceability to decisions such as responses to risk issues raised by state of the environment reports and the development of strategic plans. However, the output cannot be used to prioritize issues "at a glance." It is designed for technically aware users to analyze different issues, attach priorities, and communicate such information to nonexpert groups. Furthermore, it is but one among an array of existing strategic environmental appraisal tools available to decisionmakers. This said, the tool offers the advantages of an unweighted and essentially qualitative approach, although there is the potential for more quantitative expressions of analyses if the data are available. During development, the complexity of the presentation of the results has increased from one to several schematics. This reflects a desire to avoid oversimplification and recognition of the range of information that needs to be presented to inform regulatory decisions on risk management.

The additional schematics break out the attributes into similar groups or types of information, helping to identify the key attributes of each risk issue that need to be focused on by risk-management programs. Consequently, the underlying documentation justifying the scoring is important in providing a sound basis for analysis and presentation of the outputs.

Given the above discussion, strategic tools of this nature are necessarily imperfect and the analyses they

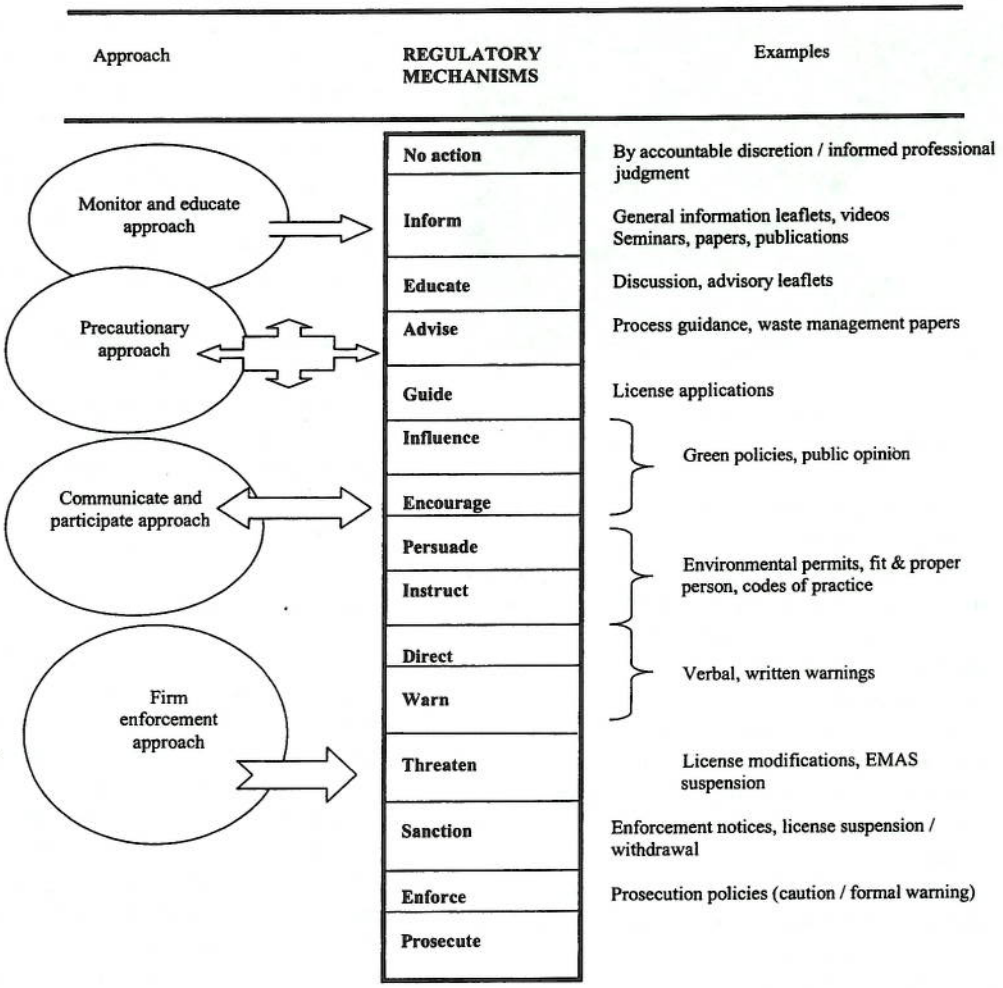


Fig. 6. Mapping of risk-management policy tools across the suite of mechanisms available for effective environmental protection.[24]

offer is only as good as the regulatory and policy decisions they inform. Notwithstanding the drive to develop practical tools and techniques that assist us in complex decision making, risk management should still reflect sensible and meaningful conclusions rather than the theoretical perspectives that may run counter to sound judgment.[30]

A structured elicitation workshop approach to using the tool was used and although more time-consuming than expected, proved more deliberative and enlightening than participants had anticipated. This aspect may be one of the most significant benefits of applying such a tool. Notwithstanding these limitations, development of the approach has allowed us to accommodate:

- inclusion of physical, social, and economic values of environmental harm without contentious weighting;
- methodological flexibility to allow for the lack of available or suitable quantitative data to characterize the environmental harm;
- broadness to allow the consideration and comparison of a diverse range of issues with differing associated environmental harm and differing levels of risk;
- uncertainty in, and lack of knowledge about, the nature and extent of the environmental harm;
- positive support of decision making and the promotion of traceability and transparency in decisions;
- improved communication of findings to different audiences with different needs and familiarity; and
- a balance between oversimplification and overcomplication in order to achieve all of the above.

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Fugacity modelling to predict the distribution of organic contaminants in the soil:oil matrix of constructed biopiles

Simon J.T. Pollard [a], Rupert L. Hough [a,d], Kye-Hoon Kim [a,e], Jessica Bellarby [b], Graeme Paton [b], Kirk T. Semple [c], Frédéric Coulon [a,*]

[a] *Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield MK43 0AL, UK*
[b] *Department of Plant and Soil Sciences, School of Biological Sciences, Cruickshank Building, University of Aberdeen, Aberdeen, Scotland AB24 3UU, UK*
[c] *Department of Environmental Sciences, Lancaster University, Lancaster, LA1 4YQ, UK*
[d] *Soils Department, The Macaulay Institute, Craigiebuckler, Aberdeen AB15 8QH, UK*
[e] *The University of Seoul, Department of Environmental Horticulture, 90 Jeonnong-dong, Dongdaemun-gu, Seoul 130-743, South Korea*

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Abstract

Level I and II fugacity approaches were used to model the environmental distribution of benzene, anthracene, phenanthrene, 1-methylphenanthrene and benzo[*a*]pyrene in a four phase biopile system, accounting for air, water, mineral soil and non-aqueous phase liquid (oil) phase. The non-aqueous phase liquid (NAPL) and soil phases were the dominant partition media for the contaminants in each biopile and the contaminants differed markedly in their individual fugacities. Comparison of three soils with different percentage of organic carbon (% org C) showed that the % org C influenced contaminant partitioning behaviour. While benzene showed an aqueous concentration worthy of note for leachate control during biopiling, other organic chemicals showed that insignificant amount of chemicals leached into the water, greatly reducing the potential extent of groundwater contamination. Level II fugacity model showed that degradation was the dominant removal process except for benzene. In all three biopile systems, the rate of degradation of benzo(a)pyrene was low, requiring more than 12 years for soil concentrations from a spill of about 25 kg (100 mol) to be reduced to a concentration of 0.001 $\mu g\, g^{-1}$. The removal time of 1-methylphenanthrene and either anthracene or phenanthrene was about 1 and 3 years, respectively. In contrast, benzene showed the highest degradation rate and was removed after 136 days in all biopile systems. Overall, this study confirms the association of risk critical contaminants with the residual saturation in treated soils and reinforces the importance of accounting for the partitioning behaviour of both NAPL and soil phases during the risk assessment of oil-contaminated sites.
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Keywords: Biopiling; Bioremediation; Fugacity; Modelling; Organic contaminants; Oil

1. Introduction

Constructed biopile technology (Battelle Environmental restoration department, 1996) is one means of reducing risks to human health and environment from soils contaminated with hydrocarbons. Risk reduction is heavily dependent on the physicochemical behaviour of risk critical compounds in the oil–soil matrix, and on their bioaccessibility and bioavailability to microorganisms (Doick et al., 2005; Allan et al., 2006). We have long been concerned with the environmental fate, partitioning and toxicity of risk critical compounds within hydrocarbon-contaminated soils (Pollard et al., 1992, 1999; Zemanek et al., 1997a,b; Whittaker et al., 1999; Pollard et al., 2004; Brassington et al., 2007). In these soils, an oil–soil matrix is universally present as the principal source of the organic contaminants that

* Corresponding author. Tel.: +44 (0) 1234 750 111; fax: +44 (0) 1234 751 671.
E-mail address: f.coulon@cranfield.ac.uk (F. Coulon).

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drive risk assessments (e.g. benzene, benzo(a)pyrene) and remedial actions at these sites.

However, within exposure assessment models for hydrocarbon-contaminated sites, the partitioning of risk critical compounds to their host matrix, the oil (Boyd and Sun, 1990; USEPA, 1991; Walter et al., 2000; Heyes et al., 2002) is rarely represented. As an oil matrix weathers, it develops into a more condensed, asphaltenic structure (Westlake et al., 1974) representing, in principle, an even stronger partition medium for contaminants in weathered hydrocarbon matrices and their post-treatment residues. Further, the oil becomes physically entrained within the soil matrix over time and hydrophobic contaminants are increasingly sequestered through partitioning into soil organic matter and/or diffusion into nanopores (Huesemann et al., 2005). As a result, contaminant molecules are released very slowly into the aqueous phase of the oil–soil matrix (Pignatello and Xing, 1996; Hatzinger and Alexander, 1997; Huesemann, 1997; Alexander, 2000). The rate of contaminant biotransformation in aged soils is thus limited by the rate of release from the matrix (Huesemann et al., 2003, 2004).

The application of fugacity modelling to the challenges of solid wastes is increasing. Previous applications include its use for directing site remediation decisions (Pollard et al., 1993; She et al., 1995), for quantifying vapour emissions from contaminated sites (Mills et al., 2004), and to predict the fate of organic compounds at landfill sites (Kjeldsen and Christensen, 2001; Shafi et al., 2006). However, there have only been limited attempts to include the source term (e.g. oil) for organic waste matrices (Nieman, 2003). Here, we investigate the capacity of oily waste source terms to act as a sink for priority contaminants within the oil–soil matrix of a biopile during bioremediation. Our research is part of an ongoing investigation by a research consortium (PROMISE) to place biopiling within a risk management framework and improve end-user confidence in this technology. Level I and II fugacity models were developed that included four phases within the soil matrix, namely: air, water, mineral soil and non-aqueous phase liquid (NAPL) to represent the source term. The model was parameterised using physical and chemical characteristics of three soils collected from sites historically contaminated with oily wastes. Our interest is in (i) to what extent this conceptualisation of partitioning in a biopile allows us to optimise treatment and (ii) what implications emerge from the modeled concentrations of key contaminants in individual media (air, water, soil) for the environmental regulation of biopiling, including the derivation of practical remedial targets for residual hydrocarbons.

2. Materials and methods

2.1. Soil characterisation

Archived soils (A, B and C; Table 1) were obtained from three sites in the UK, historically contaminated with petroleum hydrocarbons. Soil A was from a site that had undergone biopiling until the total petroleum hydrocarbon (TPH) load was reduced to the satisfaction of the regulatory authorities. Soils B and C were sampled from unremediated sites that had a long history of contamination with heavy petroleum.

Samples were prepared and characterised using standard procedures (Allan, 1989). Extractions for nitrate and ammonium analysis were performed using 4.0 ± 0.5 g (dry weight) soil and 40 ml of 1 M KCl. These were shaken on an end-over-end shaker for 30 min. Phosphate extractions were performed with 0.5 ± 0.1 g (dry weight) soil with 40 ml 2.5% v:v acetic acid using an end-over-end shaker for 2 h. Extracts were filtered through Whatman 44 paper prior to analysis on a flow injection analyzer (FIAstar). Carbon dioxide production, as a surrogate for respiration, was measured by weighing 1 ± 0.5 g (dry weight) soil into 11 ml vacuettes. Sealed vacuettes were incubated for 24 h at 15 °C and the headspace analysed for carbon dioxide using a gas chromatograph (Chrompack 9001) equipped with a methanizer and a flame ionisation detector (FID). An aliquot of between 50 and 100 µl was taken using a 250 µl gastight glass Hamilton syringe, and immediately injected onto an 80/100 mesh Poropak Q column (2 m × 1/8″ OD × 2 mm). The carrier gas was nitrogen at a flow of 20 ml min^{-1}. Temperatures of oven, injector and detector were 250 °C, 100 °C and 350 °C, respectively. A standard curve was prepared using certified gas mixtures (Linde Gases, Aberdeen). Three replicate blank vials were incubated and analysed with the samples to account for background carbon dioxide levels (Paton et al., 2006).

Microbial numbers for heterotrophic microorganisms and hydrocarbon degraders were estimated using the "most probable number" (MPN) method (Kirk et al., 2005). Soil (0.5 ± 0.2 g; dry weight) was extracted with 0.1% w:v sodium pyrophosphate in Ringer's solution using an end-over-end shaker for 2 h. Extracts (20 µl) were added to three different 96-well microtiter plates containing 180 µl media amended with 0.25 g l^{-1} INT (*p*-iodonitrotetrazolium violet) solution. The media were tryptic soya broth (TSA) for heterotrophs and Bushnell-Haas amended with 2 µl filter-sterilised diesel per well for hydrocarbon degraders or unamended for the control. The plates were incubated for two and four weeks at 25 °C for heterotrophic and hydrocarbon-degrading microorganisms, respectively.

Soil pH was measured using deionised water and a solution of 0.01 M $CaCl_2$. The measurement was performed by weighing 4 g (wet weight) into 50 ml centrifuge tubes and adding 20 ml solution. Tubes were shaken using an end-over-end shaker for 30 min and left to settle for at least 30 min. The pH was recorded when there was no change in the pH value in the second decimal point after 10 s (see Fig. 1).

2.2. Hydrocarbon extractions

Prior to extraction, samples (10 g) of each soil were blended with 10 g Na_2SO_4 to obtain a free flowing mixture.

Table 1
Soil characteristics and volumetric composition of the three biopiles

Soil and volumetric characteristics	Soil A		Soil B		Soil C	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Bulk density, kg l^{-1}	0.973	–	0.823	–	0.576	–
Moisture content, %	15	0.79	21	0.77	34	1.56
Moisture content, % at WHC*	38	3	44	1	46	1
pH in water	6.8	0.4	7.5	0.1	6.8	0.2
pH in 0.01 M $CaCl_2$	6.5	0.0	6.6	0.0	6.1	0.1
LOI**%	12	1	15	7	26	3
Org. C, %	7	0	9	4	15	1
C (TPH)NAPL, %	2.27	–	3.15	–	1.97	–
Org C soil, %	4.73	–	5.85	–	13.03	–
Dissolved org. C, µg g^{-1}	65	18	120	47	88	26
Dissolved total C, µg g^{-1}	143	11	221	92	152	27
% C	9	1	8	1	18	3
% N	5	1	2	1	1	0
Heterotrophic MPN per g in TSA	8.44×10^2	2.98×10^2	6.05×10^5	1.56×10^5	7.02×10^4	2.08×10^4
Degrading MPN per g in BH with 0.1% diesel	1.50×10^5	7.44×10^3	1.13×10^5	1.32×10^4	5.81×10^5	1.17×10^5
TPH, mg kg^{-1}	22700	–	31500	–	19700	–
Total biopile volume, m^3	625	–	625	–	625	–
Air volume, m^3	310	–	337	–	399	–
%	49.6	–	54.0	–	63.9	–
Water volume, m^3	91.1	–	108	–	122	–
%	14.6	–	17.3	–	19.6	–
Soil volume, m^3	209	–	162	–	96.1	–
%	33.5	–	26.0	–	15.4	–
NAPL volume, m^3	14.4	–	16.8	–	7.49	–
%	2.30	–	2.70	–	1.20	–

* Water holding capacity.
** Loss on ignition.

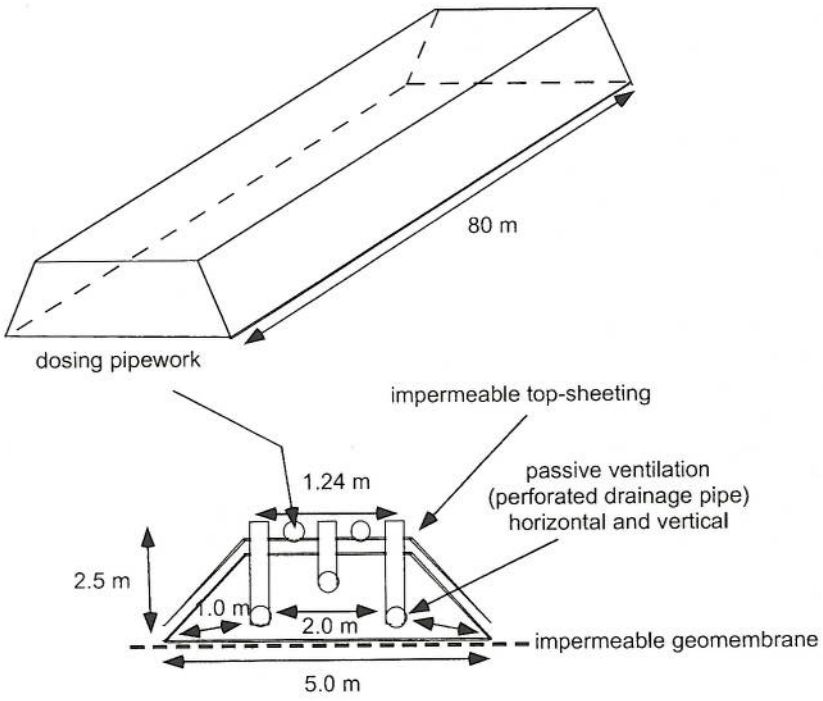


Fig. 1. Schematic and cross-section of the biopile 'evaluative environment'. The final biopile construction has a volume of 624 m^3 and weighs *ca.* 7.5×10^5 kg.

A layer of Na_2SO_4 (5 g) was placed in a series of Soxhlet thimbles followed by the soil samples. To each thimble, 1 ml of 50 mg l^{-1} *o*-terphenyl in methanol was added as a surrogate standard. Further blank (Na_2SO_4), blank spike (Na_2SO_4 with 1 ml of a 10000 mg l^{-1} diesel/mineral oil in pesticide grade methanol solution) and reference (air-dried and ground soil reference material) samples were prepared. All glass thimbles were placed into soxhlet extractors and connected to 500 ml round bottom flasks containing 200 ml dichloromethane/acetone (90:10) solution. Samples were refluxed at 30 °C for 6–8 h and extracted samples concentrated down to 1 ml by Kurderna–Danish, using a 3-ball macro synder column. Concentrations of total petroleum hydrocarbon (TPH) were determined using GC–FID on a Perkin Elmer elite 5-MS capillary column (30 m × 0.25 mm × 0.25 μm) with helium carrier gas at a flow rate of 1 ml min^{-1}. The initial oven temperature of 40 °C was raised to 300 °C at a gradient of 4.4 °C min^{-1}. The soils characterisation is presented in Table 1.

2.3. Fugacity model development

Soil characteristics (Table 1) were used to parameterise Level I and II fugacity models representative of a 'typical' constructed biopile. Initially, a Level I fugacity model (Level 1 Fugacity calculator version 1.2; Nieman, 2003) was used to examine the general partitioning behaviour and preferential partitioning in a constructed biopile environment. An evaluative environment was constructed using a typical biopile design (Battelle Environmental restoration department, 1996). It was assumed that the soil matrix consisted of four compartments: air ('A', pore space), water ('W', soil pore water), non-aqueous phase liquid ('NAPL') and mineral soil ('S') (Fig. 2). The total mass of contaminant in the system (T, mol) is described by

$$T = V_A C_A + V_W C_W + V_{NAPL} C_{NAPL} + V_S C_S \quad (1)$$

where T is the total mass of contaminant in the system, V represents the volume of each compartment (m^3), and C represents the concentration of the contaminant in each compartment (mol m^{-3}).

To estimate the fluxes between the compartments (depicted as connecting lines in Fig. 2), the relationships between C_A, C_W, C_{NAPL} and C_S were estimated by deriving partition coefficients (Eq. (2)). The partition coefficients can be used to characterise the distribution of the contaminant within the system (Eq. (3))

$$\left(\frac{C_{NAPL}}{C_W}\right) = K_{NAPLW} \quad (2)$$

$$T = V_A\{K_{AW} C_W\} + V_W\{K_{WNAPL} C_{NAPL}, K_{WA} C_A\} + V_{NAPL}\{K_{NAPLS} C_S, K_{NAPLW} C_W\} + V_S\{K_{SNAPL} C_{NAPL}\} \quad (3)$$

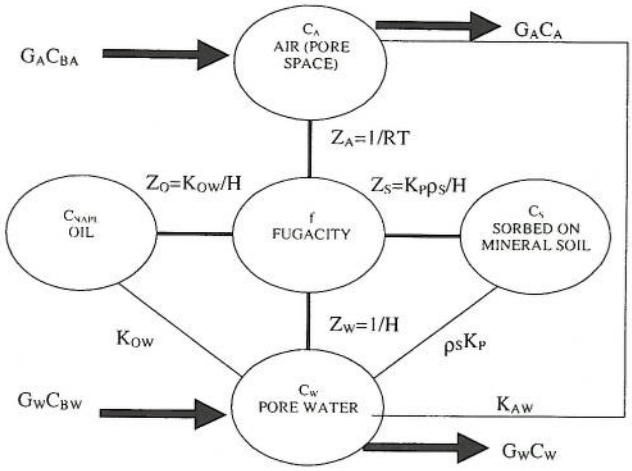


Fig. 2. Schematic of the fugacity model developed for each soil including definition of fugacity capacities used for each compartment. Z is the proportionality constant (mol m^{-3} Pa); H is the Henry's Law constant (Pa m^3 mol^{-1}); R is the gas constant = (8.314 m^3 Pa K^{-1} mol^{-1}); Temperature (K); K_S represents a partition coefficient (l kg^{-1}). ρ_S is the soil bulk density (kg l^{-1}). The inflow and outflow of air and water through the biopile system, and the losses of contaminants, are represented by the bold arrows.

where V represents the volume of each compartment in Fig. 2 (m^3), and C represents the concentration of the contaminant in each compartment (mol m^{-3}).

Under the fugacity approach, the concentration term, C, is replaced with the fugacity term Zf. This employs the relationship between concentration, C, and fugacity, f, which may be defined as the proportionality constant, Z (Eq. (4)) (MacKay, 2001). Definitions of the fugacity capacities Z_A, Z_W, Z_O and Z_S used in the Level I model are indicated in Fig. 2

$$C = Zf \quad (4)$$

To parameterise Eq. (1), the volumetric composition of each biopile was derived using a mass fraction based on the bulk density of each soil (Table 1), and a biopile volume of 625 m^3 (Battelle Environmental restoration department, 1996). The concentration of NAPL was assumed to be equal to the measured concentration of TPH (Table 1). The volumetric composition of the three biopiles is reported in Table 1. The volume of water, NAPL and mineral soil were calculated using literature-derived densities: water 1000 kg m^{-3}; NAPL was assumed to have an average bulk density of 970 kg m^{-3} (Woolgar, 1997); mineral soil was assumed to have a particle density of 2400 kg m^{-3} (Rowell, 1997). The volume of air was calculated as the total volume minus the sum of the other three volumes. A hundred moles of five priority compounds (Table 2) were introduced into the models and the partitioning of these compounds within the three soil matrices estimated.

The Level II fugacity model accounted for advection processes and degrading reactions in the form of residence times and half lives. The calculations assumed steady-state conditions – *i.e.* the amount entering the system was mass

Table 2
Input parameters

Chemical	Benzene	Benzo[*a*]pyrene	Anthracene	Phenanthrene	1-Methylphenanthrene
Molecular weight, g mol^{-1}	7.81×10^{1}	2.52×10^{2}	1.78×10^{2}	1.78×10^{2}	1.92×10^{2}
Water solubility, mg l^{-1}	1.78×10^{3}	3.80×10^{-3}	4.50×10^{-2}	1.1×10^{0}	2.69×10^{-1}
Vapor pressure, mmHg	7.60×10^{1}	5.49×10^{-9}	1.08×10^{-5}	2.01×10^{-4}	7.27×10^{-5}
Henry's Law constant, atm m^3 mol^{-1}	5.43×10^{-3}	1.80×10^{-5}	3.38×10^{-5}	3.98×10^{-5}	4.27×10^{-1}
Log K_{ow}	2.13×10^{0}	6.06×10^{0}	4.45×10^{0}	4.46×10^{0}	5.14×10^{0}
Log K_{oc}	1.81×10^{0}	6.74×10^{0}	4.10×10^{0}	4.10×10^{0}	4.17×10^{0}
$\tau_{1/2}$ Air	1.70×10^{1}	1.70×10^{2}	5.50×10^{1}	5.50×10^{1}	1.70×10^{1}
$\tau_{1/2}$ Water	1.70×10^{2}	1.70×10^{3}	5.50×10^{2}	5.50×10^{2}	1.70×10^{2}
$\tau_{1/2}$ Soil	5.50×10^{2}	1.70×10^{4}	5.50×10^{3}	5.50×10^{3}	1.70×10^{3}
$\tau_{1/2}$ NAPL	1.70×10^{3}	5.50×10^{4}	1.70×10^{4}	1.70×10^{4}	5.50×10^{3}

balanced by the amount leaving the system. If a chemical is introduced at a rate of E mol h^{-1}, then the rate of removal must also be E mol h^{-1}. If the amount in the system is M mol, then on an average the amount of time, τ, each molecule spends in the steady-state system is (Eq. (5))

$$\tau = M/E; \quad M = \tau E \tag{5}$$

There are two primary mechanisms by which a chemical may be removed from a biopile system: advection and reaction. Since a steady-state applies, we assume that inflow and outflow are equal and that a mass-balance applies. If G is the advecting medium (m^3 h^{-1}) and C is the concentration of the contaminant in G (mol m^{-3}), then the rate of advection, N, is GC (mol h^{-1}). The total influx of the chemical is at a rate $G_A C_{BA}$ in air, $G_W C_{BW}$ in water, $G_{NAPL} C_{BNAPL}$ in NAPL, and $G_S C_{BS}$ in mineral soil. Therefore, the total influx I is (Eq. (6))

$$I = E + G_A C_{BA} + G_W C_{BW} + G_{NAPL} C_{BNAPL} + G_S C_{BS} \tag{6}$$

If we assume a constant fugacity, f, to apply within the biopile system and to the out-flowing media (air and water), then we can write (Eqs. (7) and (8))

$$\begin{aligned} I &= (G_A Z_A f + G_W Z_W f) + (V_A Z_A k_A f + V_W Z_W k_W f \\ &\quad + V_{NAPL} Z_{NAPL} k_{NAPL} f + V_S Z_S k_S f) \\ &= f \Sigma D_{Ai} + f \Sigma D_{Ri} \end{aligned} \tag{7}$$

$$F = \frac{I}{\Sigma (D_{Ai} + D_{Ri})} = \frac{I}{\Sigma D_T} \tag{8}$$

3. Results and discussion

The fugacity of a chemical in a multiphase system is analogous to the partial pressure of an ideal gas and related to concentration through the fugacity capacity (Mackay, 2001). For the three soils as an entire environmental compartment, there were no significant differences ($P > 0.05$) between the estimated Level I fugacities (f) for the five priority contaminants, though the contaminants differed markedly in their fugacities (Table 4).

Here, we are principally interested in the relative phase partitioning of these contaminants (Table 3) and, from the Level II calculations, their time dependent behaviour (Fig. 3 and Table 4) within modeled biopiles. The results for phenanthrene are not presented because its Level II model output was not significantly different to anthracene.

NAPL and soil are the dominant partition media for these contaminants in each biopile systems (Table 3). The partition behaviour of the compounds is mainly influenced by their water solubility and the percentage of organic carbon in soil. In comparison to NAPL and soil phase concentrations, the water and air phase concentrations are very small except for benzene (Table 3). Benzene expresses an aqueous concentration worthy of note for leachate control during biopiling; the air phase concentrations appear insignificant in relation to NAPL and soil phase concentrations. The model provides some comfort, but odour events at biopiling facilities are sufficiently common to warrant further examination of air phase fluxes of risk critical contaminants.

Interestingly, benzene and anthracene in soil C shows a greater propensity to transfer to the soil compartment, than in soils A and B. This appears to be due to the higher percentage of organic carbon in soil C compared to the other soils (Table 3). In addition, benzo(a)pyrene being the least soluble organic compound used in these models shows a systematic preference for the soil compartment in all biopile systems. Thus, recognition of both NAPL and soil compartments, as partition media are important for risk analysts, regulators and remediation engineers. The overriding dominance of the NAPL phase for hydrophobic contaminants is theoretically established but rarely incorporated, in practice, into the exposure assessment tools used to derive soil screening levels and guideline values. This is an oversight that is likely to have a marked influence on soil assessment criteria at hydrocarbon-contaminated sites. Its significance comes into play when one considers the residual risk posed by post-treatment residues. For biopiling, there is a long-standing debate regarding the nature and extent of the hazard posed by post-treatment residues left *in situ* following treatment. For example, Zemanek et al. (1997a) showed that between 71 and 96% w:w of PAH in weathered diesel-contaminated loams were partitioned to residual oil (at 2–6% w:w of the total soil composition) in petroleum and weathered creosote-contaminated soils, with 84% w:w of benzo(a)pyrene partitioned to the residual oil phase. Woolgar and Jones

Table 3
Partitioning behaviour of the five organic compounds within the air, water, soil and NAPL phases of the three biopiles

Organic compound	Phase	Soil A		Soil B		Soil C	
		Moles	%	Moles	%	Moles	%
Benzene	Air	1.93×10^{0}	1.9	1.94×10^{0}	1.9	2.85×10^{0}	2.8
	Water	2.51×10^{0}	2.5	2.76×10^{0}	2.8	3.85×10^{0}	3.9
	Soil	4.22×10^{1}	42.2	3.75×10^{1}	37.5	6.13×10^{1}	61.3
	NAPL	5.33×10^{1}	53.3	5.78×10^{1}	57.8	3.19×10^{1}	31.9
Anthracene	Air	6.19×10^{-5}	0.0	6.23×10^{-5}	0	9.51×10^{-5}	0.0
	Water	1.30×10^{-2}	0.0	1.42×10^{-2}	0	2.07×10^{-2}	0.0
	Soil	4.25×10^{1}	42.5	3.77×10^{1}	37.7	6.42×10^{1}	64.2
	NAPL	5.75×10^{1}	57.5	6.23×10^{1}	62.3	3.58×10^{1}	35.8
Methyl-phenanthrene	Air	2.35×10^{-1}	0.2	2.25×10^{-1}	0.2	4.77×10^{-1}	0.5
	Water	3.90×10^{-3}	0.0	4.06×10^{-3}	0.0	8.21×10^{-3}	0.0
	Soil	1.50×10^{1}	15.0	1.26×10^{1}	12.6	2.99×10^{1}	29.9
	NAPL	8.74×10^{1}	84.7	8.71×10^{1}	87.1	6.96×10^{1}	69.6
Benzo(a)pyrene	Air	1.58×10^{-7}	0.0	1.75×10^{-7}	0.0	1.72×10^{-7}	0.0
	Water	6.20×10^{-5}	0.0	7.49×10^{-5}	0.0	7.02×10^{-5}	0.0
	Soil	8.88×10^{1}	88.8	8.66×10^{1}	86.6	9.51×10^{1}	95.1
	NAPL	1.12×10^{1}	11.2	1.34×10^{1}	13.4	4.95×10^{0}	4.9

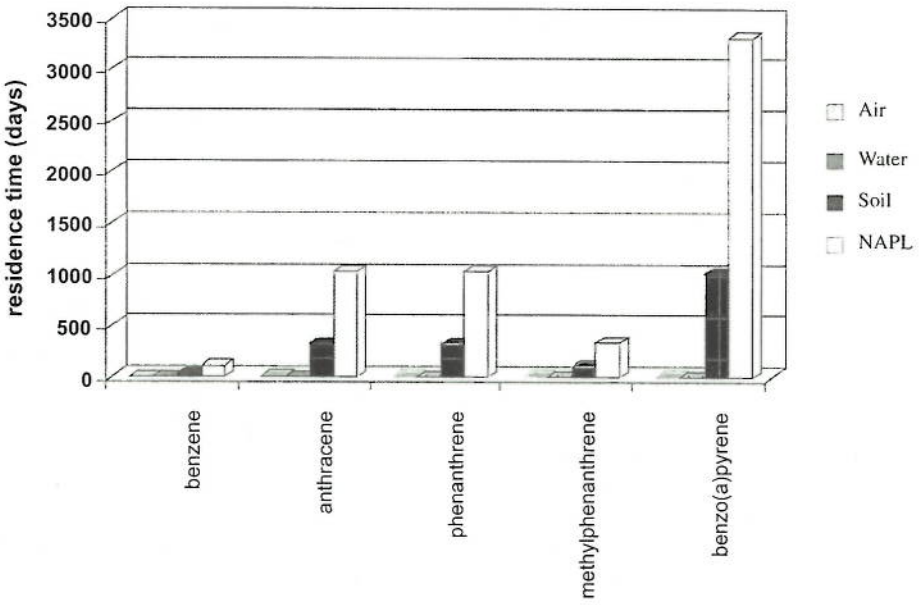


Fig. 3. Representative partitioning and degradation behaviour of the five model compounds within the soil:oil biopile matrix A.

(1999) estimated oil–water partition coefficients (termed log K_{mw}) for a series of polynuclear aromatic hydrocarbons ranging between 4.5 and 6.5 (log) dependent on the nature of the source term. Under these conditions, highly partitioned constituents are likely to be biologically inaccessible to microbial communities and resistant to biotransformation. Further, their inaccessibility may also, but not necessarily, restrict the dose available to receptors. The corollary of this debate also has implications. Attempts by remediation technologists to improve the bioavailability of these components to microorganisms through, for example, the use of biosurfactants may also result in increased human and environmental exposure. Notwithstanding the demonstration of the importance of the oil source term in this study, the behaviours modeled in Table 3 represent only a partial picture. The changes in structural composition of oil as it is biotransformed (Westlake et al., 1974; Whittaker et al., 1999) and its depletion with time mean that hydrophobic and recalcitrant contaminants become both concentrated and more tightly bound within the oil matrix as biopiling progresses. To date, the modelling above does not account for these secondary effects, but would need to if we were to present a truly representative account of partitioning behaviour in the NAPL phase over time.

In practice, biopiling timeframes are typically of the order of 3–6 months (~90–180 days). The discussion that follows

Table 4
Environmental losses including advection and degradation processes for the five model compounds in each biopile systems

		Fugacity (f) Pa	Total reaction rate ($\sum D_R f$), mol h^{-1}	Total advection rate ($\sum D_A f$), mol h^{-1}	Overall residence time (days)
Biopile soil A	Benzene	1.52×10^{1}	1.64×10^{-1}	4.66×10^{-1}	136
	Anthracene	4.87×10^{-4}	7.72×10^{-3}	2.37×10^{-3}	1335
	1 Methyl-phenanthrene	1.85×10^{0}	2.64×10^{-2}	1.47×10^{-3}	434
	Benzo(a)pyrene	1.24×10^{-6}	3.76×10^{-3}	1.14×10^{-5}	4434
Biopile soil B	Benzene	1.40×10^{1}	1.61×10^{-1}	4.32×10^{-1}	136
	Anthracene	4.51×10^{-4}	7.31×10^{-3}	2.20×10^{-3}	1355
	1 Methyl-phenanthrene	1.63×10^{0}	2.53×10^{-2}	1.29×10^{-3}	435
	Benzo(a)pyrene	1.26×10^{-6}	3.70×10^{-3}	1.16×10^{-5}	4334
Biopile soil C	Benzene	1.74×10^{1}	2.22×10^{-1}	5.35×10^{-1}	137
	Anthracene	5.81×10^{-4}	9.57×10^{-3}	2.83×10^{-3}	1356
	1 Methyl-phenanthrene	2.91×10^{0}	4.05×10^{-2}	2.32×10^{-3}	434
	Benzo(a)pyrene	1.05×10^{-6}	3.94×10^{-3}	9.61×10^{-6}	4335

with respect to the depletion times of risk critical compounds needs to be viewed in light of these practical realities. For all three soils, the majority of modeled benzene (100 mol) remained present in the NAPL compartment until 102 days when benzene was no longer present in all three biopiles (132 days; Table 4). Benzo(a)pyrene is fully eliminated from the three biopile systems after 4334 days (12 years). As shown in Fig. 3, benzo(a)pyrene remains at least 9 years in NAPL phase and ~3 years in soil phase. Elimination of anthracene and 1-methylphenanthrene from the soil phase is observed after 23 and 8 months, respectively. In contrast, anthracene and 1-methylphenanthrene remain 2.8 years and 27 months, respectively in NAPL phases (Fig. 3).

This discussion is somewhat artificial when one considers the authentic conditions under which biopiling is used. In practice, we expect the persistence (if not concentration) of these compounds in oily post-treatment residues, albeit with a restricted bioavailability. This paradox between mass and availability has proved to be a rich territory for discussion between the oil and manufactured gas plant industries and environmental regulators. In the United States, a substantive research effort has focused on integrating hydrocarbon fate and transport, petroleum microbiology and environmental diagnostics to inform regulatory processes for site management under the Superfund Program. ThermoRetec (2000), reporting for the petroleum environmental research forum (PERF), provide an authoritative account of the central importance of partitioning within soil-bound hydrocarbons in developing environmentally acceptable endpoints (remedial objectives). Drawing on a detailed understanding of NAPL and residual oil fate and behaviour, this work is now influencing the development of more realistic and defensible remediation criteria for petroleum hydrocarbon in soils for human health, groundwater and ecological receptors, and a reappraisal of the level of residual petroleum hydrocarbons that can be left at remediated sites without posing an unacceptable risk. In England and Wales, the Environment Agency (2003) have also recognised the importance of an authentic representation of partitioning in their consultation, and subsequent framework, (Environment Agency, 2005) on evaluating the human health risks from petroleum hydrocarbons in soils. We will be exploring these influences and attempting to validate the modeled behaviours described here with data from microcosms and pilot biopile trials. Ultimately, we are interested in providing a more sound evidence base for the derivation of realistic soil assessment criteria and directing remedial efforts towards risk critical compounds, exposures and environmental media.

4. Conclusions

We have demonstrated the propensity for risk critical compounds in hydrocarbon-contaminated soils to be preferentially partitioned to the NAPL and soil phases and modeled their behaviour using typical biopile design parameters. Small differences in the partitioning behaviours of the compounds studied between individual soils were dwarfed by the relative partitioning observed between the air, water, NAPL and soil phases in the evaluative environments. Modeled depletion times for individual contaminants in the context of authentic biopiling are immaterial and thus research efforts should be focused on the likely exposures of humans and other receptors to residual saturation at hydrocarbon-contaminated sites. Further, the results indicate the need for modifications to the exposure assessment models used to generate soil screening guidelines or guideline values, so to better represent contaminant fate in the multimedia systems.

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What can water utilities do to improve risk management within their business functions? An improved tool and application of process benchmarking

Brian H. MacGillivray, Simon J.T. Pollard *

Centre for Water Science, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, United Kingdom

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ABSTRACT

We present a model for benchmarking risk analysis and risk based decision making practice within organisations. It draws on behavioural and normative risk research, the principles of capability maturity modelling and our empirical observations. It codifies the processes of risk analysis and risk based decision making within a framework that distinguishes between different levels of maturity. Application of the model is detailed within the selected business functions of a water and wastewater utility. Observed risk analysis and risk based decision making practices are discussed, together with their maturity of implementation. The findings provide academics, utility professionals, and regulators a deeper understanding of the practical and theoretical underpinnings of risk management, and how distinctions can be made between organisational capabilities in this essential business process.

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1. Introduction

The provision of safe, reliable drinking water, the overarching goal of the water utility sector (AWWA et al., 2001), is within the bounds of the developed world's science, technology, and financial resources. Nevertheless, a nagging prevalence of water quality-related outbreaks remains in the developed world, with "causes" ranging from technical failures to institutional lapses and, in the extreme, negligence on the part of operating and managerial staff (Hrudey and Hrudey, 2004). Regardless of the manifestation of these incidents, one might argue that excepting "acts of God," they all derive, fundamentally, from limited organisational capacities to learn how to prevent failures; in other words, from failures to manage risk.

Traditionally, utilities managed risk through codifying standard design and operating procedures. Procedures evolve in line with the introduction of improved methods and technologies (*e.g.* novel treatment processes) and through the experiences gained from reflecting on past mishaps and near misses. From a risk management perspective, we are particularly concerned with the latter. A developmental cycle begins with a contamination event or near miss, following which incident analysis is undertaken to determine its root cause, concluding with a technical, operational or administrative solution (*e.g.* adapting design standards or operating procedures) designed to prevent its recurrence. This cycle exists at various levels, from that of the individual utility, through groups of organisations (*i.e.* utilities learning vicariously from the mishaps of others), to sectors as a whole, the latter reflected in changes to national or sector-wide codes, standards or regulations where learning is generalised, for example, regarding the pathogenic hazards associated with backwashing treatment filters. Whilst this retrospective approach to managing risk is necessary, it is a mistake to consider it sufficient for risk management. Procedures can proliferate to the point where resources are diverted towards preventing incidents that *have* happened, rather than those most likely to happen in the future (Lee, 1998). Further, a reliance on learning by trial and error, in isolation of more proactive strategies, is unsound where public health is at stake because it is not protective. Although illustrated in a water quality context, this argument extends to all aspects of the design, operation and management of utility systems (*e.g.* from process engineering to occupational health and safety management) and across many industrial (water, waste, energy, transport) sectors.

Recognition of the limitations of *post hoc* analysis is driving the water sector to supplement it with more proactive approaches to risk management, wherein utilities identify potential weaknesses and eliminate root causes of problems before failure occurs (MacGillivray et al., 2006; Hamilton et al., 2006; Pollard et al., 2004). Our research (Pollard et al., 2004, 2006; Hrudey et al., 2006; Pollard et al., 2007; MacGillivray et al., 2007a,b) has been concerned with how we can improve organisational competencies in risk management within the utility and related sectors. We have focussed on *implementation* rather than the technical aspects of the risk and decision analysis techniques employed and here, we introduce a model for benchmarking and improving the *processes* of risk analysis and risk based decision

* Corresponding author. Tel.: +44 1234 754101; fax: +44 1234 751671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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making within utilities. We describe its application within a water and wastewater utility, and end by reflecting on our theoretical and empirical contributions.

2. Benchmarking risk analysis and risk based decision making

Capability maturity models (Paulk, 1993) are simplified representations of organisational disciplines (*e.g.* software design and engineering) that codify industry practice within a maturity framework. They allow distinctions to be made between organisational capabilities (*e.g.* the ability to manage risk) by reference to the maturity of the processes applied. We have published the design (MacGillivray et al., 2007a) and application (MacGillivray et al., 2007b) of a capability maturity model for benchmarking risk management practice within the utility sectors. This model contained eleven risk management processes at five maturity levels. The premise of the maturity levels was that once each process was enshrined in procedure, with staff trained in their application, roles and responsibilities assigned, necessary resources secured, and mechanisms in place to prevent deviations from requirements and to learn from the feedback obtained, then implementation of risk management should be of consistently high quality. The demonstrable *maturity* of risk management then becomes the benchmark of an organisation's capability to manage risk, rather than simply the presence of risk policies or techniques in isolation.

We have since revised the model, responding to theoretical and empirical challenges derived from its application (see MacGillivray, 2007c). Our revision follows the spirit of the grounded theory approach (Glaser and Strauss, 1967; Strauss and Corbin, 1994), drawing primarily upon:

(i) the capability maturity modelling and quality management literatures;
(ii) normative risk analysis and management frameworks, both specific to the water and wastewater sectors and beyond;
(iii) behavioural research on decision making under uncertainty; and
(iv) our recent empirical observations.

A revised model, described here, incorporates risk analysis and risk based decision making, which are comprised of distinct practices. Risk analysis (Fig. 1; Table 1) comprises the practices of system characterisation, hazard identification, exposure assessment, evaluation of existing controls, consequence evaluation, likelihood evaluation, and risk evaluation. Risk analysis looks to the future to determine what can go wrong and how, the potential consequences and the relative likelihood of this, and finally the overall level of risk. Risk analysis is always part of a decision context (Aven and Kørte, 2003). Risk based decision making (Fig. 1; Table 2) is concerned with the identification and evaluation of risk management options and an expert review prior to selecting the optimal option(s). It is informed by criteria that establish the acceptability of risk and that set out stakeholder values and concerns, which are used to assess the relative merit of alternative options.

Both processes are presented in five maturity levels, from *ad hoc* to adaptive, characterised by the completeness of the process (*i.e.* whether all practices are undertaken) and attributes that reflect the maturity of implementation. Maturity levels codify the extent to which each process is repeatable (level 2; L2), defined (L3), controlled (L4) and adaptive (L5). Whilst the maturity attributes (Table 3) and levels (Table 4) presented are specific to risk analysis, the same principles apply to risk based decision making. Note, that to achieve a given maturity level, all positive requirements of that level and the preceding levels must first be satisfied.

3. Research methods

What can individual utilities learn about their organisational risk management maturity and how should they respond? How far should they go to improve risk management and what actions should they take? One water and wastewater utility participated in this case study. The provision of safe, reliable drinking water depends on a range of business functions spanning the design, operation and management of water supply, wastewater treatment systems. We view the integration of risk management across the breadth of these business functions as crucial to delivering a high level of competency in public health protection. Though the focus of our research is water supply, by the nature of the utility's organisation, it extended to aspects of their wastewater services. We critically assessed seven of their business functions: engineering; project management; drinking water quality management; network planning; asset management; emergency management; and occupational health and safety. The research methods included interview and document analysis, as described below.

Semi-structured interview templates were developed and applied by business function (*e.g.* asset management) and, where judged relevant, by functional discipline (*e.g.* dam safety management). Questions explored the practical form of risk management in each business function (*e.g.* "what is the process for identifying health and safety hazards within workplaces?") and its maturity of implementation (*e.g.* "are there mechanisms for quality control of risk analyses?"). Interviews (mean approximately 45 min) were conducted face to face ($n=32$) and by 'phone ($n=1$), recorded, and transcribed *verbatim* (with two exceptions, where notes were taken). Transcripts were returned to each interviewee, for comment. Finally, relevant company documentation was obtained from interviewees, the corporate intranet and the public domain (*e.g.* internet, conference articles). This included risk management policies and frameworks, risk analysis procedures and methods, accident and incident statistics and reports, water safety plans and risk analysis outputs.

Each business function's process maturity was assessed according to the lead author's judgement based on the data obtained, by reference to our model. We consider the subjectivity of this to be unimportant, because the principal research objective was

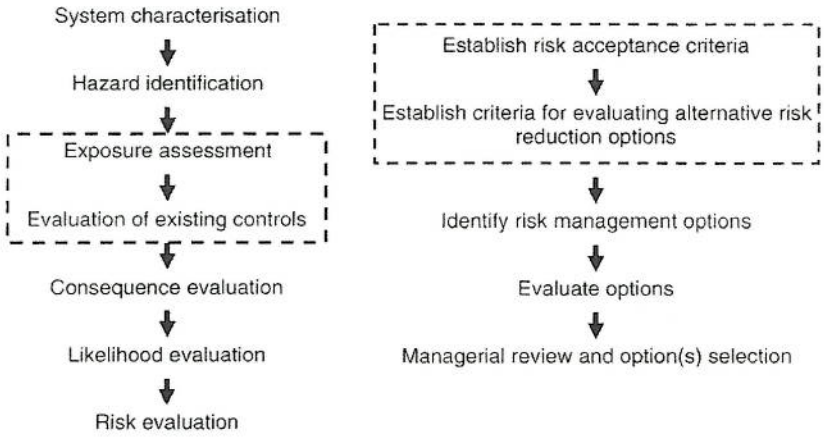


Fig. 1. Risk analysis (left) and risk based decision making practices (right). Those encased are considered key rather than critical, an important distinction in evaluating process maturity.

Table 1
Descriptions of the risk analysis practices and of the rationale for their inclusion in our model

Risk analysis practice	Description	Rationale
System characterisation	To establish and describe the system with which risk analysis is concerned (*e.g.* workplace, engineering process, project).	A comprehensive system understanding is a *sine qua non* for generating risk analysis outcomes that are valid and accepted by stakeholders.
Hazard identification	Identifying situations, events, or substances with the potential for causing adverse consequences, *i.e.* sources of harm or threats to the system.	A hazard left unidentified is excluded from subsequent analysis.
Exposure assessment	Whilst hazard identification is concerned with *what* can go wrong, precursor identification focuses on *how* and *why* things can go wrong, in other words identifying possible routes to and causes of failure.	The potential existence of a hazard does not in itself constitute a risk, as each hazard requires a process or pathway (precursor) to lead to its realisation. Thus, the value of this practice lies in both confirming the existence of pathways to failure (and therefore that a risk exists) and informing the development of risk management options focussed at root causes.
Evaluation of existing controls	The identification and assessment of existing technical, physical and administrative controls which may either reduce the likelihood of a hazardous event occurring, or serve to mitigate its severity of consequences. Assessment should address both the criticality of the controls (*e.g.* based on their inherent capacity to reduce risk, whether they are proactive or reactive, *etc.*) and their adequacy of design, management and operation.	An evaluation of existing controls: informs the evaluation of associated risk levels; serves to inform the development of risk management options through identifying latent and active control weaknesses (*i.e.* through serving as a gap analysis of existing risk management measures); and captures the historic basis for safe, reliable system operation.
Consequence evaluation	Identifying the nature of the consequences of a hazardous event occurring (*e.g.* financial, environmental) and assessing their severity of impact.	Deriving and combining measures of consequence and likelihood are required to establish the overall level of risk associated with a given hazard, so that management resources may be allocated accordingly and to assess the desirability of potential risk management measures (*e.g.* to see if they satisfy the ALARP criteria).
Likelihood evaluation	The evaluation of the likelihood (*i.e.* frequency or probability) that a hazardous event will occur and lead to a defined severity of consequence.	
Risk evaluation	Combining measures of likelihood and consequence severity to derive an overall measure of risk, either qualitative (*e.g.* high, low) or quantitative (*e.g.* expected loss of life, value at risk).	

to refine the model and illustrate its application, not necessarily to derive a maturity assessment of auditable rigour. Mechanisms to validate our findings were adopted, including sample anonymity and triangulation. Anonymity removed the potential for conflicts with the goal of adding to the body of knowledge on risk management capability (as opposed to the participant's potential desire that findings reflected positively on their organisation). Triangulation was secured through interviewing a range of representatives from each business function and cross-checking for inconsistencies in accounts, cross-checking interviewee accounts with documented sources, and providing the interviewees an opportunity to comment on drafts of the research outlined in this paper. Of the seven functions evaluated, "emergency management" was excluded from the analysis due to contradictions in the data and the limited sample of interviewees (two, compared to a minimum of three elsewhere), whilst "network planning" was excluded because of limited documentation obtained.

4. Results

We begin by summarising and discussing the observed risk analysis practices, before evaluating their relative maturity of implementation. We then turn to risk based decision making.

4.1. Risk analysis: observed practices

Table 5 summarises risk analysis practice within the sub-sample of business functions examined. Below, we provide a critical evaluation of the strengths and limitations of a selection of these practices.

4.1.1. Hazard identification

The business functions within this utility adopted a range of hazard identification methods, each with their own strengths, limitations and application contexts. In occupational health and safety management for example, hazard identification was concerned with identifying physical, chemical and biological threats to the workforce. These were primarily identified using checklists linking known hazards with processes, equipment, workplaces, or operations, and supplemented with "judgement formed from experience and knowledge of the work, past incident records, brainstorming, and system engineering techniques." The approach acknowledges the value of checklists in contexts where there is a significant body of knowledge or experience on the range and nature of potential hazards, and the notion that it is inappropriate to base hazard identification solely on lessons learned from the past, because hazards and the contexts in which they arise are fundamentally dynamic.

System engineering techniques were applied within the engineering function. Here, hazard identification was concerned with determining the root causes by which engineered systems may fail to operate within their design specifications. This was reflected in the utility's use of hazard and operability studies (HAZOP). In brief, analysts examined a process (*e.g.* disinfection) subdivided into nodes. At each node, the analysts applied guidewords (*e.g.* low, high) to process parameters (*e.g.* temperature, pressure, flow) to identify ways in which the process may deviate from its design intention.

In contrast, neither prescription nor a definitive methodological structure was evident in project management's approach to hazard identification, which was concerned with threats to the delivery of projects to time, to budget, and within the required quality parameters. Reflecting the unique nature of projects and their related hazards, this function adopted facilitated group brainstorming, informed by generic risk categories (*e.g.* "economic / business risk: the risk of exceeding project budget due to, for example, the impact of unfavourable exchange rates on the cost of minerals") to stimulate dialogue and encourage a systematic and creative approach to hazard identification.

4.1.2. Exposure assessment

The existence of a hazard does not necessarily constitute a risk because each hazard requires a pathway (a sequence of events, actions, or processes) that, if available, leads to its realisation at a receptor. Whilst hazard identification is concerned with *what* can go wrong (*e.g.* introduction of hydrocarbons within a water supply system), exposure assessment examines the *how* and *why* (*e.g.* off-take water contaminated *via* oil emissions from inadequately maintained pumps or pipes, due to an absence of procedures or inadequate supervision and training of maintenance staff). It involves identifying possible routes to and causes of failure.

Consider the drinking water quality management function within our case study utility, where risk analysis was based on an adaptation of the hazard analysis and critical control points (HACCP) methodology. The method seeks to provide a basis for understanding and prioritising human health and aesthetic hazards within the water supply chain from catchment to tap. Within the function, knowledge of the environmental behaviour of hazards (*e.g.* the environmental fate and transport of pathogens) and the system under examination, technical judgement, incident reports, survey maps, and monitoring records was synthesised to link hazards within each sub-system (*e.g.* catchment: chlorine resistant pathogens) to their sources (*e.g.* dairy farming or grazing) and to the chain of events that may lead to their realisation (*e.g.* runoff or percolation from land based activities).

Whilst variable in rigour and method, a common theme was that each function's approach to exposure assessment – where evident – tended to focus on *how* failure events may arise, rather than addressing in-depth their root causes. They neglected to explore the reasons *why* human or technical systems fail. This is an important oversight in that easily predictable causes of failure are often manifestations of deeper, underlying weaknesses (Reason, 1997). An inability to understand causal paths to failure constrains the development of risk management options targeted at the root causes of risks. Indeed, this should be the guiding basis of HACCP – in that risk (rather than hazard) management should focus at the critical points of management control; that is on those processes whose failure is likely to drive the risk (Hrudey et al., 2006).

4.1.3. Consequence evaluation

This practice involves identifying the nature of the consequences that follow a hazardous event (*e.g.* financial, environmental) and assessing their severity of impact. A range of techniques, from quantitative modelling to qualitative ranking were applied within our sub-sample of business functions. Applications of the former were largely restricted to asset management (*e.g.* event tree analysis, dam break modelling, inundation mapping, and economic impact evaluations in major dam risk analysis), with the majority of consequence evaluations being single point estimates framed by risk ranking techniques. These techniques presented consequences according to the

Table 2
Descriptions of the risk based decision making practices and of the rationale for their inclusion in our model

Risk based decision making practice	Description	Rationale
Establish risk acceptance criteria	Establishing criteria for evaluating the acceptability of risk.	In the absence of such criteria, on what basis are decisions taken on whether to mitigate or accept risk?
Establish criteria for evaluating alternative risk management options	Establishing criteria used to evaluate the relative merit of alternative risk management options (*e.g.* forecast risk reduction, technical feasibility, cost of implementation, latency of effects, environmental impacts, *etc.*) and, where deemed appropriate (*e.g.* where multi-attribute analysis is subsequently undertaken), weightings to establish their relative importance.	A range of risk management options may be considered for a particular decision context; the decision as to which is considered the best option is influenced by many factors. Different concerns and values often need to be considered simultaneously, and their relative importance may be valued differently by various stakeholders (Faber and Stewart, 2003). Making this explicit in the form of criteria can improve the credibility and defensibility of decision making, minimise the possibility that decisions will be second guessed or that their rationale be forgotten, remove barriers to stakeholder buy-in, and ensure the existence of an audit trail (SEI, 2002). More broadly, it enables value rather than "alternative focussed" decision making, the latter being characterised by the selection of an "optimal" option from a set of implied or poorly defined criteria (Arvai et al., 2001).
Identify risk management options	Generating alternative solutions for the decision problem.	Options not generated are excluded from subsequent evaluation and, ultimately, implementation.
Evaluate options	There are three elements to this: forecasting the impact of each option against the individual evaluation criteria; determining the relative merit of each option (*e.g.* via cost–benefit analysis, multi-attribute analysis); and determining risk acceptability.	Systematically evaluating the individual and cumulative merits of alternative options should provide for more credible, defensible and rational risk based decision making. Determining risk acceptability follows as it is risk management options, not risks, which are unacceptable or acceptable (Fischoff et al., 1981), *i.e.* the acceptability of risk cannot be determined without considering the costs and benefits of maintaining vs. reducing current risk levels.
Expert review and option(s) selection	The application of managerial and professional judgement in reviewing the premises, assumptions, and limitations of analyses, prior to the final decision (after Aven et al., 2007).	In line with Mintzberg (1994), we consider that decision analysis should compliment, but not replace, the knowledge, intuitions and judgement of decision makers, and further, that risk based decisions should not reflect theoretically or analytically derived perspectives that run counter to sound professional judgement (Hrudey and Hrudey, 2003). More specifically, given that risk is, at a fundamental level, an expression of uncertainty, and that the analysis of risk and decision alternatives is further subject to aleatory, epistemic and operational uncertainty (Amendola, 2001), the outputs must be treated diagnostically rather than deterministically, *i.e.*, they should provide decision support, not decisions.

nature of their impact (*e.g.* financial, environmental), and a graded scale of severity expressed by descriptive benchmarks. Their application within the sub-sample of business functions was not typically underpinned by an analytical method, relying instead on the interpretation of limited data sets (*e.g.* in occupational health and safety: cost of claims, lost time due to incidents) to derive a credible consequence evaluation. Whilst this is often a practical necessity, the indeterminacy intrinsic to this approach provides scope for individuals to bias (inadvertently or not) consequence evaluations, often in subtle and difficult to detect ways such that risk analysis outcomes may reflect the desires of vested interests (*e.g.* to secure funds, or to divert attention from flaws) rather than the corporate good. Such concerns are not unique to consequence evaluation, and provide a powerful rationale for quality control of the risk analysis process, which we discuss in Section 4.2.4 below.

4.1.4. Likelihood evaluation

This involves evaluating the probability that a hazardous event will occur and lead to a defined severity of consequence. In drinking water quality management, analysts sought to characterise the likelihood of hazardous events occurring and leading to a derogation from water quality standards or guidelines. Such judgements were informed by historic frequencies of exceedence (*e.g.* from turbidity monitoring data, *E. coli* concentrations). In some cases, these were supplemented by analysing critical variables. For example, evaluations of the likelihood of climatic and seasonal variations leading to excess levels of suspended solids in source waters were informed by analysis correlating the historic loadings of suspended solids with flow and rainfall data. However, whilst comprehensive monitoring of water quality parameters within catchments and at customer taps was routine, the absence of an overarching operational monitoring philosophy (*i.e.* at the treatment and disinfection plant level) meant that the data sets characterising hazards within water supply systems were incomplete. As one interviewee noted, "we do have online monitoring...but traditionally it's been a fairly ad hoc process...no-one has really taken a holistic view...and said – I think we should have online [pH] monitors here, chlorine residual analysers [here and]...for these reasons."

A similar theme emerged in occupational health and safety, whose risk analysis procedure stated that likelihood evaluations "may be determined using statistical analysis and calculations," but "where no past data exists or is available, subjective estimates will be required to reflect an individual's or groups degree of belief" that a particular severity of consequence will occur. It further specified that experiments and prototypes and economic, engineering or other models may be used to minimise subjective bias. Our observations revealed that modelling (*e.g.* event tree analysis) was restricted to isolated applications, whilst the availability of historic data (*e.g.* frequency rates by injury type, mechanism of injury, *etc.*) was paradoxically constrained by the organisation's good health and safety record. As one interviewee offered: "the amount of information that we generate doesn't produce sufficient data for us to analyse...and that's not necessarily because of a lack of reporting, it's just that...we actually don't produce that many incidents." This was offset, in part, by reference to external data sources (*e.g.* national health and safety databases). However, these fail to reflect the unique nature of the utility's design, construction, operation, and maintenance practices and, more broadly, their working culture.

4.2. Risk analysis: maturity of implementation

Having summarised (Table 5) and discussed the business functions' risk analysis practices, we now consider their maturity of implementation. Within each business function, the requirements of Level 2 maturity in risk analysis (Table 4) were satisfied (Fig. 2). A *repeatable* process was in place, characterised by explicit critical risk analysis practices. Level 2 is limited in two fundamental ways. One is that the key practices of exposure assessment and the evaluation of existing controls may be absent or undertaken implicitly. With the exceptions of engineering and drinking water quality management, this was true across our sub-sample (see Table 5). This is significant because a knowledge of the pathways by which hazards are realised and of the weaknesses in the design, operation and management of existing controls, is a prerequisite to developing risk management options targeted at common and root causes of failures that are yet to arise. A further defining L2 characteristic is that the rigour and quality with which critical practices are performed depends in large part on the individuals who execute and manage the work, and may therefore vary considerably. Additionally, the techniques adopted may be retrospective and historical, regardless of their applicability or currency. This is because they do not fully satisfy the requirements of a defined (L3), controlled (L4) or adaptive (L5) process. However, *fully* is the key word here, as we observed each function exhibiting some of the higher level maturity attributes and so our characterisation may be somewhat harsh. We now discuss specific attributes of their maturity in risk analysis.

4.2.1. Initiation criteria

Within many sectors, there are accepted standards of performance and codes of practice that, if adhered to, provide high degrees of control (UKOOA, 1999; Pollard et al., 2004). These standards are applied in familiar and well-characterised situations where

Table 3
Descriptions of the risk analysis process maturity attributes and their rationale for inclusion within our model

Attribute	Description	Rationale	Key aspects
Policies and procedures	The overarching principles and low-level rules guiding the execution of risk analysis.	To communicate high level commitment to risk analysis; capture and disseminate knowledge of its optimal conduct so that it is maintained within the organisational memory rather than as hidden expert knowledge (NEA/CSNI, 1999); and thus ensure its consistent, efficient conduct.	Appropriate standardisation and formalisation taking into account personnel experience and knowledge; participation of end users (*e.g.* risk analysts) in their development; matching detail with complexity of work; making explicit the rationale for conducting risk analyses; being based on an analysis of the tasks required (NEA/CSNI, 1999; Health and Safety Laboratory, 2003).
Roles and responsibilities	Assignment of personnel to risk analysis roles and responsibilities.	To avoid the "not my job" phenomenon (Joy and Griffiths, 2005), and ensure risk analysis receives appropriate focus and resource allocations.	Matching role descriptions and assignment of responsibilities with personnel competencies and authorities (NEA/CSNI, 1999). Supporting well meaning statements that "risk management is everyone's job" with specific requirements.
Initiation criteria	Stages or conditions which initiate risk analysis.	To ensure risk analyses is undertaken as required, rather than being initiated on an *ad hoc*, over zealous, or reactive basis, or marginalised as "make work."	Identifying where risk analysis is necessary vs. where adherence to codes and standards can be said to discharge the duty (Health and Safety Laboratory, 2003; UKOOA, 1999), and making this explicit in cyclical and event-based criteria.
Resource management	The planning, acquisition, and deployment of funds, techniques and staff in support of risk analysis.	Resourcing of risk analysis is particularly critical during periods of reduced budgets and downsizing, which may bring an emphasis on economic rather than safe operation (NEA/CSNI, 1999).	Sufficiency and availability of financial resources; access to sufficiently competent human resources; and a range of risk analysis techniques which reflect the complexity of the organisation's activities and working environment (Health and Safety Laboratory, 2003).
Input data management	The identification, collection, and storage of risk analysis data inputs.	The systematic identification and capture of data requirements serves to ensure analyses are underpinned by objective data evaluation, rather than reflecting best guesses in the guise of "expert judgement."	The definition of data requirements/data sources for risk analysis, either at the process level or, where not practical, on a case by case basis, and mapping these to data collection and storage systems.
Output data management	The collection, storage and dissemination of risk analysis outputs.	Risk analysis outputs must be systematically recorded to inform decision makers, for audit and training purposes, and to facilitate future reviews (COSO, 2004; CSA, 1997). Further, this ensures staff have current knowledge of the human, technical, organisational and environmental factors that govern system safety (Reason, 1997).	Documenting in-depth the risk analysis outcomes, not simply the overall level of risk (*e.g.* sources of data, assumptions used, methods followed, *etc.*). Although in theory the storage media is unimportant as long as the outputs are easily retrievable (Health and Safety Laboratory, 2003), IT-based data systems (risk registers) have significant advantages, particularly in facilitating information flow between and across layers and boundaries of the organisation (COSO, 2004).
Verification	Ensuring compliance with risk analysis policies and procedures, and providing quality control of the execution of risk analysis.	The mere existence of policies and procedures is not in itself enough to ensure that staff actions will be consistent with them (Hoyle, 2001; ISO, 2000). Errors of omission or commission (*e.g.* due to misunderstanding instructions, carelessness, fatigue or management override), may cause deviations. Similarly, procedural compliance does not ensure the quality of execution of risk analysis.	Implementation of mechanisms to ensure adherence to policies and procedures (*e.g.* auditing, "sign offs") and to sanction non-compliance. Quality control mechanisms (*e.g.* peer reviews, Delphi panels) should be implemented with explicit methods for controlling (*e.g.* establishing group consensus iteratively) or evaluating (*e.g.* quality criteria) the quality of analyses. An appropriate balance between the resources required, the constraints of bureaucracy, and the benefits of process control should be struck.
Validation	Assessing the fundamental correctness of the risk analysis process design (*e.g.* that the correct techniques are being applied, that the correct initiation criteria are in place).	The willingness and means to question the validity of current risk analysis practices is required to show due diligence and ensure that current practices are legitimate, and is further a prerequisite to the continual improvement of risk analysis.	Formalised approaches to validation include: statistical or mathematical approaches to validating technical methodologies, independent peer reviews, and benchmarking surveys; and informally may draw upon: professional networks, trade and scientific literature, *etc.*
Organisational learning	The manner in which the organisation identifies, evaluates and implements improvements to the design and execution of risk analysis.	Mechanisms for verification and validation are mere panaceas if their findings are not acted upon, *i.e.*, if they are not used to rectify deficiencies in the design and execution of risk analysis.	Reviews should: be undertaken at specified intervals and on an event driven-basis; consider a broad range of internal and external feedback; focus on improving the validity of the risk analysis process and the effectiveness of its execution, not on ensuring it complies with a given standard; treat errors of omission or commission in the execution of risk analysis not as isolated lapses requiring sanction to prevent their re-occurrence, but as opportunities to identify and resolve root and common causes of error; and be supported by a learning culture, wherein current methods and approaches to risk analysis, and their underlying assumptions, are open to question and critical evaluation.

Table 3 (*continued*)

Attribute	Description	Rationale	Key aspects
Stakeholder engagement	The engagement of stakeholders, both internal and external to the utility, for the purpose of harnessing a broad range of perspectives, knowledge, skills and experience.	The legitimacy of risk analysis outputs depends upon appropriately broad stakeholder engagement, as risk is an intrinsically multi-faceted construct, whose comprehensive understanding is often beyond the capabilities of individuals or small groups.	A team approach to risk analysis which pools the knowledge, skills, expertise and experience of a range of perspectives is preferable (Health and Safety Laboratory, 2003; MHU, 2003; Joy and Griffiths, 2005). External stakeholders may be engaged to: capture expertise (*e.g.* consultants); confer additional legitimacy on the analyses; communicate due diligence (*e.g.* regulators); and capture community values and ensure they are incorporated within the analysis.
Competence	The ability to demonstrate knowledge, skills, and experience in risk analysis to the level required (Health and Safety Laboratory, 2003).	The legitimacy of risk analyses outcomes depends to a large extent on the capacity of staff to critically evaluate available information and to supplement it with their own knowledge and plausible assumptions (Rosness, 1998), *i.e.* on staff competencies.	Definition of required staff competencies in risk analysis; evaluation and implementation of appropriate education and training vehicles to develop / maintain those competencies (*e.g.* class room learning, external workshops); providing "on the job" training under adequate supervision; designing and implementing methods for evaluating the efficacy of educating and training (*e.g.* for measuring that the required competencies have been imparted).

uncertainties and system vulnerabilities are well understood. Adhering to the historic basis for safe operations can be considered as discharging the risk management duty (Health and Safety Laboratory, 2003; UKOOA, 1999). Returning to our sample of business functions, this concept was reflected in an electrical engineer's comments: "electricity is a dangerous thing, it's a source of high energy that can be released instantaneously. Obviously you need to be in control and protected satisfactorily to make sure that there's no risk to personnel or the property...because the technology is very mature...we have our own design guidelines [for electrical engineering] that actually emphasise...issues like lifecycle cost, security of operation, reliability, safety... [and so on] I don't think it is necessary to have a formalised [risk analysis] process [in electrical engineering], because it's part and parcel of the detailed design anyway."

However, complex, uncertain and novel systems, with the potential to deviate from routine operation, may require risk analysis, so as to better understand what drives the risk from or to the plant, process or operation (UKOOA, 1999; Pollard et al., 2004). This principle extends beyond technical systems to embrace all aspects of managing a water utility. As such, an L3 attribute is the existence of initiation criteria: criteria that *initiate* the application and revision of risk analysis. Criteria observed within our sub-sample included: undertaking project risk analyses prior to full financial approval depending on the cost, complexity and novelty of the project; undertaking manual handling risk analyses in occupational health and safety management for novel, altered or relocated processes or in response to high frequency injury records or employee requests; undertaking HAZOP studies within engineering for complex or costly processes at set stages of design completeness. Timescales for revising risk analyses of various asset classes were observed in asset management. These criteria acknowledge that risk analysis is not a one-off activity, but requires regular revision to reflect system changes and the improved understanding of risks, that inevitably develops over time (*e.g.* from monitoring data, increased operator experience). In a world becoming obsessed with "the risk management of everything" (Power, 2004), an absence of these initiation criteria may drain resources, as staff are tempted to conduct risk analysis without first considering whether adherence to good practice would serve for sound risk management. At the other extreme, analysis may be applied reactively, perhaps even to provide *ex post* justifications of investment decisions (*e.g.* Health and Safety Laboratory, 2003).

4.2.2. Stakeholder engagement

A further positive characteristic of the utility's approach to risk analysis was the reflection of a broad spectrum of knowledge, skills, experience and perspectives within each function's approach to risk analysis. One benefit of their primarily qualitative approach was that it ensured that non-specialists, or what one interviewee referred to as "the people that use the systems, use the equipment and undertake the processes," could actively participate in and critically scrutinise the process. This is key, as engaging operational staff who have practical knowledge of the hazards under examination ensures a sense of ownership and engagement in the process, as opposed to accountabilities residing within a core set of head-office experts isolated from operational reality.

4.2.3. Competence

As Rosness (1998) notes, the accuracy of risk analyses depends to a large extent on the competency of analysts to critically evaluate information and integrate it with their own knowledge and assumptions. A need for education and training in risk analysis remains irrespective of the technical complexity of the methods adopted. Aside from the ubiquitous "on the job" training, two elementary programmes were observed within our sub-sample: (i) internally delivered training modules within occupational health and safety, comprising an overview of the relevant legislation, the risk analysis process, and some practical exercises; and (ii) voluntary external modules for HAZOP facilitators and project managers. However, formal definitions of the competencies required of risk analysts and metrics for assessing whether they had been imparted were absent, leading one to question on what basis education and training in risk analysis was targeted, assessed and improved. This critique is not restricted to our sub-sample; there is a broader need for research on (i) the attributes and characteristics of competent risk analysts; (ii) how they can be developed within staff; and (iii) how the expertise secured can then be measured and retained.

4.2.4. Verification: quality control

The quality control of risk analyses is intended to enhance their credibility through addressing inherent uncertainties, both epistemic, due to lack of knowledge, and operational, derived from the use of knowledge (*e.g.* analyst bias, judgements, human error; see Faber and Stewart, 2003; Amendola, 2001). This aspect was perhaps a core weakness of the sub-sample. For example, peer reviews of risk analysis were executed in a largely informal and unsystematic manner, whilst the use of facilitators was restricted to project risk analysis and HAZOP studies. That said, the role of the latter should not be underplayed, as our interviews emphasised that they did *not* drive particular outcomes or provide specific technical input, but sought to guide analysts in the application of methods and focus on the quality of process execution (*e.g.* challenging outliers during consequence evaluation, ensuring all relevant risk categories were considered during hazard identification).

With formalised quality control mechanisms being the exception rather than the norm, there was an implicit reliance on analyst competencies, a presumed absence of bias, and an assumed validity of the methods adopted. In practice, all risk analyses have inherent limitations and are based on assumptions rarely made explicit, and arguably, their applications are not scientific in a classical sense, but rather draw on the accumulated experiences, knowledge and bias of analysts (Aven et al., 2007). As such, ignorance, assumptions, value judgements, and local perspectives can distort analysis outcomes from true objectivist ideals. Given this, the utility's rescinding of the Delphi technique (Dalkey and Helmer, 1963) within their project risk analysis was disappointing. Historically, facilitated discussions and iterative anonymous voting had been used to generate consensus in risk evaluation. Characterised by group participation, anonymity and feedback loops, it minimised bias and dogma (*e.g.* reduced the reluctance of staff to abandon previously stated views). One interviewee suggested that since the approach had been abandoned, evaluations tended to reflect the subjective judgement of lone experts, which "typically went unchallenged." This may be viewed as a pyrrhic victory for those who railed against this symbol of "bureaucracy," and a timely warning that the much maligned concepts of due process, of checks and balances, can suppress greater evils.

4.3. Risk based decision making: observed practices

Table 6 summarises risk based decision making practice within the sub-sample. Below, we evaluate the strengths and limitations of a selection of these practices.

4.3.1. Establish criteria for evaluating alternative risk management options

A range of risk management measures may be considered for a particular decision. Consider drinking water quality management. Options for reducing risks to public health posed by waterborne pathogens include: enhancing the monitoring of indicator

Table 4
Descriptions of the risk analysis process maturity hierarchy, from ad hoc to adaptive

Level 5: Adaptive	Validation	A broad range of mechanisms are in place to capture feedback potentially challenging the validity of the risk analysis process (*e.g.* benchmarking surveys, professional networks, external peer reviews, mathematical validation of technical methodologies).
	Organisational learning	Norms and assumptions underpinning the design of the risk analysis process are openly questioned, critically evaluated and, where appropriate, revised in light of validation findings (i.e. double loop learning).
Level 4: Controlled	Verification	Verification extends beyond rigorous mechanisms to ensure procedural compliance (*e.g.* sign offs supplemented by in-depth audits) to provide formal quality control of risk analyses (*e.g.* peer reviews, challenge procedures, external facilitation, Delphi technique, *etc.*).
	Organisational learning	Root and common causes of errors in the execution of risk analysis (*e.g.* deficient communication, overly complex procedures, lack of education and training) are identified and resolved. Modifications to the design of the process are identified, evaluated and implemented within periodic and event-driven reviews, but remain largely reactive and externally driven (*i.e.* mirroring changes to codes, standards, guidelines, *etc.*).
Level 3: Defined	The critical and key risk analysis practices are explicitly undertaken.	
	Policies and procedures	Policies demonstrating high level commitment to risk analysis exist, supported by procedures guiding its execution, with an appropriate degree of standardisation, detail, and complexity.
	Roles and responsibilities	Risk analysis roles and responsibilities are allocated with sufficient regard for staff competencies and authorities.
	Initiation criteria	Cyclical and event-based criteria are in place to guide the initiation of risk analyses.
	Resource management	The requisite monetary, human and technical resources are identified, acquired and deployed in support of risk analysis.
	Input data management	The requisite data inputs are identified, acquired and deployed in support of risk analysis.
	Output data management	Risk analysis outputs are collected, stored and disseminated in a manner that supports decision making, satisfies audit requirements, and facilitates organisational learning.
	Verification	Basic mechanisms are in place to ensure compliance with risk analysis policies and procedures, focussing on outputs rather than tasks performed (*e.g.* sign offs on receipt of completed risk analyses).
	Validation	The validity of the risk analysis process is questioned in light of changes to regulations, codes and standards.
	Organisational learning	Non-compliances with risk analysis policies and procedures are resolved on a case by case basis (*i.e.* treated as isolated errors requiring sanction to prevent their recurrence). Improvements to the design of the risk analysis process are implemented in a reactive, *ad hoc* manner (*e.g.* in response to changes in codes or regulations).
	Stakeholder engagement	A broad cross-section of internal and external knowledge, experience, skills and perspectives is reflected within risk analysis, based on explicit guidelines or criteria for stakeholder engagement.
	Competence	Staff exhibit adequate knowledge, skills and experience in risk analysis. Education and training in risk analysis is planned and executed based on established competency requirements.
Level 2: Repeatable	The critical risk analysis practices are explicitly undertaken.	
Level 1: *Ad hoc*	Risk analysis is absent; or the critical practices are implicitly or incompletely performed.	

organisms in source waters (*e.g. E. coli*), catchment protection (*e.g.* fencing, or exclusion zones for livestock), infrastructure upgrades (*e.g.* filtration flow control), chlorine residual monitoring and operator training. The objective of each option is to reduce the risk to a level considered acceptable. However, the decision as to which option(s) is considered the best is influenced by many factors. Notwithstanding that all risk management decisions are value-laden, in best practice organisations these factors are reflected in explicit criteria used to evaluate the relative merit of alternative options.

As cost–benefit analysis is linked to determining whether risk management options satisfy the "as low as reasonably practicable" (ALARP) criteria adopted within the sub-sample, it is tempting to consider the balancing of costs and benefits as an evaluation criterion. However, we propose cost–benefit analysis is best viewed as a methodology for evaluating the relative utility of a risk management option. It does not prescribe whether one should simply balance the financial expense of implementing an option with the benefits of the risk reduction, or whether one should incorporate less tangible aspects such as technical feasibility, social values such as equity and distribution, or political concerns. In other words, it leaves the evaluation criteria unspecified. Whilst our research revealed that a broad range of criteria guided the evaluation of risk management options within our sub-sample, they were only made explicit within asset management's risk based approach to prioritising mains replacement and dam safety upgrades (Table 6). As such, one can expect what Arvai et al. (2001) termed "alternative focussed" decision making to predominate. This is characterised by an analysis of available alternatives followed by selection of the "optimal" option from a set of implied or poorly defined criteria. It is not desirable for a decision process to dictate or prescribe decisions, as an overly mechanical approach fails to recognise the human aspects of performing difficult value judgements under uncertainty (Aven et al., 2007). However, expressing the criteria against which those judgements should be taken ensures that the rationale for decisions is constructed *a priori* in a deliberative manner, rather than rationalised *post hoc*. Aside from improving risk management, explicit criteria serve to better equip utilities to manage *risk issues*, as they (i) provide a mechanism for reflecting legitimate stakeholder concerns in utility decision making (*e.g.* by incorporating public values and preferences); and (ii) provide a documented, defensible rationale for decision on risk.

4.3.2. Identify risk management options

This practice is concerned with generating alternative solutions for managing risk. Within the business functions, it was typically undertaken within creative workshops involving a diverse range of stakeholders. The value of brainstorming, which seeks to stimulate innovation through open interaction and feedback, was cited by various interviewees, one noting that it "empowers people to think: the worst [thing] that you can do is take away people's creativity." Furthermore, engaging stakeholders with diverse skills and backgrounds helps identify and address those assumptions, constraints and biases that can have a significant influence on the generation of alternatives (Aven and Kørte, 2003). Whilst primarily creative, within some functions this practice was informed by checklists of risk reduction alternatives. One example was occupational health and safety management's hierarchy of risk controls (control banding), which classified: engineering controls for hazard removal (*e.g.* substitution, isolation, modification to design, guarding and mechanical ventilation); administrative controls for preventing the occurrence of hazardous events (*e.g.* safe work practices, or procedures, training, supervision, nominating maximum exposure times); and personal protective equipment for minimising their severity of consequences.

Perhaps the most important factor was the depth and rigour of the risk analyses. Consider risk analysis within drinking water quality management. Recall that hazards identified within each sub-system (*e.g.* catchment: pathogens) were linked to their sources (*e.g.* dairy farming or grazing) and the events that may lead to their realisation (*e.g.* runoff or percolation from land based activities). Detailed surveys were then undertaken exploring the adequacy of design, management and operation of those actions, activities and processes applied to mitigate the introduction or transport of said hazards from catchment to customer tap (*e.g.* catchment protection, pre-treatment, ozonation, *etc.*). We propose that systematically identifying the underlying mechanisms through which hazardous events may occur, *before* evaluating the latent and active weaknesses in their control mechanisms, is the normative approach to identifying risk management options. The overarching purpose of risk analysis should be to develop a better understanding of the factors governing system reliability, rather than a "numbers game" (*e.g.* to simply satisfy quantitative risk acceptance criteria; Faber and Stewart, 2003). When used diagnostically, risk analysis represents an efficient tool for improving system safety and performance.

4.3.3. Evaluate options

We now turn to the evaluation of risk management options. There are three elements to this practice: (i) forecasting the impact of options against each evaluation criteria (*e.g.* technical feasibility); (ii) determining the relative merit of each option; and (iii) determining the acceptability of the residual risk, post-implementation.

Methods for achieving the former within our sub-sample of business functions included applying professional judgement, stakeholder consultations, cost-estimations, and engineering studies (*e.g.* feasibility studies in major dam safety management). This said, recall that in most business functions evaluation criteria were not defined, and so this element often tended towards the informal or implicit. For the second element, the cost–benefit approach was widely adopted for assessing the relative merit of alternative risk management options. Formal mathematical analyses were restricted to risk management options that took the form of major capital projects (*e.g.* in major dam

Table 5
Summary of the undertaking of each risk analysis practice within the sub-sample

	Drinking water quality management	Occupational health and safety management	Asset management		Project management	Engineering
			Treatment plants	Major dams*		
System characterisation	Schematics of water supply systems were produced. Data was obtained to characterise the following system elements: catchment (*e.g.* geomorphology, climate, land uses); source water (*e.g.* surface or ground water, flow and reliability, seasonal changes); storage tanks, reservoirs and intakes (*e.g.* detention times, design); treatment and distribution systems (*e.g.* processes, configuration, monitoring); current operational procedures; point sources of pollution; and consumers (*e.g.* population, demand patterns).	Checklists were used to interrogate characteristics of the work spaces and the type and methods of work to be undertaken (*e.g.* existence / location of pits, shafts, ducts, pressure vessels, access and egress routes, ventilation, isolation and lockout procedures, substances used, *etc.*).	Plant components were identified, their condition and performance evaluated through asset inspections, and current operating and maintenance regimes detailed.	Engineering assessments of dams were undertaken, drawing on technical reports, site visits, flood and earthquake loadings, dam safety standards, *etc.*	Project options were characterised through scope development and value management workshops. These detailed the project need and relevant assumptions and constraints, before characterising each option in terms including their: functional specifications, capacities, required inputs and outputs, and relative costs and benefits.	Prior to the application of HAZOP studies, process and instrumentation diagrams – which show the interconnection of process equipment and the instrumentation used for process control – were created.
Hazard identification	Chemical, microbiological, physical and radiological water quality hazards (*e.g.* chlorine sensitive pathogens) were identified on a system and sub-system (*e.g.* catchment, treatment) specific basis through a checklist-based approach.	Hazards were identified via the use of task, substance and workplace specific checklists. Where deemed relevant, this was supplemented by systems engineering techniques, incident and near miss records, and brainstorming.	A FMECA-type approach linked potential hazards (*e.g.* supernatant overflows to surroundings or temporary pipework pumps) to their direct causes (*e.g.* not enough capacity to hold or evaporate sludge received) for each component and for the plant as a whole. Informed by site visits, incident records, and feedback from operating and maintenance staff.	Significant failure modes (flood, earthquake, and static loading) were identified.	Hazards threatening the delivery of the project option(s) on time, to budget, and within the required quality parameters, were identified through facilitated brainstorming, structured with reference to generic hazard categories.	HAZOP studies identified potential deviations from process design intent (*i.e.* hazards) through the application of guide words (*e.g.* low, high, none) to process parameters (*e.g.* ozone flow).
Exposure assessment	Knowledge of the environmental behaviour of hazards and the system under examination, technical judgement, incident reports, survey maps, and monitoring records were synthesised to link hazards (*e.g.* chlorine sensitive pathogens) to their sources (*e.g.* dairy farming or grazing) and to the events which may lead to their realisation (*e.g.* runoff or percolation from land based activities).	There was an absence of explicit provisions for identifying the precursors to identified hazards, one exception being for hazards arising from manual handling activities, where checklists examined which aspects of the actions and movements, workplace layout, and working posture generated said hazards.		No inference possible.	Hazards (*e.g.* aqueduct erosion) were linked to their direct causes (*e.g.* major storm runoff; water release from failed stormwater dams).	Engineering judgement was applied to identify potential causes of deviations from design intent (*e.g.* human error: acts of omission or commission; equipment failure; and external events).
Evaluation of existing controls	Actions, activities and processes applied to mitigate the introduction or transport of hazards from catchment to customer tap (*e.g.* catchment protection, pre-treatment, ozonation) were identified via a	Health and safety risk controls were identified with reference to a control hierarchy which established their relative criticality: engineering (*e.g.* substitution, isolation, design modification, guarding), administrative (*e.g.* training, supervision,	Not observed to have been explicitly undertaken.	The influence of structural and non-structural (*e.g.* early warning systems) controls was incorporated within the modelling of failure scenarios (*i.e.* within event trees, dam break modelling, *etc.*).	Not observed to have been explicitly undertaken.	Systems or procedures designed to prevent, detect, provide early warning, or mitigate the consequences of a deviation (*i.e.* safeguards) were identified. No explicit provision for evaluating their adequacy of design,

(continued on next page)

Table 5 (continued)

	Drinking water quality management	Occupational health and safety management	Asset management		Project management	Engineering
			Treatment plants	Major dams*		
Evaluation of existing controls	checklist-type approach applied to system schematics. Critical controls were identified via set criteria. Technical data, consultations with operators, and site visits informed survey-based evaluations of their adequacy of design, management and operation with reference to key attributes (*e.g.* infrastructure; planning, procedures and legislation; monitoring; and auditing).	procedures), and personal protective equipment. No explicit provision for evaluating their adequacy of design, management or operation.				management or operation.
Consequence evaluation	This may be generalised as the judgement-based interpretation of limited data sets describing the nature and severity of consequences of past hazardous events (*e.g.* in occupational health and safety: cost of claims, lost time due to incidents) to derive a credible evaluation of the potential consequence(s) of uncertain future events. Evaluations were near uniformly characterised with reference to descriptors of the nature (*e.g.* environmental, financial) and severity of consequences of events enshrined within the utility's portfolio of risk ranking techniques. However, isolated applications of mathematical modelling (*e.g.* event tree analysis, dam break modelling, inundation mapping, and economic impact evaluations in major dam risk analysis; event tree analysis in one occupational health and safety risk analysis application) were observed.					
Likelihood evaluation	May be generalised as the judgement-based interpretation of data pertaining to the frequency of past hazardous events (*e.g.* water quality exceedence frequencies) in light of analyst(s) knowledge, experience, and assumptions. Evaluations were near uniformly characterised with reference to likelihood benchmarks within risk ranking techniques. However, isolated applications of mathematical modelling were observed (*e.g.* in major dam risk analysis, network reliability analysis, *etc.*).					
Risk evaluation	Outside of isolated risk analyses driven by consultants (*e.g.* notional costs of risk and statistical lives lost were derived in major dam risk analysis), risk was expressed in qualitative terms (extreme, high, medium or low) derived by combining estimates of consequence severity and likelihood on a risk matrix.					

safety management). More commonly, managerial judgement was used to balance costs and benefits, at times informed by cost-effectiveness evaluations of risk reduction per unit (Euro) spent. Thus, the determination of whether risks satisfied the ALARP criteria was judgement-based, rather than informed by an explicit evaluation of the costs and benefits of reducing vs. maintaining risk levels.

We present two justifications for the variable rigour and formality that characterised this practice: (i) that the resources expended in decision analysis must be justified by the benefit of better decisions, and so detailed analysis is neither desirable nor justifiable for every decision; and (ii) that evaluation criteria incorporating intangible dimensions are difficult to incorporate within the analytic framework of cost-benefit analysis.

4.4. Risk based decision making: maturity of implementation

The sub-sample's risk based decision making profile mirrors that of risk analysis (Fig. 2). However, the decision making processes were qualitatively less mature, and characterised by a lesser degree of definition. One implication is that we may expect a lesser degree of rigour and formality in risk based decision making. Perhaps this reflects an organisational culture that strongly values the roles of judgement, intuition, and creativity in decision making, and thus shies away from structure or standardisation. However, our model is intended to guide, not prescribe, decision making with the objective of encouraging a high degree of consistency, credibility, and confidence in the outcomes. In the absence of a clear framework, people struggle to identify their full range of values and concerns in a given decision context, and are ill-equipped to perform the complex trade-offs common to risk based decision making (Arvai et al., 2001; Slovic et al., 1977; Payne et al., 1992; Slovic, 1995; Matheson and Matheson, 1998). It does not require a strong grasp of decision theory to conclude that an aversion to decision frameworks, however motivated, is not conducive to sound risk management.

5. Discussion

We now critically evaluate our contribution, which is three-fold. We have (a) synthesised empirical observations with prior behavioral and normative risk research to codify the processes of risk analysis and risk based decision making; (b) placed these processes within a maturity framework that distinguishes between levels of implementation, from *ad hoc* to adaptive; and (c) provided a comparative analysis of risk analysis and risk based decision making across a range of utility business functions.

5.1. Coding of risk analysis

Consider the codification of risk analysis (Fig. 1; Table 1), best described by reference to the prominent risk frameworks that adopt an organisation-wide focus (*e.g.* COSO, 2004; AS/NZS, 1999, 2004; FERMA, 2003) and those for drinking water quality management (NZMOH, 2001; NHMRC, 2001, 2004; WHO, 2002, 2004). Our inclusion of exposure assessment is distinctive because strategic risk management frameworks tend to focus on finding sources of potential harm, to the neglect of the underlying pathways that lead to their realisation (*i.e.* how and why hazardous events may occur). This focus on root causes is mirrored in our treatment of control evaluation, which involves identifying and assessing existing technical, physical and administrative

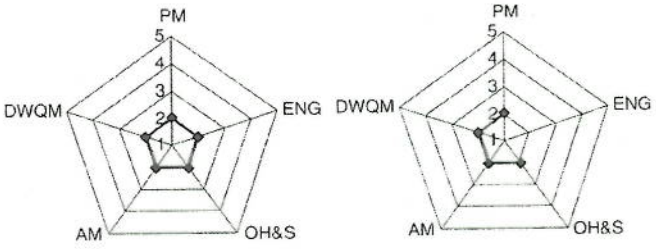


Fig. 2. Spider diagram illustrating the maturity of implementation of risk analysis (left) and risk based decision making (right) within the sub-sample (insufficient data was obtained to evaluate the latter within engineering).
Key: DWQM: drinking water quality management; AM: asset management; OH&S: occupational health and safety management; ENG: engineering; PM: project management.

Table 6
Summary of the undertaking of each risk based decision making practice within the sub-sample

		Drinking water quality management	Occupational health and safety management	Asset management	Project management
Establish risk acceptance criteria		Corporate policy was to reduce risks to a level "as low as reasonably practicable (ALARP)." The ALARP principle recognises that it would be possible to spend infinite time, effort and money attempting to reduce a risk to zero, and reflects the idea that the benefits of risk reduction should be balanced with the practicality of implementation. However, ALARP was not referred to within individual functions' risk management procedures, with the exception of OH&S and in major dam safety management. In the latter, risk acceptability considered three criteria: life safety criteria; ALARP, and the *de minimis* risk concept, in order of stringency.			
Establish criteria for evaluating alternative risk management options		Not explicitly defined. Interviewees referred to cost, time and effort required for implementation; forecast risk reduction; regulatory compliance; risks introduced (*e.g.* disinfection by-products); geographical and technical feasibility (*e.g.* site constraints); operability; manpower required; and social and political concerns.	Not explicitly defined. Forecast risk reduction, cost of implementation, and technical feasibility were referred to by one interviewee.	Defined for below ground major water mains: qualitative risk reduction, cost of implementation, and latency of effects; for major dams: cost of implementation, and forecast reduction in statistical lives lost and economic losses from dam failure events (weighted to ensure preference for reducing lives lost).	Not explicitly defined. Although project managers were explicitly required to take a cost–benefit approach in evaluating risk management options, the scope of these considerations, *i.e.* the criteria with which costs and benefits were determined with reference to, was not defined.
Identify risk management options		Options (*e.g.* infrastructure upgrades, fencing off sensitive catchments, educating and training operators) were generated by groups responsible for the risk analysis of each sub-system (*e.g.* catchment) in consultation with relevant specialists (*e.g.* engineering, operations).	Options (*e.g.* introducing standard work practices) were typically generated in brainstorming sessions involving a broad cross-section of regional/departmental staff, and, where relevant, OH&S staff.	Options (*e.g.* for wastewater treatment plants: capital projects, alterations to operating or maintenance regimes, contingency plans; for dams: structural and non-structural measures, such as installing external back up seals on concrete faced rockfill dams, or early warning systems, respectively) were generated by those groups responsible for the risk analysis of each asset class in consultation with operating and maintenance staff.	Options were typically generated by the project manager in consultation with relevant stakeholders (*e.g.* engineering staff, environmental representatives), or within the risk analysis workshops through group brainstorming. This was informed by predefined measures for: reducing likelihood of occurrence (*e.g.* audit and compliance programs, training, preventative maintenance); reducing impact of occurrence (*e.g.* contingency planning, engineering and structural barriers, early warning devices); and risk transfer (*e.g.* contracts; insurance arrangements).
Evaluate options	The impact of options against individual evaluation criteria	Methods ranged from the application of professional judgement, to the revision of risk analyses (*i.e.* to derive the forecast risk reduction), to stakeholder consultations, cost-estimations, and engineering studies (*e.g.* feasibility studies in major dam safety management). However, given that in most cases the evaluation criteria were not explicitly defined, the undertaking of this tended towards the informal or implicit.			
	Determining relative merit of options	Largely informal and judgement-based, although the use of formal cost–benefit analysis was observed within asset management's approach to prioritising major dam safety upgrades, whilst cost-effectiveness evaluations informed prioritisations of the replacement of below ground major water mains. Furthermore, risk management options that took the form of capital projects valued in excess of approximately $150,000 (US) underwent formal cost–benefit analysis as part of the capital approval process.			
	The acceptability of risk	The limited application of cost–benefit analysis in the context of evaluating risk management options meant that the determination of risk acceptability was typically judgement-based.			
Expert review and option(s) selection		Whilst our interviewees referred to peer reviews of varying formality as helping to shape the final option(s) selection across our sub-sample, the data does not allow for a meaningful analysis of the roles of judgement, experience, bias, power structures, *etc.* in shaping decision outcomes.			

controls. Here, novelty stems from our generalisation of principles relating to the control of drinking water quality hazards to require, as a normative matter, that this practice should require an assessment of control criticality (*e.g.* based on their inherent capacity to reduce risk, whether they are proactive or reactive, *etc.*) *and* of their adequacy of design, management and operation. These are important advances, because the neglect of causal pathways to failure and latent weaknesses in system defences impedes the development of risk management measures targeted at the root causes, and therefore, promotes a focus on hazard, rather than risk, management.

We have placed consequence evaluation prior to likelihood evaluation. The majority of frameworks consider the order in which they are performed to be interchangeable, or at least make no explicit reference to the matter (*e.g.* COSO, 2004; AS/NZS, 1999, 2004; FERMA, 2003). Our reasoning is that the outcome(s) should be defined prior to any evaluation of the likelihood of occurrence. If these steps are performed in reverse, likelihood evaluation tends to be concerned only with the likelihood of a hazardous event occurring (*e.g.* the probability of asset failure), rather than with the likelihood of an event occurring *and* leading to a defined outcome (*e.g.* the probability of an asset failing and leading to a given environmental impact). The former approach overestimates risk. This is not a purely theoretical danger; our research has revealed instances of its occurrence (MacGillivray et al., 2007b).

5.2. Coding of risk based decision making

Strategic risk management frameworks (*e.g.* COSO, 2004; AS/NZS, 1999, 2004; FERMA, 2003) conventionally treat risk based decision making, namely the identification, evaluation and selection of options to manage risks, in a somewhat cursory manner. And so the novelty of our coding (Fig. 1; Table 2) is best illustrated with reference to the decision theory literature. Notably, we have separated "evaluate options" into

three elements: (i) forecasting the impact of options against each evaluation criteria (*e.g.* technical feasibility); (ii) determining the relative merit of each option; and (iii) determining the acceptability of the residual risk associated with each option. We believe this provides an important advance to option evaluation, moving beyond the notion that the acceptability of a risk can be determined without considering the costs and benefits of maintaining vs. reducing risk levels (*e.g.* in using measures of risk as proxies for risk acceptability).

We also highlight our inclusion of managerial and professional review prior to the final risk management decision. Whilst not novel (*e.g.* Aven et al., 2007), it is crucial because it highlights our view that decision analysis should compliment, but not replace, the knowledge, intuitions and judgement of decision makers (Mintzberg, 1994). Further, risk based decisions should not reflect theoretically or analytically derived perspectives that run counter to sound professional judgement (Hrudey and Hrudey, 2003). More specifically, it emphasises that because risk is at heart, an expression of uncertainty (Amendola, 2001), the outputs of a decision analysis must be treated diagnostically rather than deterministically, *i.e.*, they should provide decision support, not carte blanche decisions.

5.3. Coding of maturity

Our research applies capability maturity modelling principles to the processes of risk analysis and risk based decision making (Tables 3 and 4). It allows users to distinguish the relative maturity of implementation of risk analysis and risk based decision making, presumed to correlate this with performance in managing risk. The origins and logic of the hierarchy of maturity levels, particularly regarding the selection and definition of attributes used to define process maturity, are summarised in Table 3 (for more detail, see MacGillivray, 2007c). This hierarchy is the heart of our model, and the most valuable contribution by virtue of its usefulness as discussed below.

5.4. Utility of the model for benchmarking

Throughout our work we have been concerned with improving risk management practice and we are interested in vigilance on the ground. Hence we ask, who may use the model we have developed, and what will it enable them to do that they were previously unable to? The most obvious function of the model is as a tool for research on the form and, crucially, *implementation* of risk management within industry. At a basic level, this is valuable, because published investigations of the latter tend towards the anecdotal rather than methodologically rigorous (*e.g.* Dalgleish and Cooper, 2005; Aabo et al., 2005). From an organisational perspective, its principal function is benchmarking, which enables organisations to compare themselves against others in their sector and beyond, and to identify and incorporate best practices. This is crucial because risk management remains ethereal to many in terms of practice on the ground, creating a need for the systematic evaluation of strengths and weaknesses and the sharing of best practice. It may also be used to drive improvements in the capabilities of key suppliers and partners (*e.g.* through using maturity evaluations to inform supplier selection). Finally, we consider its potential within regulation, envisaging that it may facilitate a step-change in the approach to regulating risk within utility sectors from its current focus on reactive, outcome based approaches (*e.g.* water quality standards) and prescriptions (*e.g.* codes and regulations), towards a proactive, capability based approach.

5.5. Empirical findings

Finally, we consider the contribution of our case study observations in their own right. Three observations bear emphasising: descriptive risk research; a focus on the implementation of risk management; and a cross-functional perspective. We highlight the first due to the lack of theoretically informed descriptive risk research within the water utility sector. The importance of the second is borne out by casting our eyes beyond this sector, where one observes that academic treatments of risk management tend to focus on technical and normative aspects, rather than institutional, behavioural, or descriptive facets, which our findings stress. Finally, our function-specific approach counters the concept of "enterprise wide risk management," which appears to have created a majority opinion amongst its practitioners that risk management is a generic, overarching strategic discipline rather than a devolved process with variations and nuances of application within individual business functions.

6. Conclusions

We have presented a capability maturity model for benchmarking and improving risk analysis and risk based decision making, and illustrated its application to a cross-section of water and wastewater utility functions within a single utility. The insight offered is threefold:

- a synthesis of empirical observations with behavioral and normative risk research to codify the processes of risk analysis and risk based decision making;
- an arrangement of these processes within a maturity framework that distinguishes their relative maturity of implementation from *ad hoc* to adaptive;
- a critical evaluation of the methods, techniques and maturity of risk analysis and risk based decision making across a range of utility functions.

These findings provide researchers, utility managers, engineers, asset managers, occupational health and safety representatives, public health officials, project managers, chief finance officers and regulators with a deeper understanding of the practical form and theoretical underpinnings of risk management, and how distinctions can be made between organisational capabilities. This addresses an important gap in the literature because, although the premise that institutional capacities rather than technical aspects are the fundamental limiting factor in implementing risk management has earlier origins (*e.g.* Garrick, 1988; Luehrman, 1997; Strutt, 2006), there remains a dearth of descriptive research on the practical form of risk management within the utility sectors and, particularly, how it may be embedded. The latter is the subject of our ongoing research.

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Low-cost adsorbents for waste and wastewater treatment: a review

S.J.T. Pollard*, G.D. Fowler, C.J. Sollars** and R. Perry

Centre for Toxic Waste Management, Imperial College of Science, Technology and Medicine, London SW7 2BU, UK

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ABSTRACT

The recent research interest in low-cost alternatives to activated carbon for waste and wastewater treatment is reviewed. An examination of the selection criteria and activation methods for the preparation of active carbon is followed by a critical assessment of low-cost adsorbents prepared from carbonaceous industrial wastes, agricultural by-products and mineral-derived sources. Emphasis is given to in situ reuse applications where stated in the literature and rudimentary economic analyses provided, where available, for comparative operations with commercial activated carbon.

Key words: adsorbants; carbonaceous; wastes; waste u-use; wastewater treatment

INTRODUCTION

Drinking water has been found to contain in excess of seven hundred organic compounds alone, these being derived from a wide range of municipal, industrial and agricultural operations as well as from the natural decomposition of animal and vegetable matter (Bansal, 1988). Adsorption technology is currently used extensively for the removal of organic and inorganic micropollutants from the aqueous phase (Suffet and McGuire, 1980; Slejko, 1985) and since its first introduction in the 1940's, activated carbon has become the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater to a potable water quality (Cheremisinoff, 1979; Weber and Van Vliet, 1980). The use of carbon adsorption for the direct treatment of liquid industrial waste streams is a relatively recent

*Present address: Department of Health Services Administration & Community Medicine, Faculty of Medicine, University of Alberta, Edmonton, Canada T6G 263.
**To whom correspondence should be addressed.

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practice (Lyman, 1979) but has been successfully utilised for the reclamation of metals from electroplating wastes and the removal of phenol from chloralkali plant wastewaters prior to recycling (Lyman, 1979).

Despite the prolific use of this adsorbent throughout the water and waste industries, carbon adsorption remains an expensive treatment process and over recent years, this has prompted a growing research interest into the production of low-cost alternatives to active carbon from a range of carbonaceous and mineral precursors (Bhattacharya and Venkobachar, 1984; Srivastava et al., 1987; Nawar and Doma, 1989). Many of the starting materials for these replacement adsorbents are themselves agricultural or industrial by-products, hence their reuse as secondary adsorbents contributes to the developing emphasis being placed on waste minimisation, recovery and reuse (Patterson, 1989). The aim of this review is to draw together the extensive literature which has developed around the preparation of low-cost adsorbents and to provide an assessment of their relevance and suitability for waste and wastewater treatment.

PREPARATION OF ADSORBENTS FROM CARBONACEOUS PRECURSORS

Selection criteria

The term activated carbon is used to include a broad range of carbonaceous materials which exhibit a high degree of porosity and extended interparticulate surface area (Bansal et al., 1988). Active carbons can be prepared from a huge variety of carbon-containing feedstocks by the catalytic activation of an initially pyrolysed char. Currently, the most common feedstocks for the commercial production of activated carbon are wood (mostly pine, 130 000 t per year), anthracite and bituminous coal (100 000 t per year), lignite (50 000 t per year), peat (50 000 t per year) and coconut shell (35 000 t per year). Alternative feedstocks such as olive stones and almond shells count for ~10 000 tpa (Holden, 1982; Bansal et al., 1988). The carbon contents of these precursors range from 40–90% w/w with a bulk density range of 0.40–1.45 g cm^{-3}. Production is a two-stage operation and involves carbonisation of the raw material below 800°C in the absence of oxygen typically followed by activation at elevated temperatures using an oxidant (steam, carbon dioxide or air) and sometimes a chemical catalyst. Resultant products are then sized, sieved and ground before a final conditioning. The heating rate and dwell time during carbonisation and activation and the activation atmosphere are among the parameters which affect the final pore structure, surface area and chemistry of the carbon produced (Rodríguez-Reinoso, 1986; Wigmans, 1986; 1989). Commercial carbons have a typical surface area range of ~400–1600 m^2 g^{-1}. Whilst commercial car-

bons are produced principally from pine wood and coal, numerous alternative feedstocks have been proposed (Table 1). Indeed, much emphasis is now being placed on the preparation of carbons from locally available materials for ultimate use in waste and wastewater treatment in lesser developed countries where procurement of active carbon is often difficult (Khare et al., 1988). Such adsorbents can be used in the place of commercial materials with significant economic advantages.

Bansal et al. (1988) have reviewed the criteria to be considered when selecting a potential carbonaceous precursor for active carbon. They include; (i) storage life of the raw material, (ii) volume and cost of the raw material, (iii) workability of the raw material and (iv) minimum presence of inorganics. To this list can be added; (v) density, (vi) carbon content of the feedstock, (vii) porosity of the precursor and (viii) availability of the raw material (Pollard, 1990a). Few materials satisfy all these requirements, selection often being made primarily on the basis of the availability of the raw material.

Carbonisation and activation

During carbonisation, pyrolytic decomposition of the precursor occurs (Fitzer et al., 1971) together with the concurrent elimination of many of the non-carbon elemental species (H, N, O and S). Low molecular weight volatiles are first released, followed by light aromatics and finally, hydrogen gas (Hucknall, 1985), the resultant product being a fixed carbonaceous char (Lewis, 1982). The pores formed during carbonisation are filled with tarry pyrolysis residues and require activation in order to develop the internal sur-

TABLE 1

Alternative feedstocks proposed for the preparation of activated carbon adsorbents (adapted from Hassler, 1967 and Keirsse, 1986)

Bagasse	Kelp and seaweed	Sugar-beet sludge
Lampblack	Blood	Leather waste
Bones	Lignin	Spent Fuller's earth
Lignite	Cereals	Molasses
Coal	Nut shells	Oil shale
Coffee beans	Peat	Corn cobs
Petroleum acid sludge	Cottonseed hulls	Petroleum coke
Distillery waste	Potassium ferrocyanide waste	Fish
Pulp-mill waste	Rice hulls	Fruit pits
Rubber waste	Municipal waste	Newspaper
Palm tree cobs	Jute stick	Wheat straw
Coconut coir	Sunflower seeds	Refinery wastes

face of the char. Activation may be accomplished via a chemical or physical route.

Chemical activation employs a catalyst impregnated into the raw material to influence the pyrolysis such that tar formation and volatilisation are kept to minimum (Smísek and Cerny, 1970). The most widely used chemical activants are $ZnCl_2$, H_3PO_4, H_2SO_4, KOH, K_2S and KCNS (Wigmans, 1989). The feedstock is impregnated with the catalyst, often as a near saturated solution, dried and then carbonised and activated in a single action although two separate temperatures are often used. Post activation treatment is required to remove residual catalyst which may be reclaimed for subsequent reuse. Chemical activation is performed at temperatures of between 400–800°C and used industrially for wood-based carbons. The pore size distribution of the final product is largely a function of the degree of initial impregnation (Bansal et al., 1988). A comparison of chemically and physically activated carbons (Kadlec et al., 1970) shows that the different mechanisms of activation may result in varying shapes and sizes. The precise mechanistic details of chemical activation are not well understood and the selection of an activation procedure is largely a matter of which catalysts produce a developed porosity. Nevertheless, the literature yields a large number of tried and tested activant-feedstock couples, a selection of which are shown in Table 2.

Physical activation or partial gasification refers to the direct reaction between the carbonised char and an activant in its gaseous or vapour state. As in chemical activation, the principle objective is the removal of tarry amorphous carbon from the interstitial layers of the structure in order to develop

TABLE 2

Examples of chemical activant-feedstock couples

Feedstock	Activant	Conditions	Reference
Pine sawdust	$Fe(NO_3)_3/CO_2$	850°C, 1 h, 825°C, 1 h	Alvim Ferraz, 1988
Sawdust 1	P_2O_5	350–500°C	Bansal et al., 1988
Sawdust 2	KCNS	35% v/v, 800°C	Hassler, 1967
Coconut shell	H_3PO_4	450°C	Laine et al., 1989
Coconut coir	$ZnCl_2/N_2/CO_2$	800°C	Hitchcock et al., 1983
Palm tree cobs	H_3PO_4/H_2SO_4	730°C, 6 h	Renourez and Avom, 1988
Algerian coal	KOH/NaOH	930°C	Ehrburger, 1986
Fertilizer slurry	H_2O_2/H_2O (g),N_2	450°C, 1 h	Srivastava et al., 1987
Raffination earth	H_2SO_4	10% v/v, 350°C	Korczak et al., 1989
Wood and peat	$CaCl_2$ or $MgCl_2$	400–600°C	Hassler, 1967
Olive stones	$ZnCl_2/CO_2$	600°C, 2–16 h	López-González, 1980
Petroleum coke	KOH/H_2O	700–850°C, 4 h	Bansal et al., 1988

the porosity and make accessible the internal surface area. Porosity develops with increased burn-off of disorganised carbon (Rodríguez-Reinoso, 1986). Steam, carbon dioxide and air are the most common activants, the kinetics and mechanisms of these reactions being well known for many years (Marsh and Rand, 1971; Kapteijn and Moulijn, 1986; Walker, 1986; Lizzio et al., 1990).

CARBONACEOUS ADSORBENTS FROM INDUSTRIAL WASTES

Numerous raw materials have been evaluated for the preparation of activated carbon. Many industrial wastes are high in carbon content and offer significant potential for conversion into carbonaceous chars which may then be further activated to yield porous adsorbents. Several such wastes currently pose a variety of disposal problems due either to their bulk volume, autoreactivity or physical nature (e.g. oily wastes, scrap tyres) thus the controlled pyrolysis of these wastes combined with the reuse of the porous products contributes to a minimisation of these handling difficulties.

Petroleum wastes

The petroleum refining industry generates large quantities of carbonaceous waste residues that have attracted interest as precursors for active carbon. Kogyo and Kaisha (1988) recently patented a method for the production of pitch beads, a mixture of petroleum pitch and polyaromatics. The beads were initially oxidised at 400°C and then activated at 800°C (air, CO_2). Similarly, Ali and Saleem (1988) utilised heavy vacuum bottoms from an Iraqi crude oil. The residue was initially sulphonated (H_2SO_4, 100°C), carbonised at 400°C and the resulting char steam activated at 900°C. Carbon disulphide extraction of the char prior to activation improved the adsorbents capacity for aqueous phase Methylene Blue removal. Fasoli and Genon (1976) utilised a refinery waste for the production of a supported, granular carbon. The precursor in this case was a spent sand filter used for the removal of insoluble oil residues from a refinery wastewater. The waste was carbonised in a rotary furnace and activated under a steam atmosphere. Reuse of the carbon for the same application was proposed by the authors.

Scrap tyres

Waste car tyres have also been used for their high carbon content. Stockpiled tyres pose a serious fire risk and their uncontrolled combustion may lead to the large-volume release of oils, polyaromatic hydrocarbons (PAH), phenols and heavy metals into the atmosphere (ENDS, 1990). Con-

trolled pyrolysis, however, has been employed to convert the butyl rubber and carbon black content of tyres to semi-active carbon. Luchesi and Maschio (1983) used a moving bed reactor at 400–700°C, and a variety of atmospheres to produce carbon from the rubber from stripped tyres. Resultant products exhibited surface areas of up to 320 $m^2 g^{-1}$, and demonstrated Freundlich behaviour for the removal of Orange II and Acid Black 24 dyes from the aqueous phase. Ogasawara et al. (1987) utilised a wet thermal process (water/steam 700–900°C) to prepare a highly active carbon (1260 $m^2 g^{-1}$) for vapour phase applications. In a recent review of phenol uptake from industrial wastewaters by commercial carbons in Poland, Paprowicz (1990) reported the performance of a commercial powdered carbon prepared from waste tyre rubber. Whilst a relatively low surface area of 193 $m^2 g^{-1}$ was reported, the sorbent exhibited a considerable affinity for aqueous phase phenol during subsequent batch adsorption trials.

Miscellaneous industrial wastes

An important contribution to the preparation of low-cost adsorbents has been made by Srivastava and his co-workers at the University of Roorkee, India. In one study (Srivastava et al., 1987), waste slurry generated by the combustion of liquid fuel in a fertilizer production plant was pretreated with peroxide and then air activated at 450°C to produce an adsorbent 630 $m^2 g^{-1}$ in surface area. A subsequent study evaluated the specificity of this material for the removal of Cr, Hg, Pb, Cu and Mo from metallurgical and electroplating wastewaters (Srivastava, 1989a). The adsorptive behaviour of the adsorbent was modelled to the Langmuir and Freundlich isotherms and the material exhibited a particular selectivity for CrVI, PbII and HgII. The cost of the adsorbent was estimated to be $50/tonne, 40–60-times cheaper than the commercial alternative.

The lignocellulosic component of wool carbonising waste was evaluated by Perineau et al. (1982) for the removal of ionic dyes from textile wastewaters. The selective uptake of dye adsorbates by the charred plant material was explained in terms of ionic chemisorptive interactions between the dye molecule and charged ammoniacal sorbent substrate. Active carbon has also been obtained by the carbonisation and activation (850°C) of fungal mycelum/diatomaceous earth filter cake, a biochemical waste. In this recovery/reuse study Fasoli and Genon (1976) proposed the resultant adsorbent for the on-site treatment of fermentation wastewater. A series of carbons have been recently prepared by Martínez-Sánchez et al. (1990) at the University of Alicante, Spain using chromium tanned leather waste. This precursor, high in ash (Cr_2O_3) content (22–69% w/w) was carbonised and activated at 825°C in a CO_2 atmosphere to produce a carbon with a max-

imum surface area of 108 $m^2\ g^{-1}$. No application as yet has been put forward by the authors for these adsorbents, but the on-site treatment of tanning wastewaters is an obvious and attractive possibility.

CARBONACEOUS ADSORBENTS FROM AGRICULTURAL BY-PRODUCTS

Cellulosic and lignocellulosic wastes have long been recognised as starting materials for the preparation of activated carbon. A series of investigations performed by MacKay and Roberts (1982a,b,c) evaluated the specific influence of pyrolysis conditions on the subsequent gasification and resultant microporosity obtained from lignocellulosic chars. The extensive range of precursors examined for these studies included wastes as diverse as computer paper and walnut shells, cattle manure and newsprint (MacKay and Roberts, 1982a). Much recent interest, however, has been directed specifically at agricultural by-products, especially in the Mediterranean where a wide range of prolific wastes are available.

FRUIT STONES

Rodríguez-Reinoso and his co-workers at the University of Alicante, Spain have been prominent over the last 15 years in the preparation of active carbons from locally-available agricultural by-products. Olive stones (Linares-Solano et al., 1980; López-González et al., 1980; Rodríguez-Reinoso et al., 1984; López-Garzon et al., 1984), almond shells (Linares-Solano et al., 1980; Rodríguez-Reinoso et al., 1982), apricot and peach stones (Rodríguez-Reinoso, 1989) are the prevailing raw materials. During this period of research, this group has optimised the activation procedures for active carbon preparation using a variety of chemical and physical techniques. Consequently, high quality, microporous carbons have been prepared and characterised (Rodríguez-Reinoso et al., 1982; Rodríguez-Reinoso, 1986). In a typical preparative procedure, olive stones were washed in 10% v/v H_2SO_4, sieved to ~1 mm diameter and carbonised under N_2 at 850°C for 1 h. Carbon dioxide gasification followed at 850°C for increasing time periods and the products characterised by N_2 and CO_2 adsorption, mercury intrusion porosimetry (MIP) and scanning electron microscopy (SEM; Iley, Marsh and Rodríguez-Reinoso, 1973). Application of the Langmuir equation yielded surface areas of 90–1550 $m^2\ g^{-1}$.

Caturla et al. (1988) demonstrated the excellent adsorption properties of olive stone carbons by studying the aqueous phase uptake, by these materials, of nitro- and chloro-substituted phenols, adsorbates which have long been recognised as priority pollutants by the United States Environmental Protection Agency (USEPA; Chapman et al., 1982). The

parameters found to control the adsorptive capacity of these carbons varied according to the degree of activation. Thus for narrow range microporous materials, carbon porosity was the dominant variable, whereas for carbons displaying a wider micropore range, chemisorptive effects and adsorbate dimensions showed an important function in the adsorption process.

Ferro-García et al. (1988) evaluated a range of fruit pit carbons for the specific removal of ZnII, CdII and CuII from industrial wastewaters. In this extensive study, the effect of temperature, complexing agents and accompanying anion on the adsorption of the three cations was monitored. A Langmuir interpretation yielded adsorption monolayer capacities ranging from 18–150 μmol g^{-1} for the three metals and the adsorbents were subsequently proposed by the authors for the treatment of metal finishing plant wastewaters.

In addition to the uptake of phenols and metal cations, olive stones (and almond shells) have been evaluated for the removal of industrial dyes from the aqueous phase. Linares-Solano et al. (1984) employed solution phase isothermal methods in order to complement the gas adsorption and MIP characterisation of their materials. Olive stones and almond shell precursors were carbonised in N_2 (1123 K) and activated in CO_2 (1073 K) and compared with similar materials which had been either activated directly in CO_2 or air treated at 573 K prior to CO_2 activation. Adsorbents were then screened according to their capacities for the following molecular probes: 4-nitrophenol, Methylene Blue, Orange II, Crystal Violet and Victoria Blue. The two precursors exhibited different behaviour with almond shells displaying a developed meso (pore width, d $\sim$2–50 nm) and microporosity (d $<$2 nm) and the olive stones showing a greater degree of macroporosity (d $>$50 nm). Whilst both materials yielded highly active carbons, 80–1300 $m^2 g^{-1}$ in surface area and 0.3–0.8 $cm^3 g^{-1}$ in volume, olive stones were the preferred choice of the authors for the adsorption of the larger textile dyes from solution. López-Garzon et al. (1984) continued the study of porosity in olive stone carbons with an investigation, using gas chromatographic methods, of the retention of straight, branched and cyclic hydrocarbons in the micropores of these adsorbents. Tailor-made materials derived from olive stones, activated under controlled conditions may exhibit molecular sieving properties and offer potential as isomerization catalysts for the petrochemical industry.

Coconut shell carbons

Coconut shell has long been known as a precursor for high quality, granular carbons with extensive micropore volumes and is currently responsible for $\sim$9% w/w of commercial activated carbon worldwide (Bansal et al.,

1988). Despite its commercial exploitation, however, it has been widely treated as a low-cost feedstock on account of widespread distribution in much of the developing world. Banerjee et al. (1976) prepared a carbon, 800 $m^2\ g^{-1}$ in surface area, by heating $ZnCl_2$-impregnated crushed coconut shells to 700°C then activating the charred intermediate in steam or air at 900°C. The highly adsorbing properties observed by the authors for these products make them ideal candidates as water treatment carbons. Indeed, in a study of the removal efficiencies of commercial carbons of similar surface area for aqueous Cr VI (Alaerts et al., 1989) the coconut based product was the most effective. Chromium removal was explained in terms of physiochemical adsorption of CrVI working in conjunction with the chemical reduction of CrVI to CrIII. Coconut based carbon was found to remove 94% w/w of a 20 mg l^{-1} CrVI solution after a 4 h contact time during equilibrium batch tests. Removal was found to be particularly pH sensitive and dependent on carbon dosage, particle size and CrVI concentration. Hexavalent chromium is commonly found in many industrial wastewaters, with by far the largest contribution coming from the leather tanning, textile, electroplating and metal finishing industries where CrVI concentration can vary from ten to a few hundred mg l^{-1} (Alaerts et al., 1989). With the developing world containing an increasing number of such plants, and the requirement for cheap and effective CrVI removal/recovery, coconut shell carbon adsorption displays considerable promise as a locally-available water treatment technology.

Mortley, Mellowes and Thomas (1988) characterised activated carbons from materials of varying morphology including coconut husks and shells and compared them with commercial water treatment carbons (Darco). In an exhaustive examination of the relationship between pyrolysis conditions, precursor composition and adsorptive behaviour, these workers reasoned that precursors with higher activation energies yielded higher surface areas and developed microporosities on account of the lesser degree of lignocellulosic breakdown.

Chemically activated Venezuelan coconut carbons have been recently prepared by Laine, Calafat and Labady (1989) by impregnating shells with H_3PO_4 and using a one-step carbonisation/activation procedure at 450°C. Surface areas of 1200 $m^2\ g^{-1}$ were recorded using a BET N_2 isotherm method. Hitchcock, McEnaney and Watling (1983) examined the solution phase adsorptive properties of $ZnCl_2$ activated coconut coir, the lignocellulosic fibre obtained from the mesocarp. Activated carbon fibres were prepared by carbonisation of the fibrous precursor at 800°C under N_2 followed by 18–50% burn-off (activation) in CO_2. Langmuir behaviour was observed for 4-nitrophenol adsorption, and the large amount of adsorbate retained by these materials (2.3 mmol g^{-1} for the 50% burn-off sample)

prompted the authors to propose activated coir as a possible water treatment carbon.

Rice hulls

An additional high-volume agricultural waste, prevalent in much of the developing world are rice hulls or husks. Whilst the production of rice husk carbon (RHC) has been studied since the 1940's (Tanin and Gürgey, 1987), the current interest in low-cost adsorbents has led to a re-evaluation of their water purification properties (Tanin and Gürgey, 1987; Srinivasan, Balasubramanian and Ramakrishna, 1988; Nawar and Doma, 1988; Youssef et al., 1990). Tanin and Gürgey (1987) utilised chemical ($ZnCl_2$, H_3PO_4) and physical (CO_2) activation procedures to prepare rice hull carbons which were then screened for their gaseous N_2 and solution phase isothermal adsorption capacities. Nitrogen BET analysis yielded a range of surface areas of 482–788 $m^2\ g^{-1}$. Methylene Blue adsorption conformed to a Freundlich model with the most active product being that activated with 50% w/v solution at 750°C for 1 h. In a further examination of RHC adsorption, Srinivasan, Balasubramanian and Ramakrishna, (1988) evaluated activated products for CrVI removal from industrial wastewater. Sulphuric acid washed rice hulls were activated at 800–850°C for 30 min and then ground to 20–50 mesh (ASTM) prior to adsorption studies. The results of equilibrium batch tests identified RHC as an adsorbent, comparable to commercial activated carbon, with 88% w/w and 99% w/w removal of total and hexavalent chromium, respectively. Column studies gave CrVI adsorptive capacities of 8.9 mg g^{-1} and 6.3 mg g^{-1} for RHC and commercial carbon respectively, and a feasibility study using a real plating shop wastewater, 300 mg l^{-1} as CrVI demonstrated the suitability of RHC for the treatment of CrVI bearing wastewaters. As for coconut shell carbon, the adsorption mechanism was believed to be a combination of physiochemical and reductive processes, with the charged carbon surface facilitating reduction of adsorbed CrVI ($HCrO_4^-$) to CrIII (HO_3Cr^+). Youseff, Mostafa and Dorgham (1990) have also prepared $ZnCl_2$ and steam activated RHC. Chemically activated materials (600°C, limited air) exhibited Methylene Blue capacities of 0.24–0.72 mmol g^{-1} depending on the initial $ZnCl_2$ impregnation ratio. Steam activated carbons (900°C, 12–43% burn-off), however, had poor dye affinities (0.05–0.28 mmol g^{-1}) in comparison.

In a comparative study of three low-cost adsorbents (Bhattacharya and Venkobachar, 1984), bituminous coal, crushed raw coconut shells and RHC were examined for their aqueous CdII capacities, a pollutant which often appears at unacceptable levels in smelting industry site run-off, sewage sludge and a variety of agricultural sources. Rice husk carbon was produced by car-

bonisation at 550°C, followed by steam activation at 700°C for 100 min. Activated RHC performed extremely well, exhibiting 94.4% w/w CdII removal from a 500 $\mu g\ l^{-1}$ initial solution compared with 25.4% w/w removal observed for Filtrasorb 400® , a commercial water treatment carbon. Despite this degree of performance, however, the economics of steam activation at 700°C were deemed prohibitive by these workers, and further studies were unfortunately not performed. The uptake of adsorbates by raw, untreated rice hulls (62% w/w CdII in the above study) has been the subject of study by Nawar and Doma (1989) who determined the adsorptive capacities of peat moss and raw rice hulls for two widely used industrial textile dyes, Sandocryl Orange B-3RLE and Lanasyn Black BRL ABK and compared them to a granular commercial carbon. A Freundlich treatment was applied and the factors affecting their respective removal efficiencies determined. Contact time, pH, dye structure and particle size were identified as key parameters, with the peat moss displaying the most effective removal (95% w/w, 50 ppm initial concentration, 2 h contact) followed by rice hulls (90% w/w) and the commercial carbon (87% w/w). A rudimentary economic assessment of the use of peat moss and raw rice hulls for the removal of textile dyes from industrial wastewaters estimated the relative usage costs to be 0.52 and 1.19% that of carbon for Sandocryl Orange respectively and 1.4 and 0.3% respectively for Lanasyn Black.

Miscellaneous lignocellulosic precursors

Together with the continuing evaluation of fruit pits, coconut shells and rice hulls, a multitude of alternative lignocellulosic wastes have been the subject of study for localised water treatment purposes, the composition of some being given in Table 3. Renouprez and Avom (1988) prepared active carbon from palm tree cobs, a by-product from the palm-oil industry in Cameroon. Using a variety of air (1200°C), vacuum (1200°C) and chemical (H_3PO_4/H_2SO_4, 1200°C) activation procedures, carbons, 23–1078 $m^2\ g^{-1}$ in surface area were prepared. Likewise, Chughtai et al. (1987) used cleaned Sarkanda, a tropical reed/grass as a carbon feedstock. Following impregnation with either commercial grade H_2SO_4, pure H_2SO_4 or $ZnCl_2$, the material was pyrolysed at 400–750°C in the absence of air and products screened by Methylene Blue adsorption. The optimised adsorbent (5 N $ZnCl_2$, 750°C 1 h.) exhibited a dye adsorption capacity of 223 mg g^{-1}.

Residual Spanish olive wood from the pruning and felling of olive groves in the Mediterranean was shown by López-González et al. (1985, 1988) to be a suitable precursor for activated carbon production. Gasification in CO_2 at 1043 K with increasing time periods resulted in the progressive opening of micropores in the initial char to yield a *meso*-/macroporous prod-

TABLE 3

Chemical composition (%) of selected lignocellulosic precursors

Raw material	C	H	N	VC[a]	Ash	Cellulose	Hemicellulose	Lignin
Coconut shells	52.8	5.0	0.08	69.1	0.60	33.6	25.0	38.4
Coconut husks	51.5	5.0	0.10	62.9	3.70	38.0	28.0	32.8
Coconut coir	93.9	0.7			3.10			
Bagasse	45.5	5.0	0.10	72.3	6.00	42.8	29.0	15.8
Pine wood	48.0	6.4	0.01	74.4	0.40	51.4	24.5	19.0
Pine sawdust	49.1	6.2	0.06		0.36			
Jute stick						40.0	35.0	23.0
Almond shells	47.8	6.00	0.35		0.10			
Olive stones	48.2	5.66	0.00		0.03			
Nut shells	40–45			55–60	0.55			
Palm tree cobs	44.6	6.0	0.50		2.6	60.0		

[a]Percentage of volatile components.

uct (469–854 m^2 g^{-1} in surface area) capable of adsorbing appreciable amounts of 4-nitrophenol from the aqueous phase (López-González et al., 1988). In a similar procedure (Guedes de Carvalho et al., 1984), ground Portuguese pine bark was carbonised at 600°C for 1 h under a N_2 atmosphere and then activated at temperatures between 800–1000°C by partial CO_2 gasification. Methylene Blue and iodine numbers were determined and compared with Merck and Co. Inc commercial carbon. Methylene Blue indices ranged from 80–150 for the activated bark carbon compared to 38 for the commercial adsorbent. Iodine numbers of 700–3400 and 947 were recorded, respectively. Keirsse et al. (1986, 1988) employed beechwood sawmill waste. Activated carbons produced by fluidised-bed gasification were screened according to their iodine, Methylene Blue, tannin and phenol indices. Furthermore, adsorption capacities for phenol, pentachlorophenol, dodecylbenzene sulphonate and *p*-toluene sulphonate were determined and modelled to the Freundlich isotherm.

Banerjee and Mathew (1985) produced lightweight, high quality charcoal chips from jute stick, a bulk volume agricultural waste which, in India, amounts to 3–4 Mt per year. Water digestion at 140°C under pressure prior to low temperature carbonisation (300°C) produced a high fixed carbon yield. Chemical impregnants ($ZnCl_2$, Na_2HPO_4, $(NH_4)_2HPO_4$ and $ZnSO_4$) increased the fixed carbon mass yet further to >90% w/w following a three-step carbonisation/activation procedure. The activated charcoal products were subsequently proposed for the clarification of pulp-mill wastewaters, although no data were given to substantiate this application.

A range of chemically activated Tamarind nut carbons were prepared and assessed for their water treatment properties on the basis of their phenol adsorption capacity by Srinivasan, Rao and Ramadevi (1988). Using a variety of treatments adapted from the carbon literature (Hassler, 1967), highly active products were produced by direct pyrolysis as well as activation with 10% w/v solutions of impregnated Na_2CO_3, $CaCl_2$ and Na_2SO_4. In addition, H_2SO_4 treatment and gasification over $CaCO_3$ were performed. Carbons ranged in surface area from 218 m^2 g^{-1} (H_2SO_4) to 2810 m^2 g^{-1} (direct pyrolysis) and displayed phenol uptakes of 0.3–2.0 mg g^{-1}.

Mixed lignocellulosic-resin adsorbents

Our final survey of the use of agricultural by-products concerns the preparation of mixed lignocellulosic-polymer precursors. The combination of carbonaceous wastes and polymer resins is advantageous in terms of increasing the fixed carbon mass of the carbonised char and allowing extrusion of the feedstock prior to activation, thus allowing the preparation of granular carbons. Two recent studies (Simitzis and Sfyrakis, 1988a;b) in particular, have examined carbon produced by the activation of phenol-formaldehyde resin mixed in a 20/80 blend with both olive stones and cottonseed. Steam activated (700–950°C) products (BET N_2 750 m^2 g^{-1} olive stones; 900 m^2 g^{-1} cottonseed) demonstrated similar adsorptive properties to commercial water treatment carbon in their affinities for 3- and 4-nitrophenol and Methylene Blue. In terms of the physical nature of these carbons, incorporation of the resin gives added support to the activated structure and allows formation of granular extrudates which would otherwise be impossible. Granular activated carbon is often favoured in many wastewater treatment applications on the grounds of its easy handleability and greater resistance to attrition and carbon loss during steam regeneration. The subject of attrition and supported carbons is developed in the following review of low-cost mineral and carbon-mineral adsorbents.

LOW-COST MINERAL AND MINERAL-CARBON ADSORBENTS

In addition to the cost penalty often incurred by the use of industrial activated carbon for waste and wastewater treatment, concern has also been expressed over the fragility of powdered activated carbon (PAC) with respect to steam regeneration (Panday et al., 1986). In response, several authors have documented the preparation of mineral-based adsorbents from locally-available waste materials and their subsequent application for the treatment of industrial wastes and wastewaters (Panday et al., 1986; Khare et al., 1988; Gupta et al., 1990). These sorbents, based on substrates such as fly ash,

kaolinite, Fuller's earth and china clay generally offer an increased resistance to attrition and may also exhibit selectivity towards certain aqueous pollutant species, especially ionic dyes from textile industry wastewaters. Whether used in the raw state, or alone without the incorporation of carbon, mineral adsorbents rarely require activation. However, in many instances, the mineral is used as a structural support for a surface carbonaceous char, and in these cases we witness the application of carbonisation and activation techniques similar to those described above.

Fly ash

Pulverised-fuel (fly) ash, the inorganic residue from the combustion of powdered coal (Ferraiolo et al., 1990) has received particular attention as an adsorbent for wastewater purification. Whilst the estimated global production of fly ash is 290 Mtpa (Dhir, 1986), utilisation as opposed to direct landfill of this material is less than 10% w/w of the total available. Typically 40–50% w/w in silica (SiO_2) 20–35% w/w in alumina (Al_2O_3) and 5–12% w/w in ferric iron oxide (Fe_2O_3), fly ash also contains 12–30% w/w carbon and unburnt minerals which are apparently responsible for its reported adsorption capacity (Ferraiolo et al., 1990). As with carbonaceous adsorbents, porosity, particle size distribution and surface area also contribute. Applications within the field of environmental control other then those discussed below include recovery of organic vapours (Ref. 70, Ferraiolo et al., 1990), the adsorption and photodegradation of PAH in the gaseous phase (Dunstan et al., 1989) and the dewatering of secondary sludges from biological treatment processes (Ref. 31, Ferraiolo et al., 1990).

Panday et al. (1986) reported the preparation of a range of mixed low-cost mineral adsorbents for the removal of CuII from Indian industrial wastewaters. Prepared from homogenised blends of fly ash, wollastonite and china clay, the materials exhibited Freundlich isotherm behaviour and adsorption efficiencies of 73–95% w/w for 0.1 mM CuII from aqueous solution at pH 6.5. Uptake was explained in terms of a chemisorptive surface complex between the negatively-charged silica surface and the hydroxylated Cu species in solution. Of the mixed fly ash adsorbents investigated in this study, the fly ash-wollastonite blend proved the most effective and was estimated by the authors to be 40–60-times cheaper than activated carbon. The use of both wollastonite (calcium silicate) alone and fly ash-wollastonite mixes has recently been extended by these workers to the removal of dyes from textile wastewaters (Khare et al., 1987; 1988).

Fly ash alone and coal-fly ash blends have also been examined for the removal of dyes and phenols from industrial wastewaters. Phenol occurs frequently as a hazardous pollutant in industrial wastewaters, is the basic structural unit for many synthetic organic products and is itself a degradation

product of several common pesticides (Boyd, 1982; Paprowicz, 1990). Fly ash demonstrated removal efficiencies of 40, 45 and 45% w/w for 50 ppm aqueous solutions of phenol, cresol and phenol:cresol (1:1) respectively (Kumar et al., 1987). Adsorptive capacity decreased with increasing phenol concentration, as expected. Activated carbon (Union Carbide) evaluated under identical conditions exhibited corresponding removal efficiencies of 65, 70 and 68% w/w. Whilst at low phenol concentrations adsorption onto fly ash was deemed satisfactory, kinetic studies indicated that longer equilibrium contact times were required for fly ash compared with the commercial carbon. Gupta et al. (1988) utilised a locally obtained fly ash, as supplied, for the aqueous phase adsorption of Chrome Red dye. Contact times of 2 h were required to achieve 99% w/w removal from a 5 mg l^{-1} solution. Langmuir behaviour was observed suggesting monolayer coverage, and uptake was again explained in terms of aquated metal/dye complexes at the adsorbent/adsorbate interface. Total removal of Chrome Red dye from 10 mg l^{-1} initial concentration has recently been reported by Gupta et al. (1990) by the combined use of fly ash and coal in a 1:1 blend.

Clay-carbon adsorbents

In terms of empirical chemical composition, fly ash is similar to common clay and among the mineral-based sorbents examined for waste and wastewater treatment, the phyllosilicate (layered) clays display considerable promise.

Kalapusha et al. (1984) prepared a mineral-carbon adsorbent from a spent palygorskite-montmorillonite raffination earth used to remove unsaturated hydrocarbons from aromatic petroleum products. The coked clay waste was steam activated with accompanying HCl vapour at 800–900°C in a static reactor. The resulting products were 6–12% w/w in surface carbon, exhibited Langmuirian adsorptive behaviour and had a range of surface areas of 20–140 $m^2 g^{-1}$ based on water and hexane adsorption isotherms. The mixed adsorbent was proposed for the treatment of wastewater and as a filler for rubber-based products. Korczak and Kurbiel (1987; 1989) report a mineral-carbon adsorbent prepared from a similar spent raffination earth. The starting material was spent Fuller's earth used for refining lubricating oils and contained adsorbed amounts of organic heterocyclic compounds, tarry resins and residual lubricating oil. Using a sulphuric acid activation procedure, the waste was converted to a mixed adsorbent ~ 150 $m^2 g^{-1}$ in surface area with meso- and micropore volumes of 0.254 and 0.039 $cm^3 g^{-1}$, respectively. The adsorptive behaviour of the material was modelled to the BET and Langmuir adsorption isotherms and an extensive investigation of the solution phase adsorption capacity of the sorbent for a range of common industrial pollutants exhibited the feasibility of the material for use in wastewater treatment.

Korczak and Kurbiel (1989) found the kinetics of adsorption to be controlled by an intraparticulate diffusion process. Adsorptive capacity was found to be dependent on adsorbate molecular mass, electrostatic charge and its ability to form hydrogen bonds with surrounding water molecules.

In a rudimentary cost analysis for the preparation of the aforementioned adsorbent (Korczak and Kurbiel, 1987), the mineral-carbon material was estimated to cost ~$100/tonne compared with ~$1000/tonne for a low to medium surface area commercial activated carbon. Operational costs for wastewater treatment were dependent on the additional amount of sorbent required to compensate for its reduced adsorptive capacity, but were still anticipated to be below the cost of employing industrial activated carbon. Korczak and Kurbiel (1989) paid significant attention to the dye-adsorption capabilities of the material and earmarked their adsorbent specifically for the treatment of industrial dye wastewaters. It is unclear, however, in the study to what extent the dye is removed by the carbonaceous char compared with the residual mineral surface, both of which are well documented adsorbent surfaces for ionic dyes (Kipling and Wilson, 1960; Barton, 1987).

Pollard et al. (1990a; 1991a, b) extended the work of Korczak and Kurbiel (1987; 1989) to spent bleaching earth from the edible oil industry and proposed the resulting adsorbent for the isolation of organics in mixed organic/inorganic waste streams prior to cement-based solidification (Pollard et al., 1990b). In this chemical waste treatment application, contaminating organics present in a neutralised spent pickling acid waste were adsorbed by the clay-carbon substrate and then solidified using ordinary Portland cement. Reductions of up to 37% w/w in leachable total organic carbon (TOC) were recorded together with 240–1300% increases in unconfined compressive strength for the solidified waste forms as a result of the pozzolanic activity exhibited by the thermally treated clay.

The activated spent bleaching earth prepared in this study showed many characteristics in common with the material prepared by Korczak and Kurbiel (1989). The optimised material displayed a micropore volume of 0.050 $cm^3\ g^{-1}$, a mesopore volume of 0.14 $cm^3\ g^{-1}$ and an apparent BET area of 239 $m^2\ g^{-1}$. Materials demonstrated BET linearity and an approximated Langmuirian solution phase adsorptive behaviour. On the basis of these similarities and the observed adsorption capacities for aqueous phase phenols, activated spent bleaching earth can be expected to perform well as a low-cost alternative to commercial carbon for industrial wastewater treatment.

Clay and coal-based adsorbents

Fuller's earth and calcined kaolinite have been investigated for the removal of dyes from industrial wastewaters (McKay et al., 1985; 1986). The

adsorptive nature of these clays is derived from their large interlamellar surface area, their base exchange capacity and their hydrophilicity (Siddiqui, 1968). Fuller's earth has long been exploited industrially for its decolorising properties and in many parts of the world is a cheap and readily available mineral. McKay et al. (1985) recorded the adsorption capacity of Fuller's earth for Basic and Acid Blue to be 220 and 120 mg g^{-1} respectively and thus proposed the adsorbent for the treatment of textile wastewaters. Whilst fired kaolinite demonstrated only a limited activity towards dyes, when used in its natural state it has been shown to adsorb Pb and Cd from the aqueous phase (Srivastava et al., 1989b). In this latter investigation, montmorillonite and kaolinite clays exhibited Langmuirian behaviour and uptake was believed to occur via metal silicate interactions at the charged lamellar surface. In similar trials, china clay alone was utilised for the removal of As III (Yadava et al., 1988) and ZnII (Singh et al., 1988) from distilled water. Langmuirian adsorption behaviour was again observed and the pH dependence used to infer a chemisorptive adsorption mechanism in each instance. Likewise, González-Pradas et al. (1990) used activated natural sepiolite (a fibrous silicate mineral) for the removal of aromatic amines from dilute (10^{-7} M) solution.

Coal ash and activated coal-char produced from an underground gasification facility (Humenick, Morgan and Nolan, 1987) were evaluated for the in situ treatment of contaminated groundwater, generated during gas production at the site. Adsorption isotherm studies performed using a synthetic groundwater matrix indicated that both sorbents irreversibly adsorbed phenol, *o*, *m*, and *p*-cresol from the aqueous phase. Uptake was modelled to the Freundlich and Langmuir isotherms and adsorption capacities found to be comparable to that of activated carbon.

CONCLUSIONS

Activated carbon is a costly industrial adsorbent, the procurement of which within the developing world is often problematic. Many locally available carbonaceous and mineral wastes offer potential as low-cost alternatives to active carbon and a critical review of these materials has shown that whilst they generally exhibit lower surface areas than commercial carbons, such adsorbents may demonstrate the selective uptake of some waste components when utilised for waste and wastewater treatment. Many of the studies performed to date rarely go beyond an initial evaluation of solution phase adsorptive capacity and it is recognised that there is a particular need for future studies to verify the performance of promising materials at the pilot plant scale.

The low-cost preparation of these materials relies heavily on their existence as available waste products and at present, only an estimated 3% of

worldwide carbon production finds its feedstock from alternative sources to pine, coal and peat (Bansal et al., 1988). However, the recovery and reuse of wastes as secondary adsorbents, particularly in situations where reuse is envisaged within the same industry as that producing the precursor (Humenick, Morgan and Nolan, 1987; Pollard, 1990a), may offer significant economic advantages over commercial carbon and, in addition, contribute to an overall waste reduction strategy within the industry concerned.

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A CLAY-CARBON ADSORBENT DERIVED FROM SPENT BLEACHING EARTH: SURFACE CHARACTERISATION AND ADSORPTION OF CHLOROPHENOLS FROM AQUEOUS SOLUTION

SIMON J. T. POLLARD,* CHRISTOPHER J. SOLLARS and ROGER PERRY
Imperial College Centre for Toxic Waste Management, Imperial College of Science, Technology and Medicine, London, SW7 2BU, U.K.

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Abstract—An active carbonaceous char supported on a aluminosilicate matrix has previously been prepared by the chemical activation of spent bleaching earth, a solid waste from the edible oil industry. The underlying mineral structure was characterised in this study by XRD and SEM and shown to consist of ill-defined montmorillonite lamellae, with significant loss in crystallinity from the parent material being observed. The adsorption of phenol, 3-chlorophenol and 2,3-dichlorophenol was assessed and found to conform to a Langmuir isotherm model, and a comparison with commercial powdered water-treatment carbons suggested that the surface char of the treated spent clay was sufficiently active to warrant a pilot-study investigation of this low-cost adsorbent for applications relating to wastewater treatment.

Key Words—Clay-carbon adsorbent, spent bleaching earth, montmorillonite, chlorophenols, structural characteristics.

1. INTRODUCTION

The term "activated carbon" is formally used to describe a broad range of carbonaceous materials that exhibit a high degree of porosity and extended interparticulate surface area[1]. Active carbons can be prepared from a huge range of carbon-containing feedstocks by the catalytic activation of an initially pyrolysed char, and are commercially exploited for a diverse number of adsorptive cleansing operations. Despite the extensive use of this adsorbent throughout the process industries, carbon adsorption remains an expensive treatment process and, consequently, over recent years this has prompted a growing research interest into the production of low-cost alternatives to active carbon from a range of carbonaceous industrial and agricultural byproducts[2–6]. Our own studies in this area have focussed on spent bleaching earth (SBE), a solid waste from the edible oil-processing industry typically comprising 25%–40% w/w of residual vegetable oil adsorbed onto phyllosilicate mineral clay[7]. Carbonisation of the chemically impregnated feedstock, followed by activation of the resultant carbonaceous char under a variety of thermal conditions, yielded a clay-carbon product with a developed microporosity and an associated affinity for phenol from the aqueous phase[8,9]. The microstructure of $ZnCl_2$-activated spent bleaching earth has been proposed as a microporous carbon char supported on an amorphous montmorillonite matrix and is analogous to similar reported materials derived from intercalated clay-organic precursors[10–12].

As part of a continuing research programme into the adsorptive properties of this and similar adsorbents for applications relating to environmental control[13], we now extend our structural characterisation of activated spent bleaching earth and report our investigations for the uptake of chlorophenols from the aqueous phase. These particular adsorbates are frequently encountered contaminants in the waste streams of the pesticide, pulp and paper, and wood-preserving industries[14–16].

2. EXPERIMENTAL

2.1 *Adsorbents*

Calcium montmorillonite (Fuller's earth) is a dioctahedral aluminosilicate with an idealised formula of $(Si_8)(Al_{3.15}Mg_{0.85})O_{20}(OH)_4Ca_{0.85}\cdot nH_2O$[17]. The true structure of the raw earth deviates significantly from the ideal as a result of a number of isomorphous substitutions, and acidulation with sulphuric acid prior to use for edible-oil bleaching further disrupts the mineral lattice to leave an ill-defined lamellar microstructure[18]. The simulated spent clay employed in this study consisted of 30% w/w residual crude soybean oil adsorbed onto the surface of Fulmont Premiere® acidulated bleaching earth representing an available carbon source of ~24% w/w. The optimised activation procedure for SBE previously described[9] involved impregnation of the spent clay with 25% saturated $ZnCl_2$ solution followed by carbonisation under N_2 at 450°C for 2 hours, with activation at 600°C for 1 hour. The resultant material, found to be 20.1% w/w in surface carbon, displayed a micropore volume of 0.050 cm^3g^{-1}, a mesopore volume of 0.140 cm^3g^{-1} and an apparent N_2 BET area of 239 m^2g^{-1}[9].

*Currently Postdoctoral Research Fellow, Environmental Health Program, Faculty of Medicine, University of Alberta, Edmonton, Alberta, Canada, T6G 2G3.

Reference powdered water-treatment carbons were obtained from Sutcliffe Speakman Ltd (grade 338P), Norit (UK) Ltd (grade SA4) and British CECA (grade 3SA). This series represents a range in apparent surface areas (BET N_2) from ~500 to ~1200 m^2g^{-1}. Fulmont Premiere® acidulated bleaching earth was provided by Laporte Industries, UK. CHN elemental microanalysis for the commercial materials was performed using a Perkin Elmer 240 microanalyser. The detection limits of this instrument were 0.3% w/w for elemental N and H and 0.1% w/w for C.

All other reagents were supplied by BDH in AnalaR® grade unless otherwise stated.

2.2 *X-ray diffraction*

Powder diffractograms were collected for the primary acidulated material (Fulmont Premiere®) and the optimised SBE in order to observe changes in crystallinity as a result of $ZnCl_2$-activation, and the extent of layer collapse for the mineral support as a result of additional thermal treatment. Dry sieved samples (< 150 μm) were scanned using a Phillips PW1700 instrument (Cu—K α radiation) between 2θ 1°–65° with a generating voltage of 50 kV (25 mA).

2.3 *Scanning electron microscopy*

Clay-derived adsorbents were examined by scanning electron microscopy for a visual inspection of external porosity and microtexture. Dried adsorbent samples (~20 mg; 105°C, 16h) were presented on areas of double-sided adhesive tape (0.5 cm × 0.5 cm), three of which were each mounted to the methanol-cleaned surface of a glass microslide. The slides were gold coated for 10 mins (Emscope, UK) and examined at 2000× using a Hitachi 2500 SEM and an operating voltage of 15 kV. Representative sections of surface were recorded and developed on monochrome paper (Ilford FP4).

2.4 *Equilibrium adsorption studies*

Single component, solution-phase adsorption isotherms were constructed at 20 ± 2 °C for all materials using phenol, 3–chlorophenol and 2,3–dichlorophenol adsorbates. The batch adsorption experiments were run at pH 4.1–5.9 using non-buffered solutions in order to eliminate competitive adsorptive effects from buffer components. This pH range was sufficiently below the pK_a values of the adsorbates used to ensure the predominance of the undissociated and preferred form during adsorption[19]. Equilibrium contact times of 3 hours had previously been established for this set of carbons. Dry sorbents (105°C, 16h) were sieved to < 150 μm (100 mesh) prior to use. Aliquots (100 cm^3) of 30–0.5 mM adsorbate (20–0.5 mM, 2,3–dichlorophenol on account of its reduced aqueous solubility) were added to 1.0 g sorbent samples in 120 cm^3 glass screw-cap bottles, which were then rotated at 40 rpm for 3 hours. Equilibrium adsorbate concentrations were then monitored at 500 nm by visible spectrophotometry (Perkin Elmer Lambda 3 UV/VIS spectrophotometer) using a standard colorimetric 4–aminoantipyrine method[20]. Langmuir isotherm parameters were calculated for each adsorbent-adsorbate pair.

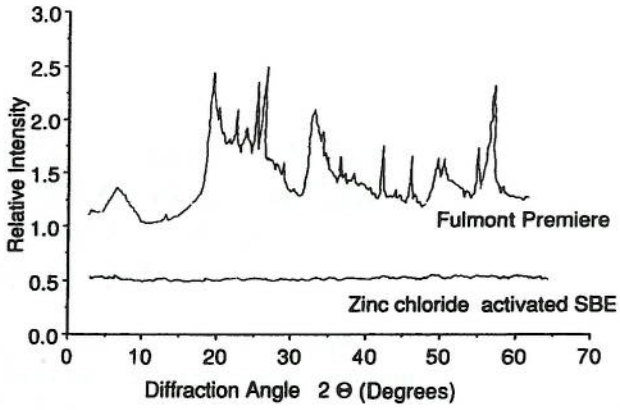


Fig. 1. XRD diffractograms for Fulmont Premiere® and activated clay-carbon adsorbent.

3. RESULTS AND DISCUSSION

3.1 *Surface characterisation*

Figure 1 illustrates the X-ray powder diffractograms of Fulmont Premiere® and $ZnCl_2$-activated spent bleaching earth. Clearly, $ZnCl_2$-activation (450°C/2hr followed by 600° C/1hr) resulted in a total loss of observable crystallinity. This loss may be interpreted in terms of the corrosive action of $ZnCl_2$ and HCl gas produced during chemical activation of the impregnated substrate. Partial loss in crystalline structure from that of the raw montmorillonite mineral is an accepted result of H_2SO_4 acidulation during the industrial production of bleaching earths[18] and further acid attack coupled with progressive dehydration of interlamellar water serves, in this instance, to accentuate the change in morphology of the underlying clay structure. Absence of the d(001) basal spacing peak in the range 2θ 0°–20° for the $ZnCl_2$-activated sample prevented quantification of the extent of layer collapse upon thermal treatment.

Several materials composed of a carbon deposit between montmorillonite lamellae have been recorded in the literature[10–12,21–23]. Sonobe *et al.*[10] reported the preparation of a polyacrylonitrile char in the two-dimensional interlamellar space of Ca-montmorillonite. The char was later graphitised at extreme temperatures (>2500°C) and the aluminosilicate template structure removed by HF treatment to reveal a graphite thin film. Similarly, Ōya *et al.* described the carbonisation of the intercalated product of montmorillonite and α-naphthylamine[22, 23]. Of interest to our own study in both cases is the gradual loss in mineral crystallinity experienced as a result of thermal treatment. Sonobe *et al.* also recorded a shift in the d(001) spacing to slightly larger diffraction-angle values, which was attributed to a narrowing of the interlamellar spacing upon char deposition[10]. Layer collapse of the Ca-analogue was noted to be initiated at temperatures as low as 200°C, but the presence of the char considerably reduced the extent of collapse. This is an important consideration for activated SBE, for which the

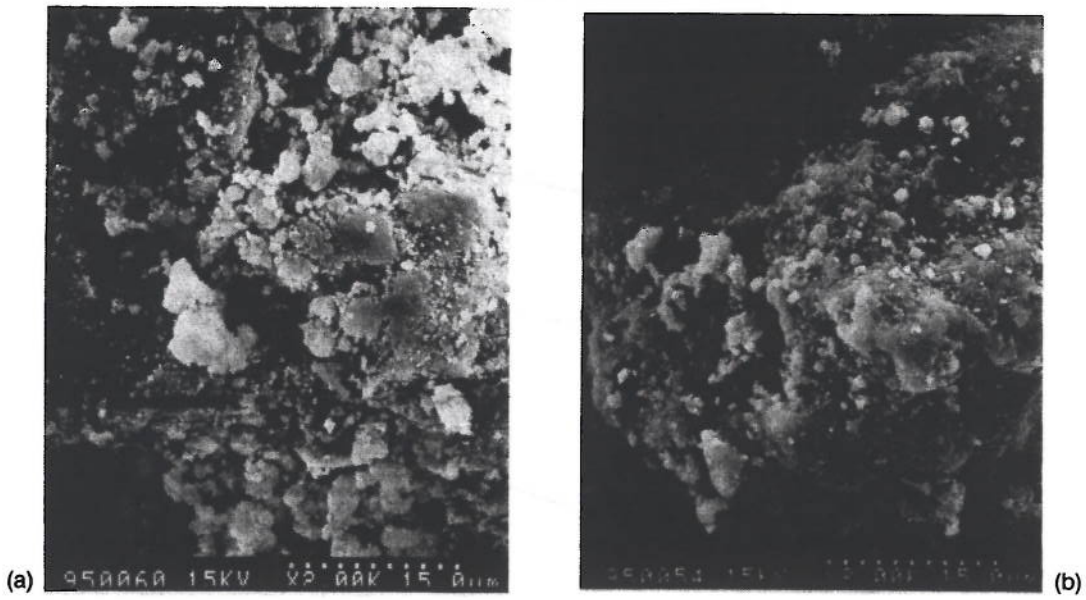


Fig. 2. SEM photographs for (a) Fulmont Premiere® and (b) activated clay-carbon adsorbent. Length bars (dashed) represent 15 μm.

adsorptive properties depend on accessibility to the interlamellar active char.

Representative SEM micrographs of Fulmont Premiere® and activated SBE are shown in Fig. 2 (a,b). The clay-carbon adsorbent was observed to be similar in external surface appearance and microtexture to the acidulated clay, retaining the ill-defined structure often referred to as being akin to a disorgan-

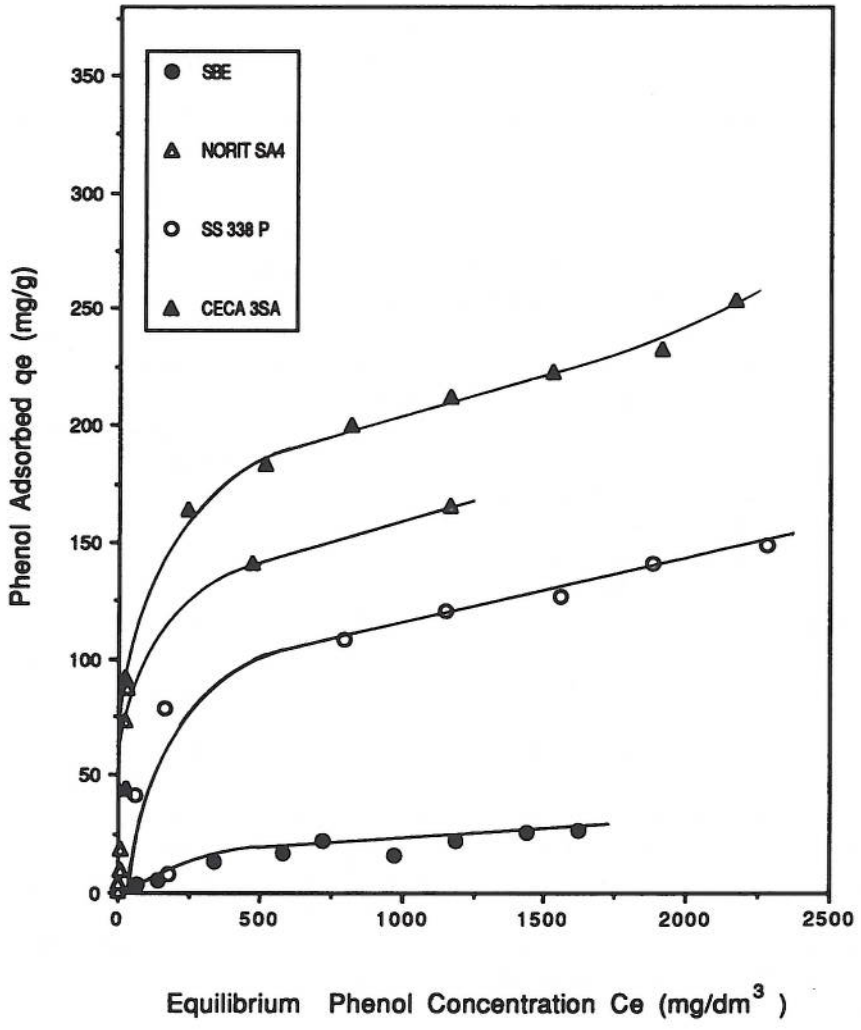


Fig. 3. Phenol adsorption isotherms for activated spent bleaching earth and commercial adsorbents.

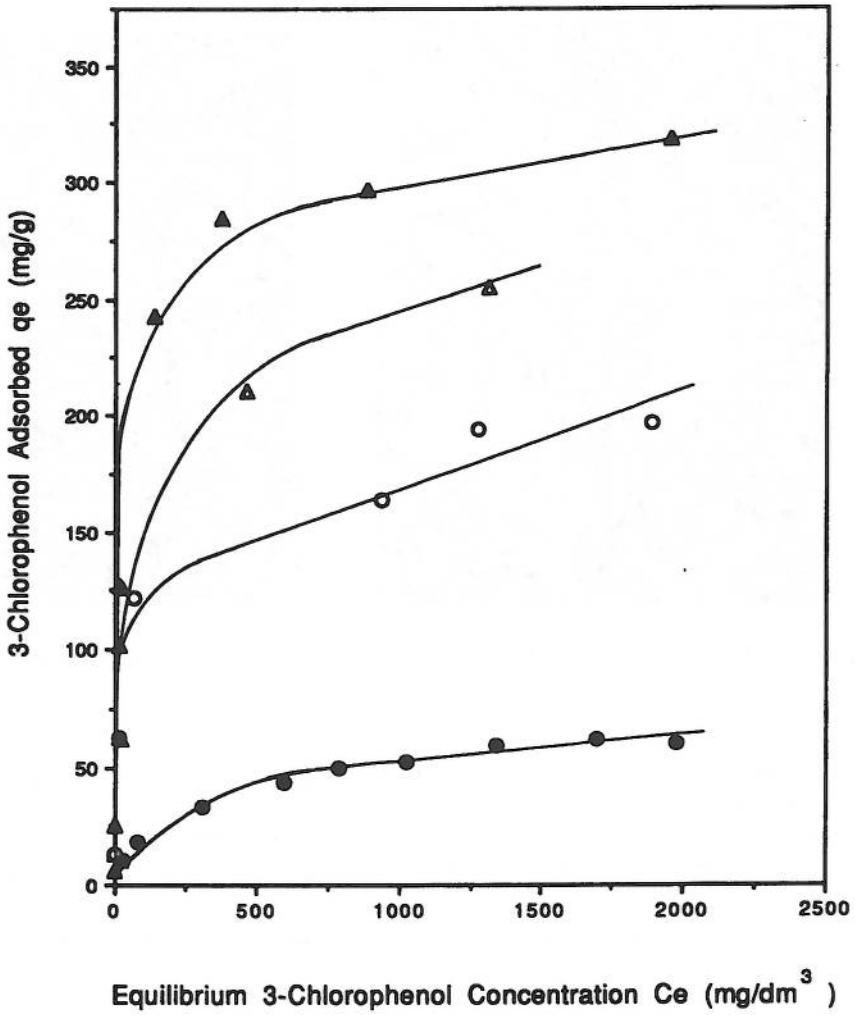


Fig. 4. 3–Chlorophenol adsorption isotherms for activated spent bleaching earth and commercial adsorbents.

ised "bundle of bank notes"[24]. Acidulation generally disrupts the structure of bleaching earths, causing them to deviate from both the exfoliated appearance usually associated with phyllosilicate materials and the hypothesised model of evenly stacked silicate lamellae[18,24,25]. The bottom edge of the particle shown in Fig. 2b, however, reveals that a basic sheet-like structure was retained from the mineral support in the clay-carbon composite materials. The surface characterisation of activated SBE thus confirms the proposed model[9] of an active carbonaceous char supported on the interlamellar surface of an ill-defined, amorphous montmorillonite matrix.

3.2 *Adsorption of phenol, 3-chlorophenol and 2,3-dichlorophenol*

Figures 3 to 5 illustrate the experimental isotherms obtained for SBE and the commercial carbons in the case of phenol, 3–chlorophenol and 2,3–dichlorophenol, respectively. A Langmuir model was subsequently applied on account of its widespread use to describe the aqueous-phase uptake of organic micropollutants by activated carbons[26–28]. While acknowledging the absence of a universal model for clays and carbons alike, this isotherm has also been employed extensively for both the adsorpion of pigments from edible oils by layer silicates[29,30], and for describing the adsorptive behaviour of clay-carbon materials analogous to activated SBE[11,12]. In addition, a Langmuir fit has previously been found to be slightly favoured over the Freundlich isotherm in our own studies for this material[8]. The model can be described by the eqn:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e}$$

where q_e is the amount of solute adsorbed per unit mass of adsorbent and C_e the equilibrium adsorbate concentration. The parameters Q^0 and b were obtained from linear plots of $1/q_e$ *vs.* $1/C_e$. Q^0 represents the solid-phase concentration corresponding to complete coverage of available adsorption sites and b can tentatively be related to the intensity of the adsorption reaction. Table 1 gives the Langmuir isotherm parameters for the selected series of adsorbent-adsorbate pairs and the parameter q_G. This parameter represents the ordinate value at which the initial (negative) curvature falls to zero, and is obtained by horizontal extrapolation from the knee-point of the

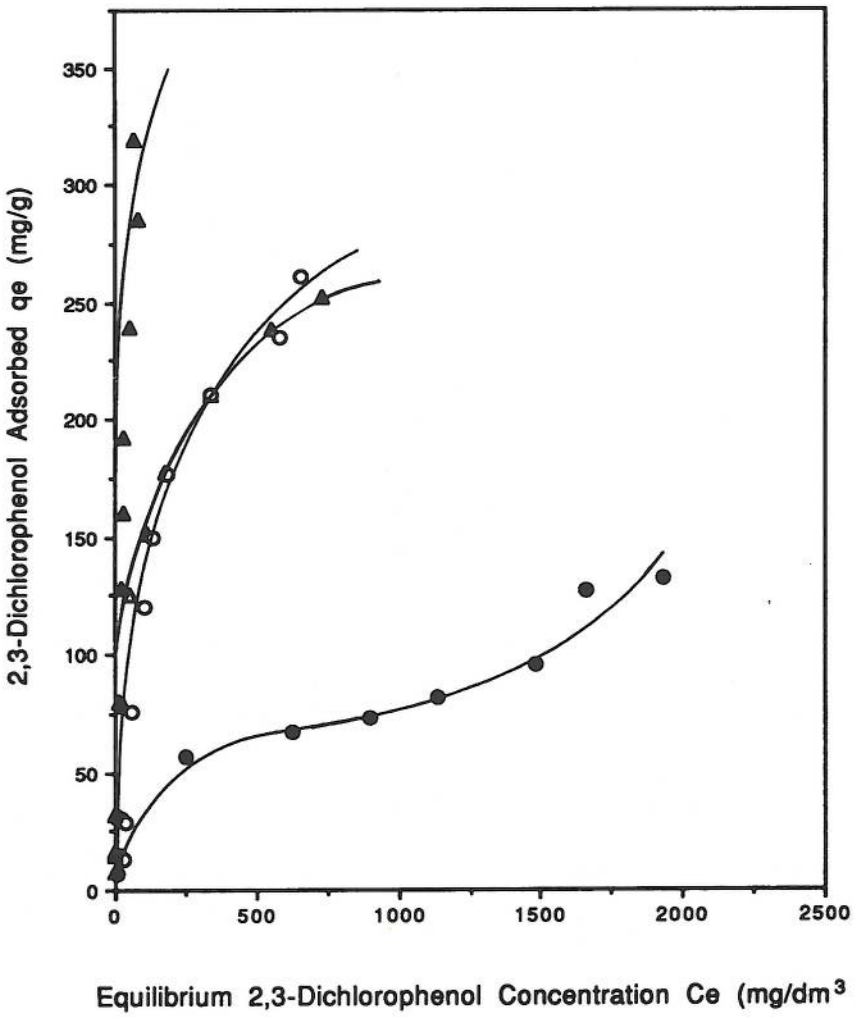


Fig. 5. 2,3–Dichlorophenol adsorption isotherms for activated spent bleaching earth and commercial adsorbents.

experimental isotherm to the q_e axis as described by Giles and Nakhwa[31]. This provided an additional quantitative method of assessing the adsorptive capacity of materials which do not exhibit a strictly limiting adsorption plateau.

SBE exhibited near-Langmuirian behaviour and showed an increasing affinity (Q^0, q_G) for individual adsorbates with increase in molecular weight and hydrophobicity along the series: phenol < 3–chlorophenol < 2,3–dichlorophenol. Both the adsorptive behaviour and range in Q^0 values compare favourably with those noted by Korczak and Kurbiel[12] for a mineral-carbon adsorbent derived from spent clay used in the raffination of lubricating oil. These workers evaluated their material for the removal of organic carbon from pesticide wastewaters and reported values of 4.85 mg g^{-1} and 0.00056 dm^3 mg^{-1} for the Langmuir parameters Q^0 and b, respectively. The poor adsorptive performance observed was explained by these investigators in terms of bound acidic oxy-

Table 1. Adsorption isotherm parameters

Adsorbate	Adsorbent	q_G (mg g^{-1})	Q^0 (mg g^{-1})	b (dm^3 mg^{-1})	r^2
Phenol	SBE	20	33.3	2 E–03	0.98
	Norit SA4	150	46.3	114 E–03	0.85
	SS 338 P	106	141.3	7 E–03	0.99
	CECA 3SA	207	221.7	16 E–03	0.73
3–chlorophenol	SBE	54	53.7	40 E–03	0.97
	Norit SA4	255	255.3	41 E–03	0.99
	SS 338 P	181	164.7	65 E–03	0.99
	CECA 3SA	295	341.1	13 E–03	0.77
2,3–dichlorophenol	SBE	64	91.6	18 E–03	0.97
	Norit SA4	>250	124.4	89 E–03	0.86
	SS 338 P	>255	347.6	3 E–03	0.93
	CECA 3SA	>320	142.0	370 E–03	0.98

Table 2. Elemental microanalysis and apparent carbon activities

Adsorbent	C (%w/w)	H (%w/w)	N (%w/w)	q_{GC} phenol (mg g^{-1} C)	q_{GC} 3- chlorophenol (mg g^{-1} C)
SBE	20.1	0.92	<0.30	100	269
Norit SA4	85.4	0.60	<0.30	176	299
SS 338 P	82.4	0.69	2.53	129	220
CECA 3SA	81.1	0.49	9.18	255	364

gen groups inhibiting the chemisorption of phenolic adsorbates at the adsorbent surface. Extensive characterisation of this analogous material[12] demonstrated that the adsorption kinetics were controlled by an intraparticulate diffusion process, with adsorptive capacity dependent on adsorbate molecular mass, electrostatic charge, and the hydrogen bonding with surrounding water molecules. In an additional study, Kalapusha *et al.*[11] reported Langmuir isotherm behaviour for an adsorbent produced by steam activating a spent palygorskite-montmorillonite mineral used initially to remove unsaturated hydrocarbons from aromatic petroleum products.

Commercial carbons displayed corresponding adsorptive behaviour (q_G) in accordance witn their reported apparent BET surface areas; SS 338P (500 m^2g^{-1}) < Norit SA4 (650 m^2g^{-1}) < CECA 3SA (1200 m^2g^{-1}), the disubstituted chlorophenol being most strongly adsorbed. Such behaviour is in agreement with similar studies performed with commercially available carbons and increasingly chlorinated phenolic adsorbates[28]. Construction of full isotherms for 2,3–dichlorophenol was restricted due to the reduced aqueous solubility of this compound.

The diminished adsorptive performance observed for SBE in comparison with the commercial carbons is primarily attributed to the reduced active-carbon content (20.1%w/w) of activated SBE (Table 2). The capacity of the mineral support alone for these adsorbates was found to be negligible. A comparison of uptake on a gram carbon basis, however (Table 2), suggested a high activity for the surface char of SBE within the range of the selected water-treatment carbons. Application of this adsorbent for wastewater treatment, therefore, would require correspondingly higher doses for equivalent micropollutant removal. Cost-benefit analyses and pilot-scale studies to determine mass transfer coefficients, breakthrough curves, and competitive adsorption effects will therefore be required further to this study before activated SBE can be finally affirmed as applicable for the removal of chlorophenols from industrial waste waters.

4. CONCLUSION

The structure of activated spent bleaching earth can be confirmed as comprising an adsorptive carbon char supported on the interlamellar surface of an amorphous montmorillonite matrix. The activity of the carbonaceous deposit for the phenolic adsorbates examined was considered sufficient to propose a pilot-study investigation for removal of chlorophenols from industrial waste waters of varying organic strength. Low-cost alternatives to commercial carbon, such as activated spent bleaching earth, are of particular relevance to developing countries where economic restraints severely limit the widespread application of industrial adsorbents[32]. With these countries sharing an increasing percentage of world vegetable oil production and processing[33], spent bleaching earth may represent a locally available bulk feedstock for conversion into a clay-carbon adsorbent.

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THE REUSE OF SPENT BLEACHING EARTH: A FEASIBILITY STUDY IN WASTE MINIMISATION FOR THE EDIBLE OIL INDUSTRY

Simon J.T. Pollard *, Christopher J. Sollars & Roger Perry

Imperial College Centre for Toxic Waste Management, Imperial College of Science, Technology and Medicine, South Kensington, London, UK, SW7 2BU.

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Abstract

Spent bleaching earth, a solid waste from the edible oil industry can be converted to a clay–carbon adsorbent for potential reuse in the adsorptive cleansing of vegetable oils. Commercial and laboratory-prepared adsorbents were screened for their ability to remove coloured pigments, impurities and trace contaminants from rapeseed and crude coconut oils. Activated spent bleaching earth demonstrated efficient removal of benzol[a]pyrene from crude coconut oil reducing the concentration from 12·8 μg kg^{-1} in the crude oil to 1·3 μg kg^{-1} (89·8% w/w removal) in the treated product at a 2·0% w/w adsorbent dose. Soybean and rapeseed process wastes activated under identical conditions exhibited similar removal efficiencies of 89 and 86% w/w, respectively. This compared with a reduction in benzo[a]pyrene concentration to 10·8 μg kg^{-1} for virgin bleaching earth (15·6% w/w) and to less than 0·1 μg kg^{-1} for commercial powdered activated carbon (> 99·2% w/w). Activated spent bleaching earth exhibited limited removal of chlorophyll derivatives (27% w/w) and negligible uptake of the β-carotenoids and phosphorus from degummed rapeseed oil compared with the virgin bleaching earth which showed effective bleaching of chlorophyll derivatives (98% w/w), the β-carotenoids and removal of phosphorus (71% w/w). Adsorptive differences between these materials are interpreted with reference to interactions at the surfaces of acidulated montmorillonite and activated carbon. Processing incentives for the recovery and reuse of spent clay are discussed.

Key words: Edible oils, decolourisation, spent bleaching earth polynuclear aromatic hydrocarbons, active carbon.

*Current address: Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, UK, EH9 3JJ

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INTRODUCTION

The adsorptive cleansing of edible oil is performed on an industrial scale using acidulated calcium montmorillonite clay (bleaching earth) to remove a variety of undesirable impurities which would otherwise impart colour, odour and taste to the refined product. These include chlorophyll, β-carotene (and their derivatives), residual soaps, fatty acids, phosphatides and trace metals (Patterson, 1976; Norris, 1982). Activated carbon is also periodically used in an admixture with virgin bleaching earth for the removal of trace quantities of polynuclear aromatic hydrocarbons (PAH) from edible oils (Biernoth & Rost, 1967; Norris, 1982; Larsson *et al.*, 1987). These contaminants, some of which are suspected human carcinogens, are occasionally present in crude oils in quantities sufficient to be of concern to edible oil processors.

Spent bleaching earth (SBE), the principal solid waste product from the edible oil industry, routinely contains in excess of 20% w/w residual oil which can rapidly oxidise to the point of spontaneous ignition as a consequence of clay-catalysed auto-oxidation reactions (Svensson, 1976; Sonntag, 1979). For many years, the conventional route for the disposal of this waste has been direct landfill, but recent changes in environmental legislation and a growing concern for the safe disposal of catalysts (Agoos, 1986; Habermehl, 1988) have led to restrictions being placed on the dumping of spent clay (McDermott *et al.*, 1989). A re-evaluation of waste management options for this material is therefore required.

'Waste minimisation' is an umbrella term used to denote any process which results in a reduction of the waste stream prior to treatment or disposal (Patterson, 1989). Source reduction, waste recovery, reuse, and recycling are examples of waste minimisation strategies. The reuse of SBE and the concomitant recovery of residual oil has been a recurrent focus of research within the edible oil industry for nearly 50 years. Clay regeneration has been attempted by steam (Penninger, 1979), alkali (Smith *et al.*, 1977) and solvent extraction

(Orth, 1980; Ong & Sinkeldam, 1983; Kheoh, 1986), wet oxidation of adsorbed oil (Kalam & Joshi, 1988*a*, *b*) and by thermal treatment methods (Bahl & Dayal, 1977). Most recently, extraction of oil from the clay surface using supercritical carbon dioxide has been investigated (Anon., 1992). Alternative disposal options for SBE have included biological treatment by landfarming, its proposed use as a fuel supplement (McDermott, 1982; Daido, 1987) and as a potential chicken feed (Blair *et al.*, 1986).

As part of our own investigations into the reuse of SBE, we have previously reported the conversion of a laboratory-synthesised soybean filter cake to a low-cost adsorbent (Pollard *et al.*, 1991*a*, *b*). In this process, residual soybean oil present in the spent earth is first carbonised and then activated on the clay surface to yield a clay-supported active carbon (Pollard *et al.*, 1990; 1992) (Fig. 1). The present feasibility study investigates the reuse of activated SBE for the removal of pigments and trace contaminants from crude vegetable oils. In an assessment of bleaching performance, activated SBEs were screened together with selected commercial adsorbents for the removal of colour from degummed rapeseed oil (an oil high in chlorophyll derivatives) and benzo[*a*]pyrene B[*a*]P) from crude coconut oil (with which trace PAH in some edible oils are occasionally associated).

METHODS

Materials

Degummed rapeseed oil and crude coconut oil were obtained from a commercial UK supplier. Virgin bleaching earth was supplied by Laporte Industries, Widnes, UK. Norit SA4 powdered activated carbon was supplied by Norit (UK), Glasgow and Brimac CC bone char obtained from British Charcoals and Macdonalds, Greenock, UK. Additional powdered carbons were obtained from BDH Chemicals, UK (decolourising charcoal) and Chemviron Carbon, UK (Grade C). An admixture of 4 parts virgin bleaching earth to 1 part Norit SA4 was prepared by powder blending and represented an adsorbent blend used commercially for the occasional removal of PAH from edible oils.

An optimised procedure for the preparation of zinc chloride activated SBE (clay–carbon adsorbent) from a laboratory-synthesised filter cake containing 30% w/w soybean oil has been previously described (Pollard *et al.*, 1991*a*). Two additional control materials were included in this study: (1) carbonised SBE, in which the residual oil was pyrolysed on the montmorillonite support without chemical activation, and (2) deactivated SBE, in which the chemically activated char was subsequently oxidized in air at 850°C to the point of complete carbon burn-off. These materials allowed comparison of the activated materials with the carbonised char and the mineral support, respectively.

Actual ex-factory spent soybean and rapeseed filter cake process wastes were activated using the optimum amount of zinc chloride established using the laboratory-synthesised material. Adsorbent properties are summarised in Table 1.

Benzo[*a*]pyrene (99%) was supplied by the Commission of the European Community, Community Bureau of Reference, Brussels, Belgium.

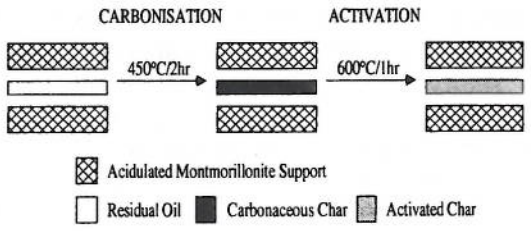


Fig. 1. Schematic structural model for the preparation of zinc chloride activated spent bleaching earth.

Methods

Colour, chlorophyll and phosphorus removal from rapeseed oil

Adsorbent samples were pre-dried (105°C, 16 h) and sieved to a particle size of less than 150 μm. Subsamples (1·25 g) were then used to bleach degummed rapeseed oil (100 g) in open 250 ml pyrex beakers at 95°C for 35 min atmospheric pressure with constant stirring. Bleaching was performed under the fume hood in batches of six samples at a time using a thermocoupled stirrer–hotplate (RS Instruments). Bleached oils were then simultaneously vacuum-filtered whilst hot (Whatman No. 3 paper) using a Buchner apparatus and vacuum manifold.

Colour removal from degummed rapeseed oil was determined at 60°C using a colorimetric method (EEL Absorptiometer Model 4, Evans Electroselenium Ltd, UK). Absorption was monitored over wavelength bands 601 (λ_{max} 430 nm) and 602 (λ_{max} 470 nm) in 3·2 cm ($1\frac{1}{4}$ inch) glass cells using a distilled water blank. Evans activity (EA; bleaching performance) is expressed as the sum of the two values and is representative of general colour removal rather than the uptake of specific chromogenic compounds. An increase in Evans activity denotes increased bleaching performance.

Lovibond red and yellow values were obtained at 60°C in 6·6 cm ($5\frac{1}{4}$ inch) glass cells using a Lovibond colorimeter (Colourscan, Tintometer Ltd, UK). A reduction in these parameters is indicative of the bleaching of carotenoids in oils. Residual chlorophyll-derivative concentrations in the degummed rapeseed oil were analysed using a λ_{max} of 600 nm. Residual phosphorus contents in bleached rapeseed oils are indicative of phosphatide impurities and were determined for crude and bleached rapeseed oils by X-ray fluorescence using a Phillips PW 1400 XRF system. This technique has previously been found to be comparable to graphite-furnace atomic absorption spec-

Table 1. Adsorbent properties

Adsorbent	Base material	Apparent N_2 BET surface area ($m^2\ g^{-1}$)	Carbon content (% w/w)	pH
Commercial				
virgin bleaching earth	acidulated calcium montmorillonite	397	0·23	3·0–3·2
Norit SA4	peat-based active carbon	629	86·4	9·8
Brimac CC	hydroxyapatite bone char	100	9·8	9·3
BDH decolourising charcoal	wood charcoal	515	79·1	3·7
Chemviron c	Coal-based active carbon	866	73·3	NA
clay: carbon 4:1	virgin clay: Norit SA4 blend	NA	69·2	NA
Synthesised SBE				
activated SBE	spent bleaching earth	239	20·1	4·1
carbonised SBE (control)	spent bleaching earth	270	8·7	NA
deactived SBE (control)	spent bleaching earth	15	<0·3	
Ex-factory SBE wastes				
activated rapeseed SBE	spent bleaching earth	143	16·7	NA
activated soybean SBE	spent bleaching earth	193	16·6	NA

NA, not available; SBE, spent bleaching earth.

trometry for residual phosphorus determinations (Morgan *et al.*, 1985).

Benzo[a]pyrene removal from crude coconut oil

Crude coconut oil was liquefied in a microwave oven for 1 min prior to bleaching. Selected adsorbents (2·00 g) were then used to open-bleach the crude oil (100g) at 95°C for 35 min. Bleached oils were filtered as above and stored in a freezer prior to analysis. Bleaching curves of adsorbent dose in the range 0–3·5% w/w against residual B[*a*]P concentration were constructed for the activated filter cakes and Norit SA4 to observe the lower adsorption threshold in each case.

B[*a*]P concentrations in open-bleached coconut samples were determined by reversed-phase HPLC. Bleached coconut oil samples (2·00 g) were dissolved in HPLC grade petroleum ether (40–60°C fraction, Vickers, UK) and diluted to 10 ml in volumetric flasks. Clean up was performed on a deactivated alumina (Supergrade IV; ICN Biomedicals GmbH, Germany) gravity column with petroleum ether elution. The last 60 ml of a 100 ml eluate was collected and reduced first using a rotary evaporator and then under a stream of dry nitrogen for 20 min in a crimp-top vial (Hewlett-Packard, UK). The residue was re-diluted to 200 μl in HPLC grade tetrahydrofuran (Vickers, UK), shaken vigorously to disperse the residue in the solvent and stored in the freezer.

Chromatographic analysis (Hewlett Packard HP1090 Series M chromatograph) was performed on a 20 cm RF Chromsep 20 PAH column (ChromSpher). Gradient elution (60–100% ACN over 20 min; flow rate 1·7 ml min^{-1}) was employed using acetonitrile in HPLC grade water. Programmed fluorescence detection was performed for B[*a*]P with excitation and emission wavelengths of 384 and 406 nm, respectively at slit widths of 10 nm. A sample injection volume of 20·0 μl was used throughout.

RESULTS AND DISCUSSION

Colour removal from degummed rapeseed oil

Table 2 shows the bleaching performance of commercial and laboratory-prepared adsorbents. A range of base materials and porosities are represented among the commercial adsorbents including predominantly mesoporous materials (pore widths 2–50 nm; Brimac CC bone char, virgin bleaching earth) and microporous carbons (pore widths < 2 nm; Chemviron C, BDH decolourising charcoal).

Virgin bleaching earth exhibited its characteristic superiority for the removal of chlorophyll derivatives, the β-carotenoids and phosphorus from degummed rapeseed oil and demonstrated a high Evans activity confirming efficient overall colour removal (Table 2). In comparison, the colour removing performance of activated SBE was negligible. Noteworthy is the behaviour of the carbonised SBE which exhibited intermediate adsorptive characteristics in terms of Evans activity and β-carotenoid removal.

The removal of coloured pigments from edible oils by mineral-based and carbonaceous adsorbents can be interpreted with reference to the accepted mechanisms of adsorption in each case.

Properties of bleaching earth credited with a role in the removal of colour and trace impurities from edible oils include pore size distribution, particle size, extent of acidulation, total surface area and moisture content (Siddiqui, 1968; Brimberg, 1982; Zyla & Olszar, 1984; Morgan *et al.*, 1985). Adsorption of coloured pigments at the protonated surface of montmorillonite is generally accepted as involving a combination of acid–base (Brønsted) interactions and physical adsorption (Siddiqui, 1968; Fahn, 1976; Morgan *et al.*, 1985; Taylor *et al.*, 1989).

In contrast, activated carbons adsorb largely on the basis of their extended surface area and highly

Table 2. Bleaching performances of commerical and laboratory-prepared adsorbents

Bleaching parameter	Colour removal			Chlorophyll ($\mu g\ kg^{-1}$)	Lovibond colour (absorbance)		Phosphorus ($\mu g\ g^{-1}$)
	601	602	EA		Red	Yellow	
Rapeseed blank	0	0	0	6650	4·5	69	17
Commercial							
virgin bleaching earth	44	56	100	140	1·0	7	5
Norit SA4	0	0	0	1080	4·1	68	12
Brimac CC	0	0	0	2450	4·4	68	14
BDH decolourising charcoal	0	0	0	970	4·1	69	3
Chemviron C	0	0	0	620	3·4	68	12
clay:carbon 4:1	41	37	78	160	0·9	7	10
Synthesised SBE							
activated SBE	0	0	0	4840	4·8	69	18
carbonised SBE	29	35	64	610	1·0	11	10
deactivated SBE	0	0	0	5750	4·2	68	15

developed microporosity. Many activated carbons also exhibit some surface acidity but this is believed to be more a consequence of carboxylate functionality at the edges of their extended polynuclear structure (Bansal *et al.*, 1988) rather than direct protonation. Hence, this lack of protonation may account for the reduced Evans activity observed for these adsorbents. Chlorophyll derivatives removed by the carbons in this study are more likely to have been adsorbed on a physical basis, the molecular dimensions of the isolated chlorophyll *a* molecule (1·2 nm × 1·5 nm; Taylor *et al.*, 1989) being suitable for physisorption across the micro- and mesopore size range in these materials.

Whilst approximately 27% w/w of the available chlorophyll derivatives were removed by the activated SBE, no Evans activity was observed. Comparison with the carbonised SBE control suggests that the $ZnCl_2$ activation process employed causes a deterioration in bleaching capacity at the protonated silicate surface.

The commercial materials exhibited a range of phosphorus-removal capacities, the most significant uptake being demonstrated by virgin bleaching earth and the BDH decolourising charcoal. Lovibond red and yellow values remained essentially unaltered by the commercial carbonaceous adsorbents whilst the virgin bleaching earth again indicated significant removal of both the lighter (yellow) and deeper (red) chromogenic carotenoids present in the degummed rape sample. Whilst β-carotene is reported to be removed by both bleaching earth and activated carbons (Sonntag, 1979), these results indicate the varying specificity exhibited by a range of commercial adsorbents for carotenoids, chlorophylls and phospholipids and highlight the competitive nature of adsorption for these substances from rapeseed oil.

Benzo[a]pyrene removal from crude coconut oil

Residual B[*a*]P concentrations remaining in open-bleached coconut oils treated using a number of selected adsorbents are presented in Fig. 2 with 10%

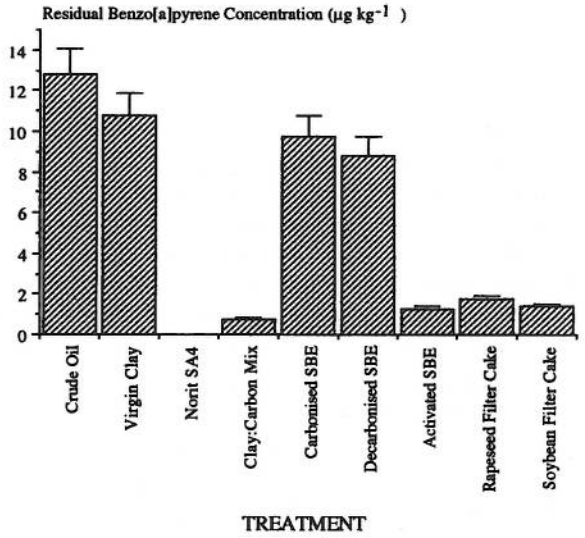


Fig. 2. B[*a*]P removal, by industrial and laboratory-prepared adsorbents, from crude coconut oil.

error bars indicating the analytical error associated with triplicate determination of B[*a*]P in the crude sample.

Norit SA4, a standard carbon for PAH removal from edible oils, reduced the B[*a*]P concentration from a mean value of 12·8 $\mu g\ kg^{-1}$ in the crude oil to trace levels ($<0{\cdot}1\ \mu g\ kg^{-1}$) at a 2·0% w/w adsorbent dose. The admixture of Norit SA4 with virgin bleaching earth removed all but 0·8 $\mu g\ kg^{-1}$ B[*a*]P. Virgin bleaching earth alone, however, displayed a limited capacity for B[*a*]P. Carbonised SBE and deactivated SBE likewise adsorbed limited amounts of B[*a*]P. In comparison, the $ZnCl_2$ activated SBE demonstrated an appreciable capacity for B[*a*]P, reducing the residual concentration in the bleached coconut oil to 1·3 $\mu g\ kg^{-1}$.

A comparison of PAH removal for these materials with the colour removal data confirms the differential mechanisms for the adsorptive behaviour of bleaching

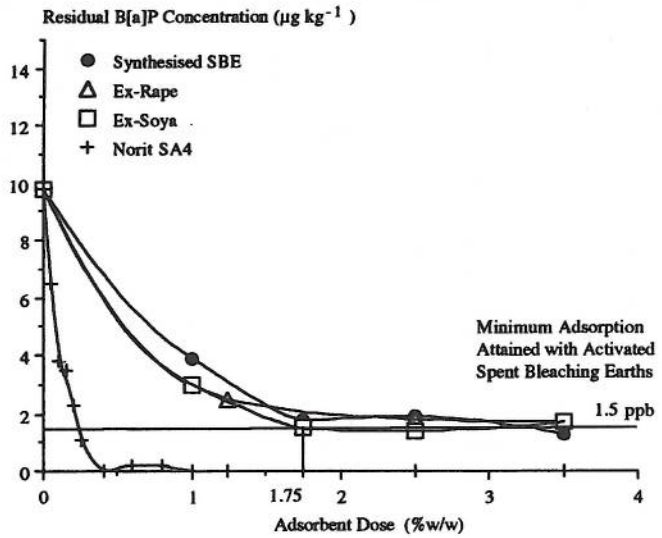


Fig. 3. B[*a*]P bleaching curves from crude coconut oil for activated filter cakes and Norit SA4 carbon.

earth and activated carbon. These results suggest that the adsorption of coloured pigments and PAH from edible oil are distinct and at the extreme, associated with the surface properties of acid-activated montmorillonite and active carbon, respectively. This is to be expected on account of the non-polar nature of PAH adsorbates which are more effectively adsorbed by van der Waals attraction at the microporous carbon surface than at the protonated surface of acidulated montmorillonite. Uptake of B[*a*]P by the activated SBE is therefore attributed directly to the active carbon present on the interlamellar surface of this material (Pollard *et al.*, 1991*a,b*, 1992).

Real process wastes activated under optimised conditions were examined for B[*a*]P removal from a second coconut oil sample and compared with the laboratory-synthesised activated SBE (Fig. 2). Bleaching curves were constructed for these three adsorbents in order to assess the required dose during reuse and for comparison with the corresponding curve for Norit SA4 (Fig. 3). At a 2·0% w/w dose, activated spent rape and soybean filter cakes exhibited similar behaviour to the laboratory-synthesised activated SBE, with residual B[*a*]P levels of 1·8, 1·4 and 1·3 μg kg^{-1}, confirming them as suitable adsorbents for PAH removal. These values correspond to B[*a*]P removal efficiencies of 86, 89 and 90%. Norit SA4, in comparison, reduced B[*a*]P to trace levels (< 0.1 μg kg^{-1}) at a 1% w/w dose. In these curves, our activated SBE adsorbents demonstrated a limiting capacity for B[*a*]P with residual B[*a*]P concentrations of approximately 1·5 μg kg^{-1} remaining at approximately 1·75% w/w dose.

Processing considerations

Handleability, bulk density and particle compatibility are of principal concern when processing admixtures of finely powdered adsorbents for edible oil bleaching. An excess of fine particles in some powdered activated carbons occasionally causes 'burst-through' problems during filtration of the bleaching admixture, and extremes in bulk density can result in settling during powder blending and/or bleaching. These problems often lead to ineffectual cleansing of the oil or even spoiled batches of the refined product at considerable expense to the processor. Such processing problems may be overcome by using admixtures of activated SBE (which has adsorptive properties similar to activated carbon) and virgin bleaching earth for the concurrent removal of PAH and pigments from edible oils. Activated SBE has an apparent bulk density of approximately 0·6–0·7 g cm^{-3} compared with approximately 0·5 g cm^{-3} for the virgin bleaching earth (Pollard, 1990), values which are similar enough to alleviate concerns over particle incompatibility.

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MICROPOROUS CARBONS FROM *MORINGA OLEIFERA* HUSKS FOR WATER PURIFICATION IN LESS DEVELOPED COUNTRIES

S. J. T. POLLARD,*[1] F. E. THOMPSON[1] and G. L. MCCONNACHIE[2]

[1]Department of Chemistry and [2]Department of Civil Engineering and Building Science, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, Scotland

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Abstract—High quality activated carbon can be prepared from the waste husks of *Moringa oleifera*, an indigenous tropical plant material. Steam activated husks exhibited a well-developed micropore volume of 0.57 $cm^3\,g^{-1}$ and a corresponding apparent surface area of 734 $m^2\,g^{-1}$, as determined by BET N_2 adsorption hysteresis. In an assessment of aqueous phase adsorptive performance, activated *Moringa* carbon was found to be comparable to commercial powdered activated water treatment carbons (PACs) and exhibited a Langmuir monolayer coverage constant (Q^0) of 1.89 mmol g^{-1} for phenol adsorption from the aqueous phase. Cultivation of *Moringa oleifera* in developing countries for the coagulant properties of its seed extract provides a well founded economic incentive for the utilisation of treated waste husks as activated carbon during *in situ* water purification.

Key words—activated carbon, *Moringa oleifera*, microporosity, water purification, low-cost adsorbents, less developed countries

NOMENCLATURE

A_m = molecular cross-sectional area (m^2)
b = Langmuir adsorption coefficient
C_{BET} = BET constant
C_e = equilibrium concentration of solute (mol dm^{-3})
dW/dR = micropore distribution function (<2 nm)
K_F = Freundlich constant (mol g^{-1})
n = Freundlich constant
N_A = Avogadro constant (mol^{-1})
qe = amount solute adsorbed per unit mass adsorbent (mol g^{-1})
Q^0 = Langmuir monolayer coverage constant (mol g^{-1})
Θ_n = phase transition during thermal decomposition of substrate (°C)
p/p^0 = partial pressure of N_2 in equilibrium with adsorbent surface
SSA = specific surface area ($m^2\,g^{-1}$)
R_P = effective pore diameter (nm)
$S_{mes+mac}$ = external surface area ($m^2\,g^{-1}$)
S_{tot} = apparent BET surface area by N_2 adsorption ($m^2\,g^{-1}$)
V_{ads} = volume N_2 adsorbed ($cm^3\,g^{-1}$)
$V_{mes+mac}$ = pore volume attributable to meso and macropores ($cm^3\,g^{-1}$)
V_{micro} = micropore volume ($cm^3\,g^{-1}$)
x_m = adsorption monolayer capacity from experimental isotherm (mol g^{-1})

INTRODUCTION

The provision of safe, potable water to communities in less developed countries (LDCs) is regarded as a necessary condition for overall development, and remains a central objective of the World Health Organisation (Reid, 1982). Water and wastewater treatment in developing countries can, however, aspire towards arbitary environmental quality guidelines that reflect idealised operating procedures instead of achievable targets that are realistic and cost-effective. This can result in attempts to implement inappropriate solutions that exceed the available resources and practical capability of many communities (Pinfold *et al.*, 1993). In acknowledgement of these difficulties, a substantial research effort has focused on low-cost approaches to water purification and wastewater treatment in LDCs (Shultz and Okun, 1984). Processes that reduce overall treatment costs through the application of indigenous, natural products are particularly attractive because they lessen reliance on imported water treatment chemicals, have negligible transportation requirements and offer genuine, localised and appropriate solutions to water quality problems (Jahn, 1982).

The preparation of low-cost adsorbents for water purification, waste and wastewater treatment has recently been reviewed by Pollard *et al.* (1992). For example, a wide range of lignocellulosic agricultural by-products have successfully been converted into activated carbons, including coconut coir (Hitchcock *et al.*, 1983), jute stick (Banerjee and Mathew, 1985), sarkanda grass (Chugtai *et al.*, 1987), palm-tree cobs (Renouprez and Avom, 1988), rice husk (Nawar and Doma, 1989) and tamarind nut shells (Bhargava and

*Present address: Aspinwall & Company, 13 Melville Street, Edinburgh EH3 7PE, Scotland.

Sheldarkar, 1993a–c). The suitability of these precursors is determined by their local and bulk availability, carbon content and the presence of inherent microstructure within the substrate itself (Hardman, 1992). Viability of their ultimate use may be determined as much by these factors as by the adsorptive capacity, regenerative characteristics and physical form of the subsequent carbon product.

In this study we describe the preparation and characterisation of activated carbon from *Moringa oleifera* seed husks. This precursor is suitable due to its widespread distribution across the tropical developing world and because of the recognised potential of *Moringa* seed extract as a low-cost, natural coagulant aid for turbidity control in several LDCs including the Sudan, Central India and Malawi (Subbaramiah and Rao, 1937; Jahn, 1982; McConnachie, 1993). Preparation of the endosperm extract in rural communities typically involves prior removal of the husk and crushing of the seed with clarified water to produce a suspension which is then filtered prior to use (Jahn and Dirar, 1979). Waste husks could potentially be pyrolysed and gasified with steam to produce activated carbon for the *in situ* purification of stored household water containing excessive taste and odour contaminants. The following examination of preparative requirements and adsorptive characteristics served to demonstrate the technological viability of this process.

EXPERIMENTAL METHODOLOGY

Thermal analysis

Finely divided (1 mm dia.) *Moringa oleifera* husks (Peter B. Dow & Company, Gisborne, New Zealand) (10 mg) were placed in the quartz sample crucible of a Stanton Redcroft thermobalance (STA 780) and heated at 10°C min^{-1} under dry, flowing nitrogen (30 cm^3 min^{-1}) from 25 to 900°C. Carbonisation temperatures of 360°C and 485°C and dwell times of 0 and 30 min were selected following examination of the differential thermal profile (DTA) of *Moringa* husk which clearly exhibited thermal behaviour characteristic of the pyrolytic decomposition of hemicellulose, cellulose and lignin composite units in plant materials (Shafizadeh, 1984) (Fig. 1). Decomposition temperature ranges and mid-points were verified by the thermal analysis of purified cellulose powder and alkali lignin (Aldrich Chemical Co., U.K.).

Laboratory-scale preparation

Carbonisation and steam activation of *Moringa* husks was conducted using an adapted Carbolite CTF 12/65 rotary furnace fitted with an internal silica sleeve (Fig. 2). Successive charges (30 g) of substrate were placed in a customised pyrex combustion boat and purged with dry nitrogen for 10 min. For carbonisation, samples were heated under N_2 at a fixed rate of 15°C min^{-1} and held at the selected temperature ±3°C for the predetermined dwell time. Following carbonisation, the char was removed to a N_2-flushed desiccator and the yield determined. Following CHN microanalysis (Perkin Elmer 2400 microanalyser) and phenol screening (below), steam gasification of carbonised *Moringa* char was conducted using a steam delivery rate of 4.5 cm^3 min^{-1} from an adjacent steam generator. Prior to activation the empty silica vessel was flushed with steam for 15 min. Samples of *Moringa* char (0.5 g) were then placed in silica boats and partially gasified at 850°C in the furnace for dwell times of 5 and 15 min, respectively. Under these conditions, the basic endothermic reaction of steam with carbon (1) is the equilibrium with the water gas shift reaction (2) and so partial gasification of *Moringa* substrate with carbon dioxide (3) becomes of additional importance (Wigmans, 1989):

$$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad (1)$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \quad (2)$$

$$C(s) + CO_2(g) \rightarrow 2CO(g). \quad (3)$$

Following activation, samples were removed to the desiccator immediately to cool, were homogenised and sieved to <250 μm, then washed with 40 cm^3 2M HCl followed by 3 × 40 cm^3 deionised water to remove residual ash and vacuum filtration (Whatman 45 μm cellulose nitrate membrane). Finally *Moringa* carbons were oven-dried overnight at 85°C and desiccated awaiting CHN microanalysis, estimation of C/H quotient and determination of carbon burn-off, where:

$$\text{carbon burn-off} = \frac{\%\text{C in raw substrate}}{\%\text{C in char normalised for percentage yield}} \times 100\%. \quad (4)$$

Solution phase screening and isothermal analysis

The adsorptive efficiencies of carbonised and activated chars were screened using a single point, aqueous phase phenol adsorption test. Preliminary tests established that contact times of 24 h. would ensure steady-state conditions. pH values of the non-buffered solutions (Milli-Q SP deionised water) were measured prior to and following phenol adsorption and were in the range 5.4–7.4, ensuring predominance of the undissociated form (Ward & Getzen, 1970). Char samples (0.5 g) were added to 50 cm^3 aliquots of a 10^{-2} M phenol (BDH, U.K.) solution in 250 cm^3 Erlenmeyer flasks and shaken using a temperature-controlled shaker bath (70 one-inch strokes min^{-1}) for 24 h at 37 ± 2°C, this value being representative of stored drinking water temperatures in tropical climates (Jahn, 1982). Phenol removal has been used extensively as an indicator of progressive char development and, for simple screening purposes, can be expressed as a removal efficiency (in mol % removal) where:

$$\text{removal efficiency} = \frac{\text{mol phenol adsorbed per g adsorbent}}{\text{mol phenol in initial solution}} \times 100\%. \quad (5)$$

Following uptake, suspensions were vacuum-filtered (Whatman No. 1) and residual phenol concentrations analysed at 270 nm using a direct u.v. spectrophotometric method (Shimadzu UV-160A). For raw, carbonised and activated *Moringa* materials, and for 2 reference commercial water treatment carbons (Ceca Acticarbone TE and Eurocarb YAO), 7-point adsorption isotherms were constructed using accurately weighed amounts (0.005, 0.01, 0.05, 0.1, 0.2, 0.5 and 1.0 g) of adsorbents added to 100 cm^3 of 10^{-2} M phenol solution in 250 cm^3 Erlenmeyer flasks as above. Solution phase adsorptive behaviour was modelled to the Freundlich and Langmuir isotherms [equations (3) and (4), respectively] on account of their widespread use to describe the aqueous phase uptake of organic micropollutants by activated carbons:

$$q_e = K_F C_e^{1/n} \quad (6)$$

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \quad (7)$$

where q_e is the amount of solute adsorbed per unit weight asdorbate; K_F, $1/n$, and b are characteristic constants; C_e the residual solution phase concentration; and Q^0, the solid phase concentration corresponding to complete monolayer coverage of available adsorption sites. K_F has been used as a relative measure of adsorption capacity and can thus be taken as an indicator of surface area, as can Q^0. $1/n$ and b are related to the enthalpy of adsorption and indicate the intensity of reaction. The former model is purely empirical and the latter assumes maximum adsorption occurs when the surface is covered by a uniform monolayer of adsorbate (Voice and Weber, 1983; Pollard *et al.*, 1992). Estimation of phenol specific surface area (SSA) was performed employing the method of Giles and Nakhwa (1962), assuming the phenol molecule is adsorbed flat-on to the carbon surface and using a molecular cross-sectional area (A_m) for the phenol molecule of 0.522×10^{-18} m^2 (Puri, 1980):

$$\mathrm{SSA} = x_m N_A A_m \quad (8)$$

where x_m is the ordinate value at which the initial (negative) curvature falls to zero, obtained by horizontal extrapolation of the knee-point on the experimental isotherm to the q_e axis; N_A the Avogadro constant; and A_m the molecule cross-sectional area of the phenol molecule.

Continuous gas phase isothermal analysis

Activated *Moringa* carbon was analysed by continuous gas phase adsorption hysteresis for surface area characterisation and pore size distribution analysis using a single channel Omnisorp Model 100 instrument (Centre for Environmental Control and Waste Management, Imperial College, London) and a method adapted from Pollard *et al.* (1991). A representative carbon sub-sample (0.1027 g) was outgassed at 250°C for 8 h. under a vacuum of 10^{-6} torr. A full N_2 adsorption/desorption isotherm was obtained at −196°C using a constant, calibrated N_2 flow rate of 0.27 cm^3 min^{-1} and an adsorption cut off p/p° of ~0.98 (160 torr). Surface characterisation: apparent N_2 BET surface area (linear region $p/p^\circ = 0.05$–0.30); t-plot analysis (t = thickness of adsorbed monolayer; linear region $t = 0.5$–0.9 nm), and pore size distribution was performed using the associated instrument software, which employs the BJH method of meso- and macropore size distribution (Barrett *et al.*, 1951) and the Horváth–Kawazoe model (1983) for analysis of the micropore size distribution (pore widths <2 nm).

Scanning electron microscopy

Activated *Moringa* carbon was examined by scanning electron microscopy (SEM) for a visual inspection of external porosity and microtexture. Oven-dried samples were presented on areas of double-sided adhesive tape (0.5 cm × 0.5 cm), mounted on the methanol-cleaned surface of a aluminium microstub. The slides were gold coated for 5 min (Emscope, U.K.) and examined at various magnifications using a Cambridge Stereoscan 90b instrument and an operating voltage of 10 kV. Representative sections of surface were recorded and developed on monochrome paper (Ilford FP4).

RESULTS

Pyrolytic decomposition of Moringa husks

Figure 1 illustrates the sequential thermal decomposition processes occurring in *Moringa* husk during carbonisation by means of the experimental and differential thermograms (TG, DTG and DTA). For reference, accounts of lignocellulose thermochemistry are provided by Mackay and Roberts (1982), Shafizadeh (1984) and Shukry *et al.* (1990). briefly, Θ_1 (Table 1) is indicative of substrate dehydration (20–105°C), with transitions Θ_2, Θ_3, and Θ_4 characteristic of pyrolytic decomposition processes

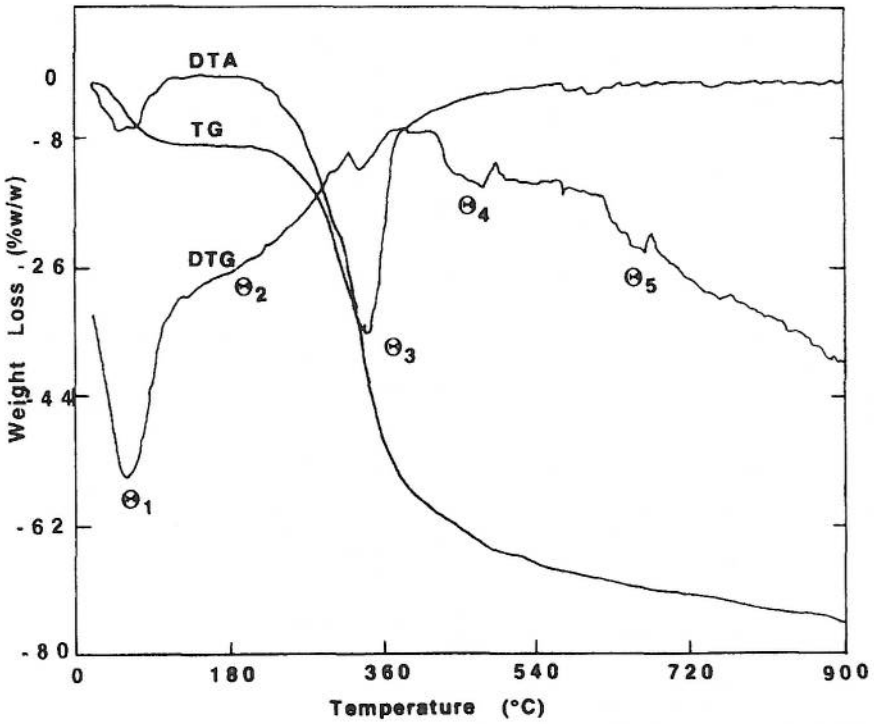


Fig. 1. Pyrolytic behaviour of raw *Moringa* husk by thermal analysis.

Table 1. Thermal analysis of lignocellulosic materials

Phase transition (°C)	Substrate *Moringa* husk	Aldrich® cellulose powder	Aldrich® alkali lignin
Θ_1 (dehydration)	20–105 (55)	30–130 (70)	30–135 (70)
Θ_2 (hemicellulose)	120–280 (180)		155–275 (210)
Θ_3 (cellulose)	255–360 (345)	315–370 (345)	280–395 (350)
Θ_4 (lignin)	420–485 (460)		400–520 (465)
Θ_5 ("rearrangement")	615–685 (650)		630–740 (685)

Table 2. Elemental microanalysis and apparent carbon activities

Moringa substrate	Overall yield (%ʷ/w)	C (%ʷ/w)	H (%ʷ/w)	N (%ʷ/w)	C/H quotient	Carbon burn-off (%)	Phenol removal (mmol g^{-1}) (mol %)
Raw husk	100	46.89	7.06	3.00	6.6	0	0.38 ± 0.01 (19)
Carbonised 360.0	33.7	66.31	3.90	3.29	17.0	52	0.44 ± 0.01 (22)
Carbonised 360/30	34.1	68.75	3.81	1.49	18.0	50	0.42 ± 0.01 (21)
Carbonised 485/0	28.7	74.76	3.20	1.27	23.4	54	0.64 ± 0.01 (32)
Carbonised 485/30	27.6	75.20	2.93	1.36	25.7	56	0.61 ± 0.01 (30)
Activated 850/5	9.6	82.35	1.45	14.58	56.8	83	1.42 ± 0.03 (71)
Activated 850/15	1.1	00.97	0.23	0.01	4.2	98	ND

in hemicellulose (120–280°C), β-1,4-glycosidic bond cleavage in cellulose units (255–360°C) and thermal depolymerisation in lignin (420–485°C), respectively. Progressive heating results in char formation via internal thermal rearrangement (Θ_5) of the sugar anhydride sub-unit residues, eventually providing pseudographitic layers with microporous interstices (Mackay and Roberts, 1982) that can be further developed during their activation with steam. *Moringa* husk appears to have structural similarities with lignin, with a minimal contribution of hemicellulose sub-units as evidenced by negligible weight loss during Θ_2. This is advantageous for carbon production because significant hemicellulose contributions would otherwise result in substantial volatilisation during carbonisation and, subsequent heavy carbon loss. Selection of carbonisation and activation temperatures is always a compromise between carbon and structural development, both of which progress with increasing temperature, hence the selection of 360°C and 485°C as initial carbonisation temperatures, which correspond to the completion of Θ_3 and Θ_4 processes, respectively.

Aromaticity of carbon product

CHN microanalyses, char yields and carbon burn-off values are presented in Table 2 with the phenol adsorption efficiencies of the carbonised and activated products. C/H quotients reflect the degree of aromaticity or extent of thermal rearrangement experienced by the carbonised sub-units (Lewis, 1982) and increase with structural development of first the carbonised, and subsequently, the activated carbon product. Examination of Table 2 allows identification of the 485°C/30 min *Moringa* char as the primary candidate of steam gasification trials on the basis of retained carbon and apparent structural development. Continued loss of yield following a 30 min dwell at 485°C, however, appears to eliminate extended carbonisation times, the husks clearly sensitive to elevated processing temperatures. Steam activation, performed at a

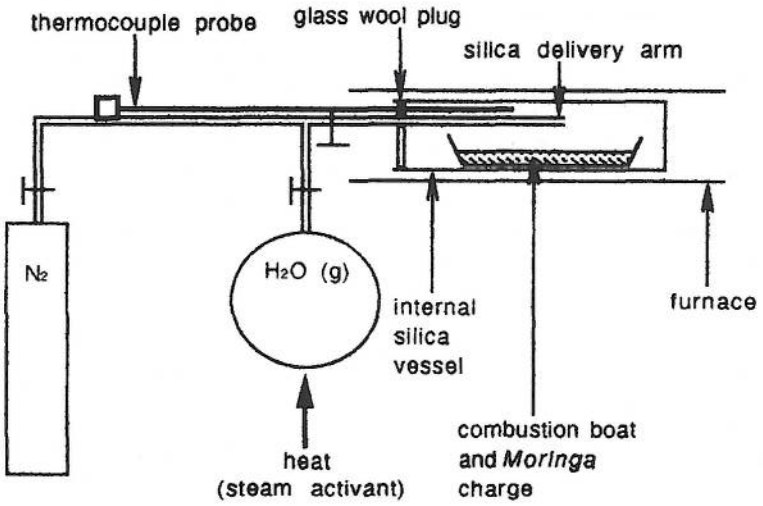


Fig. 2. Schematic of experimental apparatus.

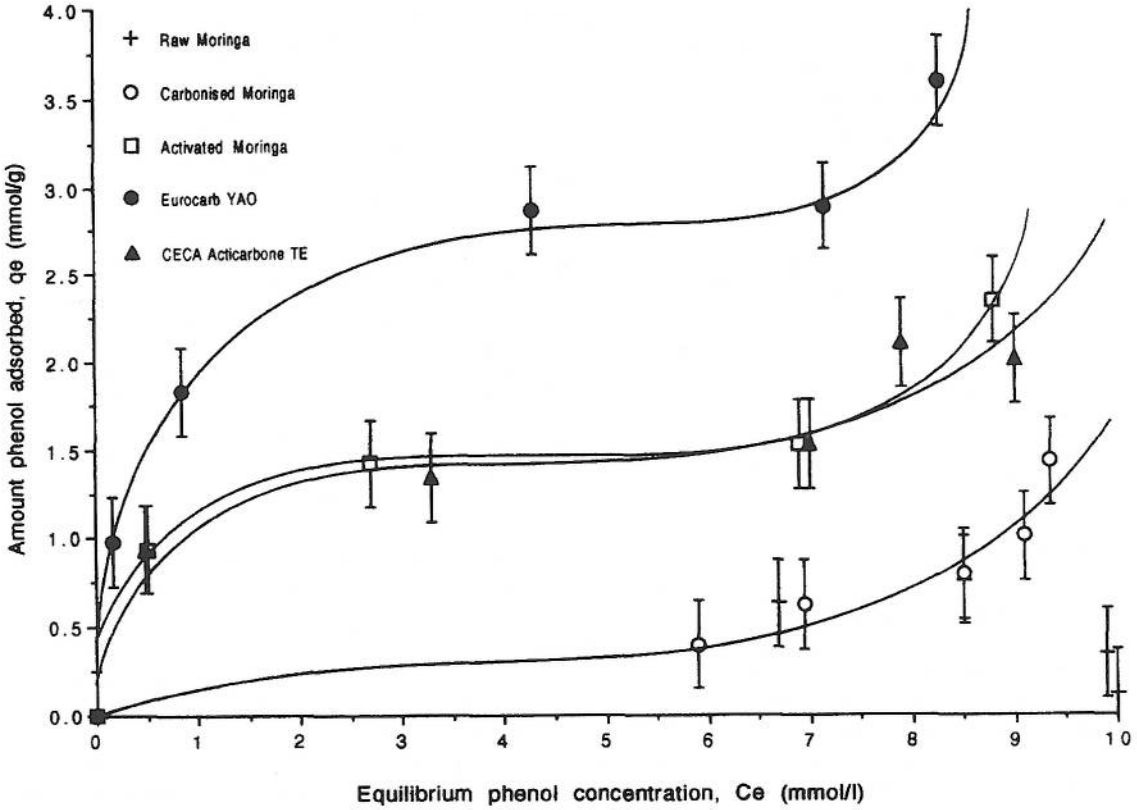


Fig. 3. Phenol adsorption: experimental isotherms for study adsorbents.

minimum feasible temperature of 850°C, resulted in successful development of microstructure as evidence by a substantially enhanced phenol uptake during screening (1.42 mmol g^{-1}, equivalent to 71 mol % removal efficiency from the 10 mM solution) and a further increase in the C/H quotient of the activated product. Maximum phenol removal efficiency was observed for the 5 min gasified char and this product subsequently subjected to detailed isothermal analysis for water treatment applications.

Phenol adsorption isotherms and microporosity of Moringa carbon

Experimental phenol isotherms for raw, carbonised and activated *Moringa* are compared in Fig. 3 with those for selected comparable reference carbons. With the exception of the raw husk, which demonstrated erratic isothermal behaviour, the adsorbents demonstrated sigmoidal behaviour typical of Type II isotherms (Shaw, 1980) and characteristic of monolayer followed by multilayer adsorption. Linearised Langmuir and Freundlich plots with correlation coefficients are provided in Figs 4–5 for relevant carbons. Deviations from idealised model behaviour are attributed to multilayer adsorption evidenced by the S-shaped experimental isotherm. The related isothermal parameters are listed in Table 3. Activated *Moringa* carbon exhibited an intermediate specific surface area and monolayer coverage coefficient (Q^0) between the commercial lignocellulosic-based PACs, Eurocarb® YAO and Ceca® Acticarbone TE. Phenol specific surface areas (SSA) for *Moringa* carbon determined using (i) the Giles and Nakhwa method (1962); and (ii) by conversion of Q^0 were 465 $m^2 g^{-1}$ and 594 ± 79 $m^2 g^{-1}$, respectively. Progressive development of porosity in the activated product from the carbonised *Moringa* char is confirmed by increases in the relevant isothermal parameters (x_m, SSA, Q^0, K_F) and the skeletal morphologies observed in representative SEM micrographs of activated *Moringa* surfaces (Figs 6 and 7).

Table 3. Phenol adsorption isotherm parameters

Parameter	Giles and Nakhwa		Langmuir		Freundlich	
Adsorbent	x_m (mmol g^{-1})	SSA ($m^2 g^{-1}$)	Q^0 (mmol g^{-1})	b (dm^3 $mmol^{-1}$)	K_F ($dm^3 g^{-1}$)	n
Carbonised 485/30	0.60	188.6	NA	NA	0.02 ± 0.18	0.52
Activated 850/5	1.48	465.2	1.89 ± 0.25	1.98	1.12 ± 0.15	3.80
Eurocab® YAO	2.78	873.9	3.05 ± 0.27	2.93	1.80 ± 0.08	3.31
Ceca® Acticarbone TE	1.34	421.2	1.53 ± 0.94	0.4	1.05 ± 0.12	0.38

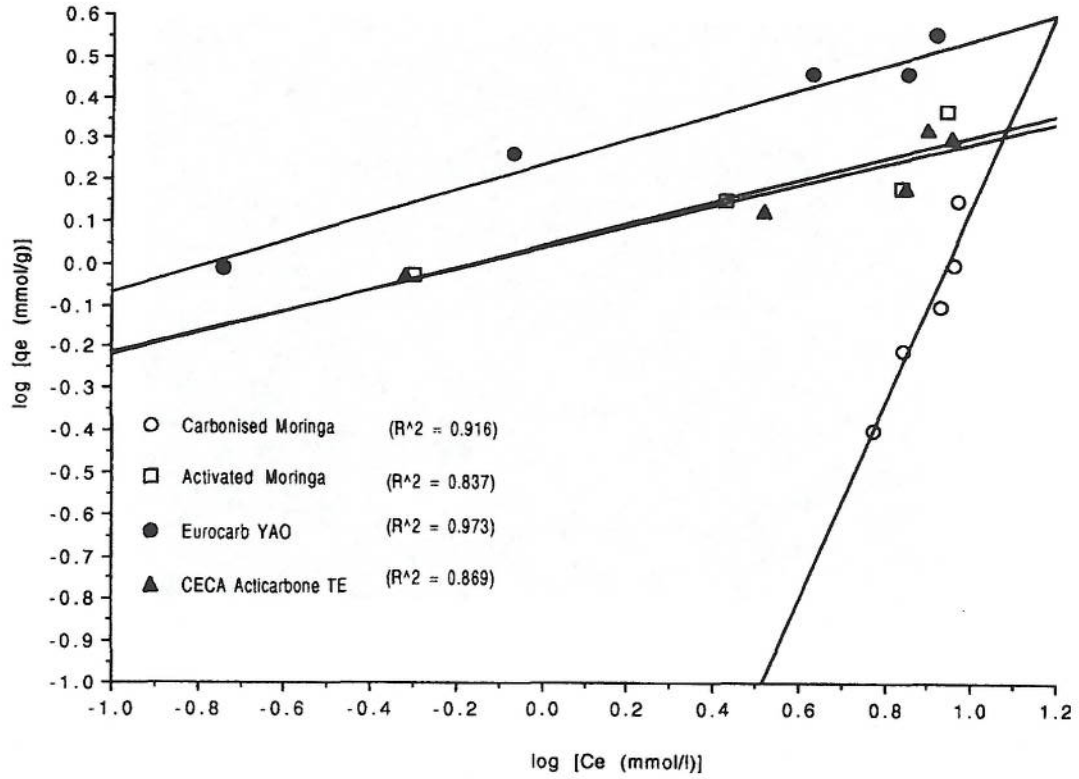


Fig. 4. Phenol adsorption: Freundlich isotherms for study adsorbents.

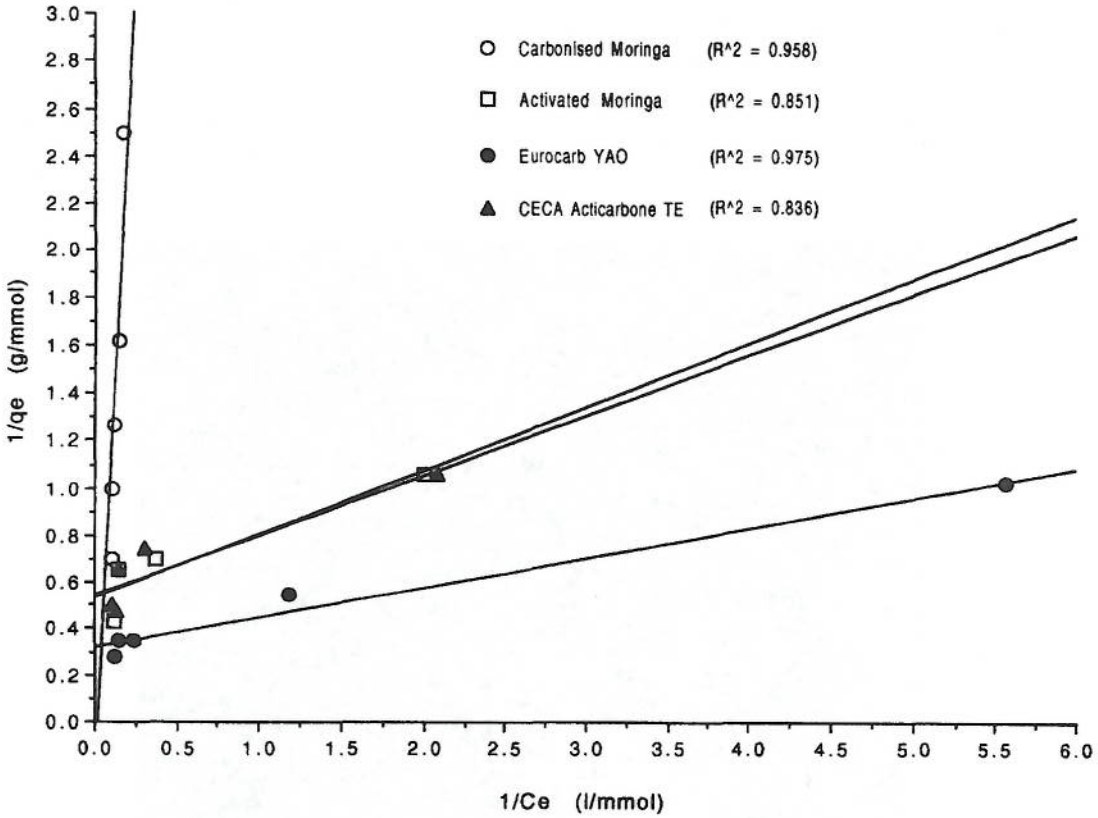


Fig. 5. Phenol adsorption: Langmuir isotherms for study adsorbents.



Fig. 6. Representative SEM micrograph of activated *Moringa* carbon surface (808 ×).

The adsorption-desorption isotherm of N_2 on *Moringa* carbon at −196°C is shown in Fig. 8 and compared with that of a peat-based commercial carbon obtained in earlier studies (Pollard *et al.*, 1991). Surface area and porosity data obtained by continuous gas phase hysteresis for the two adsorbents is shown in Table 4. Apparent surface areas for *Moringa* and the peat-based commercial product determined using the linearised BET equation and a molecular area of 0.162×10^{-18} m^2 for N_2 at −196°C (Gregg and Sing, 1982) were 734 m^2 g^{-1} and 704 m^2 g^{-1} respectively, demonstrating the superior quality of the *Moringa* product. For microporous solids, the BET model takes no account of micropore filling processes (Sing, 1989) and true surface areas may be significantly greater than these apparent values. For *Moringa* carbon, the contribution from the external surface area ($S_{mes+mac}$) was determined to

Table 4. Summary of continuous volumetric adsorption data

Parameter / Absorbent	Activated *Moringa*	Peat-based PAC (Norit® SA4)
Mass (g)	0.1027	0.2770
V_{ads} (cm^3 g^{-1})	4352.2	49667.0
C_{BET}	168.8	161.9
S_{tot} (m^2 g$_{-1}$)	734.3	704.5
$S_{mes+mac}$ (m^2 g^{-1})	77.9	283.9
V_{micro} (cm^3 g^{-1})	0.569	0.141
$V_{mes+mac}$ (cm^3 g^{-1})	0.071	0.285
Microporosity (% v/v)	88.9	33.1

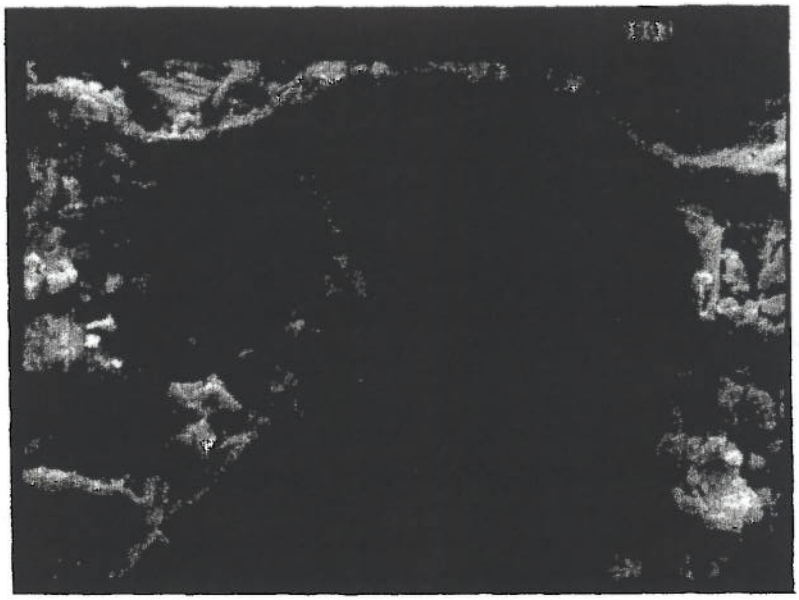


Fig. 7. Representative *Moringa* carbon surface showing skeletal structure of activated surface (1610 ×).

be 78 $m^2 g^{-1}$, this representing the meso- and macropore surface alone (pore widths 2–200 nm). Mesopore and micropore distributions were determined using the Barrett *et al.* (1951) and the Horváth–Kawazoe models (1983), respectively. A basis for the application of these models to the characterisation of microporous carbon adsorbents and the significance of their limitations is provided by Pollard (1990). *Moringa* carbon exhibited near Type I isothermal behaviour according to the BDDT classification (Brunauer *et al.*, 1940), and Type H4 de Boer hysteresis (Sing *et al.*, 1985) with an onset of isotherm closure at $p/p^0 \sim 0.4$, indicative of the presence of microporosity within the structure. Angular deviation of the experimental isotherm plateau from the strict horizon (compared to classical microporous solids) reflects partial mesoporosity, desirable for solute transport to adsorption sites. Activated *Moringa* demonstrated a substantial micropore volume of 0.57 $cm^3 g^{-1}$ compared to 0.18 $cm^3 g^{-1}$ previously determined for a peat-based water treatment carbon of similar surface area (Pollard *et al.*, 1991). The pore volume of *Moringa* carbon above 2 nm was determined to be 0.07 $cm^3 g^{-1}$ yielding a micropore volume contribution of ~89%v/v to the total pore volume. The Horváth–Kawazoe plot (Fig. 9) illustrates the extent of micropore development, with the micropore distribution function ($dW/dR = 6.7$, $R_p = 0.54$ nm) exceeding that previously determined for peat-based carbon ($dW/dR = 4.9$, R_p 0.63 nm; Pollard *et al.*, 1991) by a factor of 1.4 in peak height. These results clearly indicate the viability of *Moringa* husks as a suitable precursor for the preparation of microporous activated carbon with adsorptive properties similar, if not superior, to some commercial carbons from industrialised countries.

DISCUSSION

The potential applications for low-cost active carbons in developing countries include the adsorption of excessive concentrations of Fe, Mn from groundwater supplies, taste and odour compounds from "foul-smelling" stored water, adsorption of bacterial and viral pathogens in stored water and the tertiary treatment of domestic and industrial wastewaters with excessive nutrient or contaminant load (Jahn, 1982; Bhargava and Sheldarkar, 1993a). The current emphasis on natural treatment processes for direct water purification in developing countries seeks to address a number of broad-based developmental problems associated with poor water quality: (a) an overall need for the provision of safe, potable water to rural communities in the developing world (Reid, 1982); (b) an established requirement for appropriate water and wastewater treatment processes that can be implemented at a local level (Schulz and Okun, 1984); and (c) a specific need for low-cost adsorbents for the removal of micropollutants and taste and odour compounds from contaminated and "foul-smelling" water supplies. Among these problems lie some

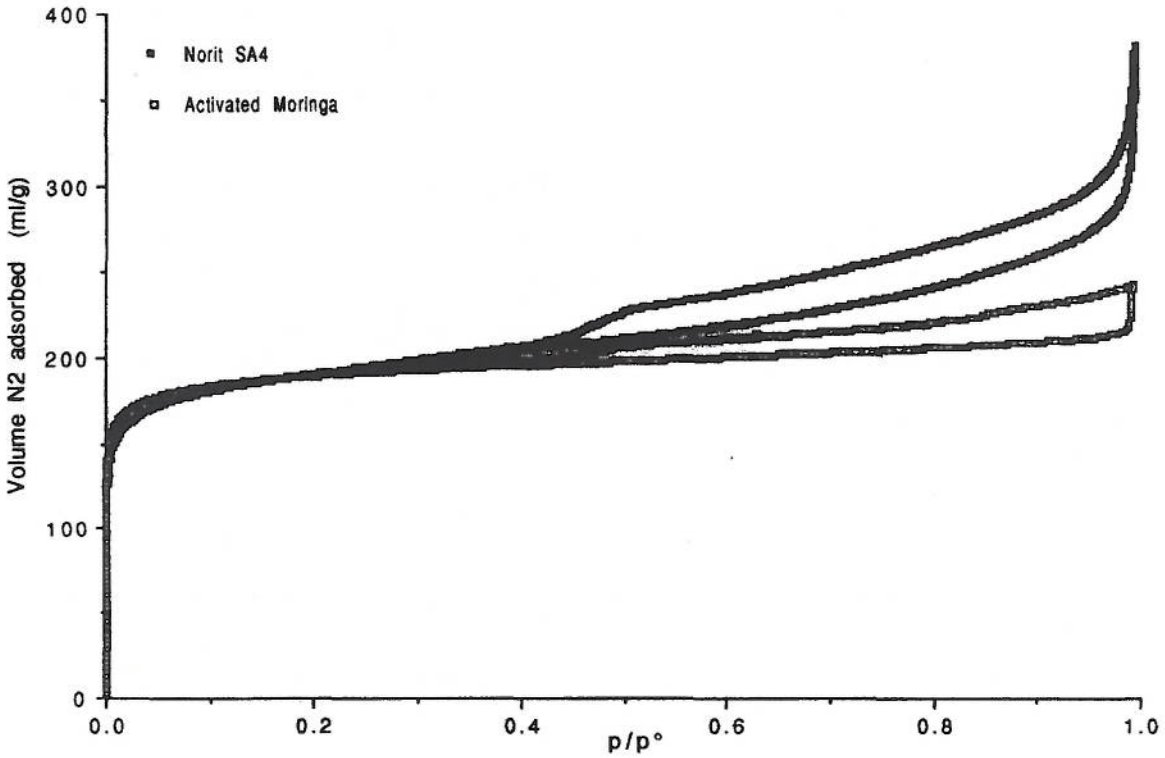


Fig. 8. Experimental isotherms for N_2 adsorption at −196°C on commercial water treatment carbon and activated *Moringa* husk.

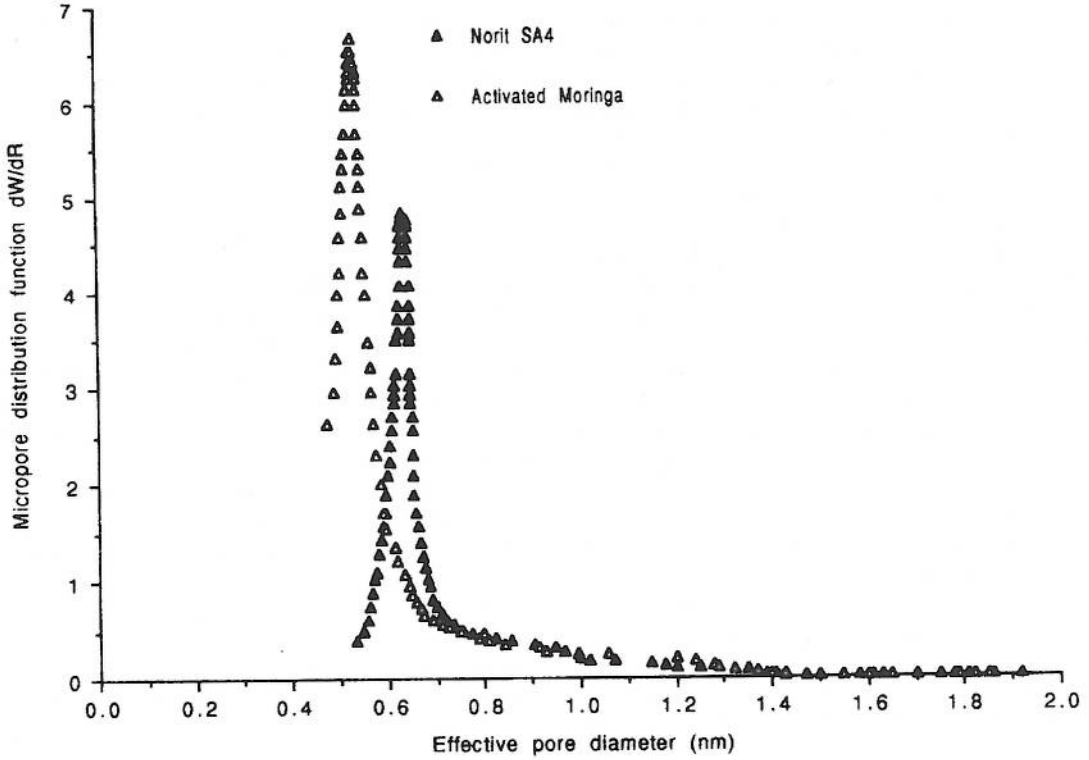


Fig. 9. Horváth–Kawazoe plots of micropore distribution in commercial water treatment carbon and activated *Moringa* husk.

specific objectives related to low-cost carbon production: (d) a need for locally-available, low-cost precursors to activated carbon that allow successful application of adsorption technology without enforcing reliance on commercial carbon from industrialised countries (Khare *et al.*, 1988; Pollard *et al.*, 1992); and (e) a need for simple, preparative procedures for low-cost activated carbon that incur negligible environmental impacts. The latter usually places a requirement for physical activation (partial gasification) on the preparative process because activation of carbon precursors with $ZnCl_2$, H_3PO_4, H_2SO_4 and other chemical activants can lead to process difficulties (corrosion of plant) and pollution problems with rinsewater if full activant recovery is not feasible. Furthermore, leaching of residual activant from the activated product may prove problematical, especially if water purification applications are being considered. Examples of successful gasification plants currently operating in developing countries have been described by Hardman (1992). On this basis of the above criteria, *Moringa* carbon is clearly a potential candidate for the direct purification of drinking water by adsorption and may have additional uses as (i) an effective replacement for sand in fine or dual filter units operating at low filtration rates; and (ii) in tertiary wastewater treatment, providing it can be produced in sufficient quantity.

Precedents already exist for the use of ashes, chars and soils for the treatment of stored water in LDCs (Jahn, 1982). For example, the water purification characteristics of certain adsorptive "plant ashes" added to storage jars containing drinking water are well known by indigenous peoples throughout the developing world. In certain parts of India, "foul-smelling" water is mixed with wood ash from the sal-tree (*Shorea robusta*) and then cloth-filtered before use. In Kerala, India, burnt coconut shells, carbon adsorbents with an extended microporosity (Bansal *et al.*, 1988), are frequently added to well water supplies. Carbonaceous materials are generally collected from the ashes of the fire for these applications, but these materials generally have poor adsorptive capacities and hence require high dosages (Jahn, 1982). The adsorptive capacities of the chars obtained could be substantially enhanced if *controlled* pyrolysis and activation were applied rather than uncontrolled combustion and use in the form of "plant ash". Furthermore, selective use of specific precursors for activated carbon has substantial advantages over the indiscriminate use of fire ash of mixed, and often low adsorptive quality. Use of *Moringa* carbon, therefore, is fully consistent with accepted water purification practices for rural communities in many developing countries and is especially attractive because of the highly-developed microporosity attainable with this substrate. An additional advantage of the recovery and reuse of waste *Moringa* husk is that increased utilisation of the plant may encourage further development of localised *Moringa oleifera* plantations with long-term

benefits for rural communities in terms of natural water purification.

Within the range of activated carbons prepared from similar lignocellulosic precursors, *Moringa* carbon compares very favourably in terms of apparent surface area ($734\ m^2\ g^{-1}$) and phenol adsorptive capacity ($1.89\ mmol\ g^{-1}$). For example, Renouprez and Avom (1988) prepared carbons with N_2 BET surface areas of $23–1078\ m^2\ g^{-1}$ from palm tree cobs using a variety of physical and chemical activation procedures. Likewise, Tanin and Gürgey (1987) prepared rice hull ash carbons with a range of surface areas from 482 to $788\ m^2\ g^{-1}$. Tamarind nut shell carbons, prepared and assessed for their water treatment properties on the basis of their phenol adsorption capacity were highly active with surface areas of $218\ m^2\ g^{-1}$ (H_2SO_4 activant) to $2810\ m^2\ g^{-1}$ (direct pyrolysis) and reported phenol uptakes of $3–32\ \mu mol\ g^{-1}$ (Srinivasan *et al.*, 1988). Activated *Moringa* in this study exhibited a micropore volume ($0.57\ cm^3\ g^{-1}$) comparable to the highly adsorptive materials prepared by Linares-Solano *et al.* (1984) from olive stones and almond shells. These materials displayed a developed meso- and microporosity, with the olive stones showing a greater degree of macroporosity (pore widths 50–200 nm). Whilst both materials yielded highly active carbons, $800–1300\ m^2\ g^{-1}$ in surface area and $0.3–0.8\ cm^3\ g^{-1}$ in total pore volume, olive stones were the preferred choice for the adsorption of textile dyes from industrial waste waters. Potential substrates of comparable importance to *Moringa oleifera*, currently being grown for the coagulant properties of their seed extracts, include *Moringa peregrina*, Nirmali (*Strychnos potatorum*), Tamarind nuts (*Tamerindus indica*), and Guar (*Cyamopsis psoraloides*) (Shulz and Okun, 1984). *Moringa peregrina* seeds have an average endosperm mass of 0.32 g compared to 0.23 g for *Moringa oleifera* (Jahn, 1982) and are of particular future interest.

CONCLUSION

High grade microporous activated carbon can be prepared from waste seed husks from the *Moringa oleifera* tree. Beneficiaries of a development in the utilisation of the waste husks would be communities using natural *Moringa* polyelectrolytes for turbidity control (e.g. Sudan, Egypt, Niger, Southern and Central India). Future work will focus on developing an optimised and implementable preparative procedure for *Moringa* carbon, evaluating the adsorptive properties of carbons produced from similar plant material wastes and demonstrating *in-situ* the pilot-scale use of *Moringa* carbon in passive uptake storage jars and downflow treatment columns.

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THE PRODUCTION OF ACTIVATED CARBON FOR WATER TREATMENT IN MALAWI FROM THE WASTE SEED HUSKS OF *MORINGA OLEIFERA*

A. Michael Warhurst*, Gordon L. McConnachie** and Simon J. T. Pollard*

** Department of Civil and Environmental Engineering, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK*
*** Aspinwall & Company, 13 Melville Street, Edinburgh EH3 7PE, UK*

ABSTRACT

Moringa oleifera is a multi-purpose tree whose seeds can be used as a coagulant in water treatment. The seed husks are currently discarded as a waste, but research has shown that they can be converted into activated carbon by carbonisation at 485°C under N_2 for 30 minutes, followed by activation in steam at 850°C for 5 minutes. Here we report an improved method of carbon production, using a single-stage steam pyrolysis activation that is more appropriate for the intended use. Steam pyrolysis at 750°C for between 30 and 120 minutes produced a high quality microporous activated carbon at a yield of between 11 % and 17 %, with increases in soak time giving improved pore development and more mesoporosity. The apparent N_2 BET surface area of the *M. oleifera* carbon produced by soaking at 750°C for 120 minutes was 730.0 $m^2 g^{-1}$, similar to that of the carbon produced previously by the two-stage process, 734.3 $m^2 g^{-1}$. The phenol adsorptive capacities of the carbons pyrolysed at 750°C were similar to a commercial carbon. These results show that it is possible to produce high quality activated carbon from the waste seed husks of *M. oleifera* using a simple one-stage 750°C steam pyrolysis. This provides a low-cost method of producing activated carbon locally in developing countries for use in water treatment. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd.

KEYWORDS

Activated carbon; appropriate technology; developing countries; low-cost adsorbents; *Moringa oleifera*; multi-purpose tree; steam pyrolysis; water purification.

INTRODUCTION

Moringa oleifera is a multi-purpose tree that is found in many tropical areas, where it grows rapidly and is able to survive periods of low rainfall (Morton, 1991). The tree produces large seed pods, which can either be harvested while young and green for food ('Drumstick' in India), or left to dry on the tree. The dried seeds can be crushed to produce a high quality vegetable oil, and the pressed cake can then be used as a coagulant (see below). Parts of the tree are also used in medicine; the leaves contain hypotensive agents (Faizi *et al.*, 1994) and the roots are abortifacient (Nath *et al.*, 1992). The coagulant properties of the crushed *M. oleifera* seed appear to have been discovered first by experimentation by villagers in Sudan (Jahn, 1988),

and further research has found the coagulant to be as effective as aluminium sulphate in many situations, and its use is being developed on both a village and waterworks scale (Jahn, 1986; McConnachie *et al.*, 1994).

The seed husks are currently discarded as waste when seed is prepared for oil and/or coagulant production. However, it has been found that these husks can be converted into a high quality microporous activated carbon (Pollard *et al.*, 1995). Activated carbon has many uses in drinking water and wastewater treatment, including the removal of taste and odour-producing chemicals (Lalezary-Craig *et al.*, 1988), algal toxins (Donati *et al.*, 1994), pesticides (Miltner *et al.*, 1989) and metals (Budinova *et al.*, 1994). Since commercial activated carbon is expensive, it is seldom possible to use it in water treatment in developing countries. However, substantial research effort has been directed towards the preparation and utilisation of low-cost alternatives to commercial carbon using locally available agricultural by-products (Pollard *et al.*, 1992). A low-cost method of producing activated carbon from *M. oleifera* waste could allow economic use of activated carbon even in poorer countries, and contribute to an appropriate technological solution to improving potable water quality in the developing world.

Previous research by Pollard *et al.* (1995) found that carbonisation of husks under N_2 at 485°C for 30 minutes, followed by steam activation for 5 minutes at 850°C, produced a highly microporous carbon with adsorptive properties similar to commercial activated carbons. This is a complex production process, involving two heating stages, and the use of N_2 gas. In a developing country both chemical and energy costs are high, so any reduction in, or elimination of, the use of chemicals, and any reduction of the energy required for the process will improve the economic case for carbon production. Several simplified activated carbon production processes have been investigated by other workers, with a one-stage 600 - 700°C steam pyrolysis carbonisation being particularly effective (Gergova *et al.*, 1994). The research presented here demonstrates that a simple steam pyrolysis procedure can be used to make a good quality activated carbon from the waste husks of *M. oleifera*, and reproduce the activity and microporosity previously demonstrated at the laboratory scale under more conventional activation conditions.

MATERIALS AND METHODS

Materials

M. oleifera husks were obtained from Malawi, where they had been produced as a waste product from the production of *M. oleifera* seed. Because of the nature of the seed-husk separation process, this husk material also contained powdered seed, and was not of an even particle size, varying between powder and particles several mm in dimensions. Two commercial reference carbons were used in the phenol adsorption tests, one powdered, Acticarbone TE (CECA S. A., France), and one granular, YAO 14x40 ref. 779 (Eurocarb, Bristol, UK).

Carbonisation/activation of husks

Carbonisation of *M. oleifera* husks was performed in a Carbolite 12/65 tube furnace, with a purpose-made quartz tube inserted into it (Multi-Lab, Newcastle, UK). This tube connected to Quickfit connections at one end, and a ball and cup joint at the other, allowing flow-through of a controlled gaseous atmosphere. Charges of 30 g of *M. oleifera* husks were placed in a customised quartz combustion boat (Multi-Lab), loaded into the quartz tube and positioned in the centre of the furnace. The temperature of the sample was monitored by a thermocouple probe (type K probe, connected to a P. I. 8013 thermometer from Portec, Milton Keynes, UK) which entered the silica tube through one of the Quickfit connectors and whose tip was positioned just above the sample. Steam, generated by a flask of water on a heating mantle, entered the quartz tube through one of the Quickfit joints at a rate of approximately 2 ml (liquid water) per min. A condenser was connected to the ball and cup joint at the other end of the tube, and the condensed material was collected in a beaker.

The sample was heated at a fixed rate of approximately 20°C min^{-1} to the appropriate temperature, and held at this temperature (±10°C) for the time specified. After the furnace had cooled to between 200 and 300°C, the carbonised husks (char) were removed, allowed to cool for a few minutes and then weighed to determine the yield. The char was then moved to a desiccator for storage. Chars, duplicated for each set of temperature and time, were later mixed, homogenised and sieved to <250 μm, then dried in an oven at 110°C overnight, prior to testing for adsorptive capacity.

Aqueous adsorption testing of chars with phenol

A preliminary screening test of the adsorptive capacity of the chars was conducted using a simple single point, aqueous phase phenol adsorption test (Pollard *et al.*, 1995). Char samples (0.5g) were added to 100 ml of 0.01 M phenol (BDH, UK) solution in 250 cm^3 Erlenmeyer flasks, which were sealed with Suba-seals, then shaken at 90 strokes min^{-1} in a temperature controlled shaker bath for 24h at 25°C. Following uptake, suspensions were vacuum-filtered through a Whatman cellulose nitrate 0.45 μm membrane filter and residual phenol concentrations were analysed at 270 nm using a u.v. specqtrophotometer (Shimadzu UV-160A). All determinations were at least duplicated.

N_2 BET adsorption testing of chars

Activated chars were analysed by continuous volumetric N_2 adsorption analysis for surface area characterisation and pore size distribution analysis using a Coulter Omnisorp Model 100 instrument (Centre for Environmental Control and Waste Management, Imperial College, London, UK). A representative carbon sub-sample of approximately 0.3g was taken from each char under test and outgassed at 250°C for 8 h under a vacuum of 10^{-5} torr. A full N_2 adsorption/desorption isotherm was obtained at liquid N_2 temperatures using a constant, calibrated N_2 flow rate of 0.27 cm^3 min^{-1} and an adsorption cut off p/p^o of -0.98. Analysis of the data was done using the associated instrument software, which employs the N_2 BET method of calculating apparent surface area, the t-plot analysis for comparing micropore, mesopore and macropore volumes, the BJH method of mesopore and macropore size distribution (Barrett *et al.*, 1951) and the Horváth-Kawazoe model (1983) for analysis of the micropore size distribution (pore widths <2 nm). The BJH method employs the Kelvin equation for determination of the pore size distribution and assumes a cylindrical pore shape, as does the Horváth-Kawazoe model. The appropriate use and limitations of these models have been discussed previously (Pollard, 1990).

RESULTS

Characteristics of char production

The yields obtained under various temperatures and times are shown in Table 1. The steam pyrolysis process gave reproducible yields, with duplicate runs differing by less than 1%. As the soaking temperature was increased, the yield reduced. There was little effect on yield of different soak times at 500 and 600°C, but at higher temperatures the yield was considerably reduced by longer soak times.

The material condensed from the off-gases contained both a black, tarry component and a yellowish-white material. The condensate had a strong, unpleasant smell.

Characterisation by phenol adsorption

The single point phenol adsorption test showed that phenol uptake increases as yield reduces (Table 1 and Figure 1). However, all three chars produced at 750°C showed similar adsorptive behaviour, in spite of the increased burn-off in S750/120, with 11.4% remaining, as compared to S750/30, with an approximately 50% higher yield of 16.6%. All the chars produced at 750°C had a phenol adsorptive capacity similar to the commercial powdered activated carbon, Acticarbone TE, though lower than the commercial granular carbon Eurocarb YAO (Table 1).

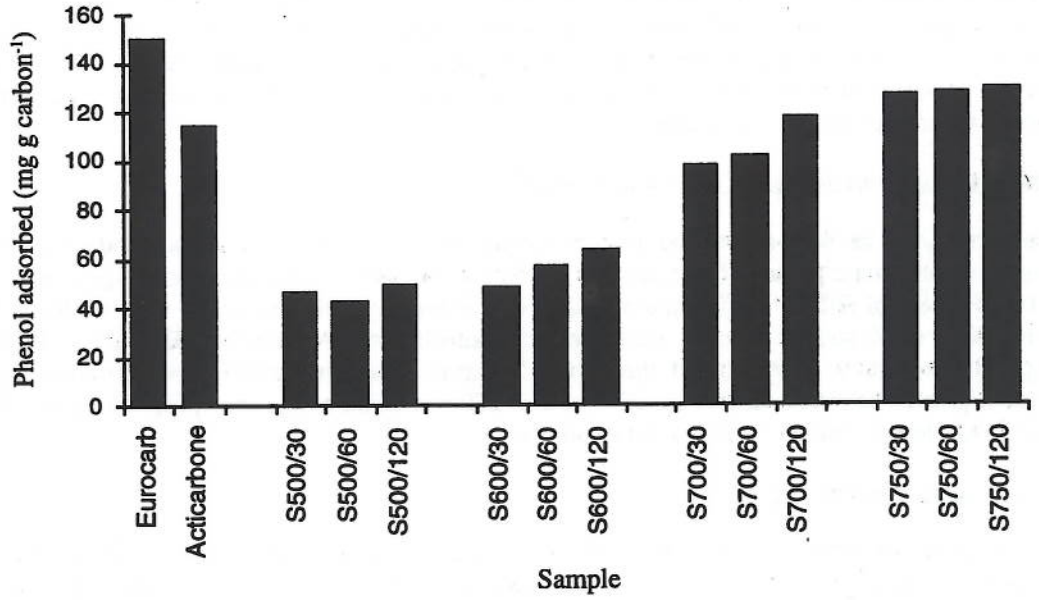


Figure 1. Phenol adsorption results.

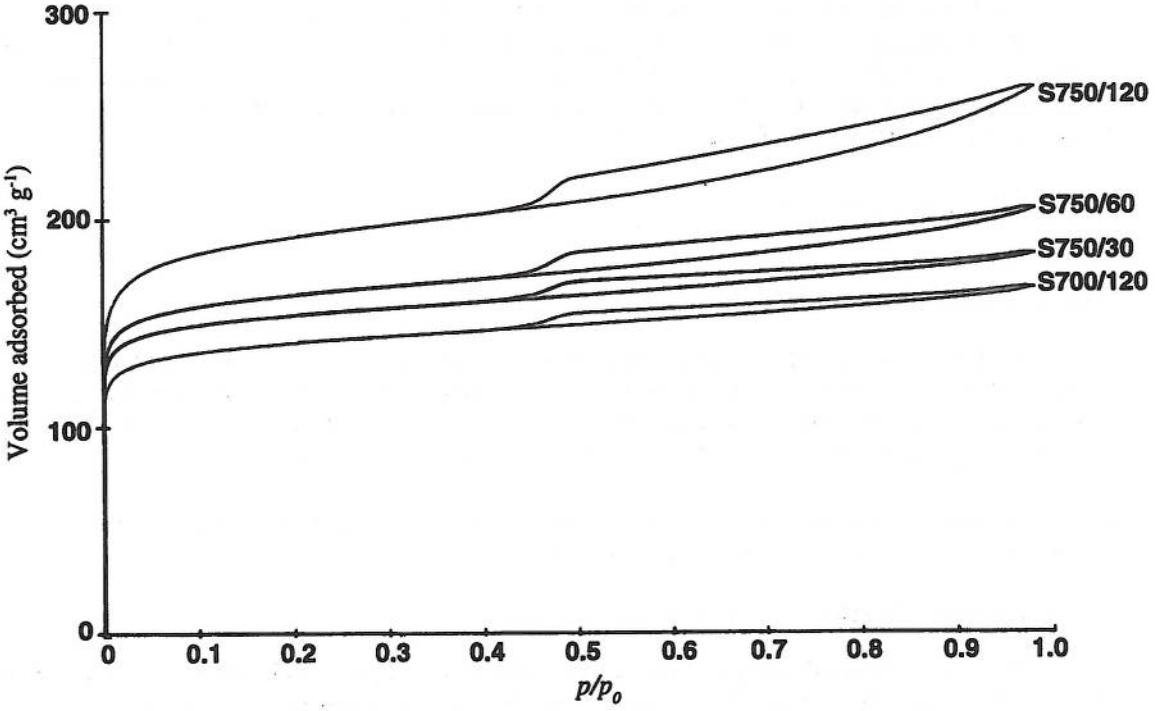


Figure 2. Nitrogen adsorption isotherms.

Characterisation by N_2 BET adsorption

Nitrogen adsorption isotherms were determined for the four carbons with the highest burn-off, and highest phenol adsorption (Figure 2). All isotherms exhibited Type I/Type IV (microporous/mesoporous) characteristics with closed loop hysteresis but tight initial micropore filling. The hysteresis loop was classified as H4 (Gregg and Sing, 1982), more indicative of slit or plate-like pore configurations, hence the need for caution in interpretation of the surface area and micropore volume data (Pollard, 1990). The carbon with the lowest burn-off, S700/120, exhibited Type 1 isotherm characteristics, according to the BDDT classification (Gregg and Sing, 1982), with limited hysteresis. As burn-off increases, the isotherm increases in Type 4 characteristics, toward a more mesoporous structure. The width of the hysteresis loop also increases at higher burn off, and moves away from a horizontal plateau, which is indicative of increased mesoporosity.

The purpose of the analysis of the N_2 adsorption isotherm data in this work is to enable comparison between the carbons produced, and limited comparison with those carbons produced by other workers. Used in a comparative sense, the data is useful in assessing the effects of different preparative techniques and in optimising carbon production (Pollard *et al.*, 1991).

The apparent surface areas for the carbons were determined using the linearised BET equation and a molecular area of 0.162×10^{-18} m^2 for N_2. This apparent surface area increased with increasing burn-off (Table 2), to a maximum of 730.0 m^2 g^{-1} for S750/120. This compares well with the surface area of 734.3 m^2 g^{-1} found for the *M. oleifera* carbon produced in previous work (Pollard *et al.*, 1995).

The t-plot analysis of micropore, mesopore and macropore volumes and surface areas demonstrates that these also increased as burn-off increased (Table 2). The maxima were found in the S750/120 carbon, with a micropore volume of 0.25 ml g^{-1}, a combined mesopore and macropore volume of 0.1 ml g^{-1} and a mesopore and macropore surface area of 112 m^2 g^{-1}. As expected, the mesopore and macropore volumes are particularly strongly affected by increased burn-off, with S750/120 having almost double the volume of S750/60, whilst the micropore volume only increases by just over 10 %. This leads to a fall in percentage of the pore volume that is due to micropores, from 82% in S750/60 to 72% in S750/120. The micropore volume of S750/120 is about half that found in the previous *M. oleifera* work, but the mesopore and macropore volume is 40 % higher.

Table 1. Char yields and phenol adsorbance results

Sample	Production conditions		Yield		Phenol adsorbed	
	Temperature	Soak time	%		mg/g carbon	
	°C	min	mean	± s. d.	mean	± s. d.
S500/30	500	30	24.1	± 0.1	46	±2.9
S500/60	500	60	24.7	± 0.1	43	±3.9
S500/120	500	120	23.5	± 0.2	49	±2.6
S600/30	600	30	22.0	± 1.3	48	±1.8
S600/60	600	60	22.4	± 0.4	57	±0.4
S600/120	600	120	22.0	± 0.8	63	±0.6
S700/30	700	30	19.7	± 0.2	97	±0.2
S700/60	700	60	18.5	± 0.1	101	±2.6
S700/120	700	120	17.3	± 0.4	117	±1.1
S750/30	750	30	16.6	± 0.2	126	±0.2
S750/60	750	60	15.1	± 0.1	127	±2.7
S750/120	750	120	11.4	± 0.5	129	±2.0
Acticarbone					114	±2.0
Eurocarb					150	±8.9

The Horváth-Kawazoe plots of micropore distribution (not shown) had a single, sharp peak at an effective pore diameter of just less than 0.6 nm, with the height of this peak (dW/dR representing the micropore distribution) at a maximum in S700/120 (dW/dR = 15.5), and a minimum in S750/120 (dW/dR = 9.7), providing further evidence of the reducing proportion of micropores in the carbons with higher burn-off.

DISCUSSION

These results have shown that it is possible to produce a high quality activated carbon from the waste husks of *M. oleifera*, using a simple one-stage, 750°C, steam pyrolysis. Carbon produced by soaking at 750°C for 120 minutes has a similar N_2 BET apparent surface area to that produced by a two-stage process, carbonisation at 485°C followed by steam activation at 850°C, though it is less microporous and more mesoporous and macroporous.

As burn-off increases, it seems that both microporosity and the larger pores develop, presumably by widening of micropores to mesopores (Wigmans, 1989), whilst more micropores are being opened. It is likely that if higher temperatures are used for the steam pyrolysis, at some point the surface area will begin to reduce, as the pores are burnt out. It is possible, though, that a carbon pyrolysed at 800°C might have an apparent surface area higher than that of S750/120, though this would probably be at the expense of reducing yield. Further work is intended on higher temperature carbons. The balance between yield and adsorptive capacity is an important consideration in the application of this process; S700/30 and S700/120 have a single-point phenol adsorption capacity within a few percent of each other, but the yield of S700/30 is 50 % higher, and it requires 90 minutes less heating time, therefore saving energy. Future work will include evaluation of the most effective and economical method of producing carbons suitable for the adsorptive roles required (discussed below).

The characteristics of the carbons produced in this work appear to be similar to those produced by Gergova *et al.* (1994) by steam pyrolysis of plant materials. This work found that steam pyrolysis at 700°C for 120 minutes led to a BET surface area of 820 $m^2\ g^{-1}$ in apricot stones, 574 $m^2\ g^{-1}$ in almond shells and 541 $m^2\ g^{-1}$ in cherry stones, comparable with those found in this work. Rodríguez-Reinoso *et al.* (1995) used a more conventional two-stage carbonisation and activation process to compare the actions of steam and CO_2 as activating agents. Their work found that microporosity widening occurred from the early stages of the activation process when steam was used as an activating agent at either 750 or 800°C, as has been found in these experiments. In contrast, microporosity widening occurs later with CO_2 as an activating agent. Steam was found to produce a wider range of pore size distribution than CO_2, with a larger development of mesoporosity and macroporosity, both of which are useful for adsorbing larger molecules and providing transport routes to the micropores.

Table 2. Results from N_2 isotherm analysis, compared with the *M. OLEFERA* carbon produced in earlier work Pollard *et al.*, 1995)

Sample	N_2 BET surface area (m^2/g)	Micropore volume (ml/g)	Mesopore & macropore surface area (m^2/g)	Mesopore & macropore volume (>2 nm, ml/g)	Volume in micropores (%)
S700/120	539.8	0.20	55.3	0.030	87
S750/30	588.1	0.21	61.8	0.032	87
S750/60	625.1	0.22	75.6	0.048	82
S750/120	730.0	0.25	111.6	0.098	72
N_2 485/30, S850/5 (Pollard *et al.*, 1995)	734.3	0.57	77.9	0.07	89

The composition of the off-gases and condensate was not determined in this study, but work on steam pyrolysis volatiles from apricot stones and coconut husks found that typical components of lignocellulosic gases include derivatives of phenol, guaicol, veratrol, syringol, resorcinol, free fatty acids and the esters of fatty acids (Razvigorova *et al.*, 1994). Whether it would be possible to find a use for this material is not clear, otherwise it will have to be disposed of; fortunately it is likely to be readily biodegradable.

This research project will be continuing in association with The Polytechnic, the University of Malawi, in Blantyre, Malawi, where we will be developing the techniques for bulk production of the activated carbon in Malawi. In addition to the seed husks, we intend to investigate the possibility of producing carbon from the seed pods, which make up more than 50 % of the mass of the fruit, and which are currently discarded. We will also be examining applications of the carbon, particularly concentrating on water quality problems produced by algal blooms, including taste, odour and toxins, since algal blooms are a problem in reservoirs in Malawi and other regions of southern Africa (Scott, 1991). Further work is also underway in association with the Environmental Engineering group at the University of Leicester, Leicester, UK, to develop market analyses and business plans for *M. oleifera*-derived oil, coagulant and activated carbon.

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CHARACTERISATION AND APPLICATIONS OF ACTIVATED CARBON PRODUCED FROM *MORINGA OLEIFERA* SEED HUSKS BY SINGLE-STEP STEAM PYROLYSIS

A. MICHAEL WARHURST[1], GORDON L. McCONNACHIE[1] and SIMON J. T. POLLARD[2]*

[1]Department of Civil and Environmental Engineering, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, U.K. and [2]Scottish Environment Protection Agency, Environmental Strategy Directorate, Erskine Court, The Castle Business Park, Stirling FK9 4TR, U.K.

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Abstract—The seed husks of the multipurpose tree *Moringa oleifera* are potentially a waste product that may be available in large quantities, and previous work has demonstrated that a microporous activated carbon can be produced from them by carbonisation under nitrogen followed by activation in steam. This research examines the efficacy of a simpler and cheaper activation process, single-step steam pyrolysis activation, with a view to promoting the production of low-cost activated carbon in the developing world.

Husks were heated in a steam atmosphere to 750°C for 30 or 120 min, or 800°C for 30 min, then the resulting carbons were tested to determine their iodine numbers and adsorption isotherms for phenol, 4-nitrophenol and methylene blue. Phenol and 4-nitrophenol were adsorbed rapidly by all three carbons, with 80–90% w/w adsorbed in the first 30 min, whereas methylene blue adsorption was slower. Pyrolysis at 800°C for 30 min produced a carbon (yield 12.2% w/w) with an iodine number of 703 mg g^{-1}, a phenol specific surface area (SSA) of 629 m^2 g^{-1}, a 4-nitrophenol SSA of 664 m^2 g^{-1} and a methylene blue SSA of 211 m^2 g^{-1}. The carbon produced at 750°C for 120 min (yield 11.9% w/w) had similar properties, but the one produced at 750°C for 30 min (yield 16.6% w/w) had a less developed porosity. The adsorbance characteristics of the two best carbons were superior to those produced previously by the conventional two-stage carbonisation–activation, and were competitive with commercial carbons. These results demonstrate that steam pyrolysis activation of *M. oleifera* husks could provide a low-cost, local source of high quality activated carbon in the developing world. © 1997 Elsevier Science Ltd. All rights reserved

Key words—activated carbon, appropriate technology, *Moringa oleifera*, steam pyrolysis, water treatment

NOMENCLATURE

- b = Langmuir adsorption coefficient
- BET = Brunauer, Emmett and Teller method for surface area calculation
- C_e = equilibrium concentration of solute (mol l^{-1})
- q_e = amount of solute adsorbed on the adsorbent (mol g^{-1})
- Q^0 = Langmuir monolayer coverage constant (mol g^{-1})
- K_f = Freundlich constant (mol g^{-1})
- n = Freundlich constant
- SSA = specific surface area (m^2 g^{-1})
- x_m = Giles and Nakhwa adsorption monolayer capacity from experimental isotherm (mol g^{-1})

INTRODUCTION

In recent years there has been a focus on the use of appropriate, low-cost technology for the treatment of drinking water in the developing world (Gupta and Chaudhuri, 1992; Pollard *et al.*, 1992; Cairncross and Feachem, 1993). One major cost associated with water treatment in these countries is the importation of water treatment chemicals and other materials. Exchange rates are frequently unfavourable, and foreign currency is scarce, making the importation of chemicals and materials a significant burden on the water treatment budget. Extreme variability in exchange rates often affects a water authority's budgeting capability, and can cause unpredictable losses and price increases.

One solution to these problems is the indigenous production of treatment materials, either by local production of chemicals, or the use of alternative, locally available, treatment materials. One example of the latter is use of a coagulant which is contained in the seeds of the tree *Moringa oleifera* (common names include Drumstick and Horseradish tree), a multi-purpose, drought-tolerant tree which grows in many areas, including Northern India, Africa and the Caribbean (Morton, 1991). The seeds of this tree contain a coagulant protein (Gassenschmidt *et al.*, 1995; Ndabigengesere *et al.*, 1995) which can replace conventional coagulants such as aluminium salts, in both domestic (Jahn, 1988) and larger scale water

*Author to whom all correspondence should be addressed [Fax: (01786) 446 885; Tel: (01786) 457 700].

treatment (McConnachie *et al.*, 1994). In addition, the seed contains a high quality oil, which has many uses (Morton, 1991).

A potential waste product from the production of the coagulant and oil is the seed husk. We have previously shown that this husk can be converted into a high quality, microporous activated carbon (Pollard *et al.*, 1995), that could potentially be used to replace imported carbons in applications such as removal of taste and odour compounds from water supplies. Our initial work on the production of carbon from *M. oleifera* husk used a two stage carbonisation–activation process, involving heating the husk to 485°C for 30 min under nitrogen, followed by exposure to a steam/nitrogen mixture at 850°C for 5 min (Pollard *et al.*, 1995). This process required nitrogen, which might have to be imported into a developing country, and two heating stages, involving significant energy input. Reappraisal of the literature, however, showed that other workers (Gergova *et al.*, 1994) had successfully used a single-step steam pyrolysis activation to make carbons from a variety of materials.

Preliminary tests on carbons produced from husks at a variety of temperatures demonstrated that steam pyrolysis activation produced high quality carbon (Warhurst *et al.*, 1996). More detailed examination of carbons using nitrogen adsorption allowed selection of optimum carbons based on a balance between surface area development, microporosity and product yield (Warhurst *et al.*, 1996, 1997). Three carbons were chosen for further characterisation: S750/30, which had been heated to 750°C then held at that temperature for 30 min; S750/120, also heated to 750°C, but held for 120 min; and S800/30, which was heated to 800°C and held for 30 min. The yields and BET N_2 surface areas were as follows: S750/30, 16.6% w/w, 588 $m^2 g^{-1}$; S750/120, 11.9% w/w, 730 $m^2 g^{-1}$; S800/30, 12.2% w/w, 710 $m^2 g^{-1}$ (Warhurst *et al.*, 1997). The carbon produced using the conventional two-stage process had a similar surface area of 734 $m^2 g^{-1}$, and a yield of 9.6% w/w, though this carbon was acid-rinsed to remove water-soluble ash (Pollard *et al.*, 1995). For comparison, a commercial peat-based activated carbon, Norit SA4, was found to have a surface area of 705 $m^2 g^{-1}$ (Pollard *et al.*, 1995).

The aim of this work was to characterise three steam-pyrolysed carbons using molecular probes in the solution phase, so as to facilitate comparison with commercial activated carbons used in developing countries, and provide a sound basis for carbon production in the developing world.

EXPERIMENTAL DETAILS

Materials

M. oleifera husks were obtained from Malawi, where they had been produced as a waste product from the production of *M. oleifera* seed for use in pilot and full-scale testing of its coagulant properties. Because of the nature of the seed/husk separation process, this husk material also contained powdered seed, which was not of an even particle size, varying between a powder and particles several millimetres in diameter.

Carbonisation–activation of husks

Carbonisation of *M. oleifera* husks was performed in a Carbolite 12/65 tube furnace containing a purpose-made quartz tube (Multi-Lab, Newcastle, U.K.), connected to Quickfit connections at one end and a ball and cup joint at the other, allowing flow-through of a controlled gaseous atmosphere. Charges of 30 g of *M. oleifera* husks were placed in a customised quartz combustion boat, loaded into the quartz tube and positioned in the centre of the furnace. The temperature of the sample was monitored by a thermocouple probe (type K probe, connected to a P.I. 8013 thermometer) positioned just above the sample. Steam, generated by a flask of water on a heating mantle, entered the quartz tube at a rate of approximately 2 ml (liquid water) min^{-1}. A condenser was connected to the ball and cup joint at the other end of the tube, and the condensate was collected in a beaker.

The sample was heated at a fixed rate of approximately 20°C min^{-1} to the appropriate temperature, and held at this temperature (±10°C) for the time specified. After the furnace had cooled to between 200 and 300°C, the carbonised husks were removed, allowed to cool in air for a few minutes and then weighed to determine the yield. The carbon was then moved to a desiccator for storage. Carbons, at least duplicated for each set of temperature and time, were later mixed, homogenised and sieved to $<250\ \mu m$, dried in an oven at 110°C overnight, then stored in a desiccator over silica gel.

Adsorption kinetics

The adsorption kinetics of the model adsorbates phenol, 4-nitrophenol and methylene blue (BDH, U.K.) on selected carbons were determined in advance of isotherm measurements. The adsorption times used were 48, 31, 24, 8, 4, 2, 1, and 0.5 h each for phenol and 4-nitrophenol, and 100, 72, 48, 31, 24, 8, 4, 2, 1 and 0.5 h for methylene blue. Carbon samples of 0.5 g were added to 100 ml of 10 mM adsorbate solution in 250 cm^3 Erlenmeyer flasks, which were sealed with Suba-seals, then shaken at 90 strokes min^{-1} in a temperature controlled shaker bath at 25°C. After the required time, the samples were filtered and analysed as described below for the adsorption isotherms.

Adsorption isotherms

Seven-point, single-adsorbate adsorption isotherms were constructed for phenol, 4-nitrophenol and methylene blue, at 50, 35, 20, 15, 10, 7 and 3 mM of phenol and 4-nitrophenol, and 30, 20, 15, 10, 7, 3 and 1 mM of methylene blue. These "molecular probes" represent adsorbates of distinct molecular cross-section, so providing information on the characteristic porosities of *M. oleifera* carbons. Carbon samples of 0.5 g were added to 100 ml of adsorbate solution in 250 cm^3 Erlenmeyer flasks, sealed with Suba-seals, then shaken at 90 strokes min^{-1} in a temperature controlled shaker bath for 24 h at 25°C. Following uptake, suspensions were vacuum-filtered through Whatman No. 542 filter paper, diluted as necessary, then acidified with 1 drop of 1 M HCl per 10 ml sample. Residual adsorbate concentrations were determined using a u.v. spectrophotometer (Shimadzu UV-160A), at 270 nm for phenol, 329 nm for 4-nitrophenol and 665 nm for methylene blue.

The isotherms were then analysed using the Langmuir and Freundlich models. The Langmuir model assumes that a monolayer of the adsorbate adsorbs to the carbon surface,

leading to the equation:

$$q_e = \frac{Q^0 b C_e}{1 + bC_e} \quad (1)$$

where q_e is the amount of solute adsorbed on the adsorbent (in mol g^{-1}), C_e is the equilibrium concentration of solute (in mol l^{-1}), Q^0 is the Langmuir monolayer coverage constant in (mol g^{-1}) and b is the Langmuir adsorption coefficient. The constants are derived from a plot of $1/C_e$ against $1/q_e$.

The Freundlich model is purely empirical, and is expressed as:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where the Freundlich constants K_f and n are derived from a plot of log C_e against log q_e.

Adsorbate-specific apparent surface areas were derived by conversion of Q^0, using the reported cross-sectional areas of the model adsorbates. The molecular cross-sectional areas used for the three adsorbates were: 5.22×10^{-19} m² for phenol (Pollard *et al.*, 1995), 5.25×10^{-19} m² for 4-nitrophenol (Pollard *et al.*, 1991) and 3.9×10^{-19} m² for methylene blue, assuming end-on adsorption (Barton, 1987).

A further estimate of the adsorbate-specific surface area was obtained by the method of Giles and Nakhwa (1962), in which the "knee point" on the adsorption isotherm is extrapolated to the q_e axis and taken as the point of monolayer coverage. This extrapolated point, x_m, can then be converted to an apparent surface area as done with Q^0.

Iodine number determination

Iodine numbers were determined using a method based on ASTM D4607-86 (ASTM, 1991b). A three-point isotherm was used, with an equilibration time of 30 s, and the residual iodine concentration was determined by titration with sodium thiosulphate (BDH, U.K.) with starch as an indicator. The iodine number was operationally defined as the quantity of iodine (BDH, U.K.) adsorbed (in mg g^{-1} carbon) at a residual iodine concentration of 0.02 N.

RESULTS

Adsorption kinetics

Adsorption kinetics were determined for phenol on carbons S750/120 and S750/30, for 4-nitrophenol on carbon S800/30 and for methylene blue on carbon S800/30. The results are shown in Fig. 1. Adsorption of phenol and 4-nitrophenol on the carbons was rapid, with 90% w/w of the 4-nitrophenol adsorbed by S800/30 after 48 h being already adsorbed after 0.5 h, and 80% w/w of the phenol adsorbed by

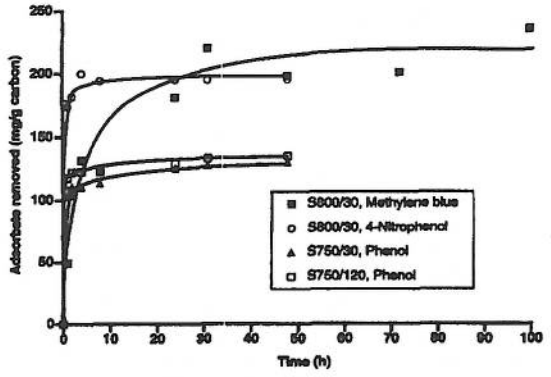


Fig. 1. Adsorption kinetics.

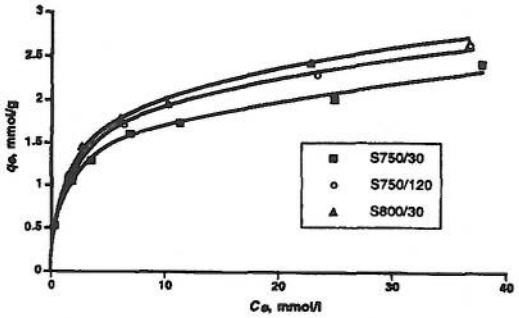


Fig. 2. Phenol adsorption isotherms.

S750/120 after 48 h adsorbed in the first 0.5 h. A comparison of the phenol adsorption kinetics of carbons S750/30 and S750/120 demonstrated that the S750/120 carbon adsorbed more phenol, and adsorbed it slightly faster, with 88% w/w of the final amount adsorbed in 1 h, as against 80% w/w on the S750/30 carbon.

The methylene blue uptake was substantially slower, with only about 30% w/w of the final total adsorbed in the first 0.5 h, and about 80% w/w adsorbed after 24 h. The variability of the methylene blue results in this experiment (and in its adsorption isotherm) makes it more difficult to identify the precise time at which its adsorption reaches a plateau. It was decided that a 24 h equilibration time would be used for the isotherm experiments, which would approximate equilibrium conditions for the phenol and 4-nitrophenol adsorbates, though the methylene blue would not be fully equilibrated.

Adsorption isotherms

Phenol, 4-nitrophenol and methylene blue adsorption isotherms for the three carbons are shown in Figs 2, 3 and 4, respectively. For all the adsorbates, the S800/30 carbon showed the highest adsorptive capacity, with S750/120 slightly lower and S750/30 the lowest. The difference between the carbons was particularly marked in the adsorbance of methylene blue, where the S750/30 carbon adsorbed substantially less than the others.

The isotherms were analysed using the Langmuir and Freundlich models, the results of which are shown in Table 1, along with the regression

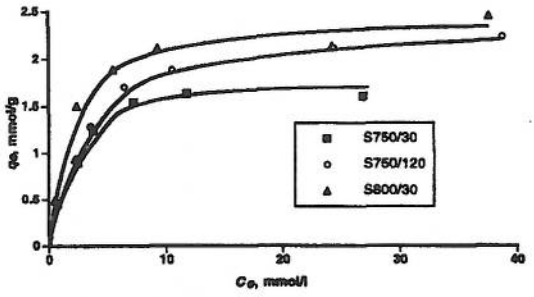


Fig. 3. 4-Nitrophenol adsorption isotherms.

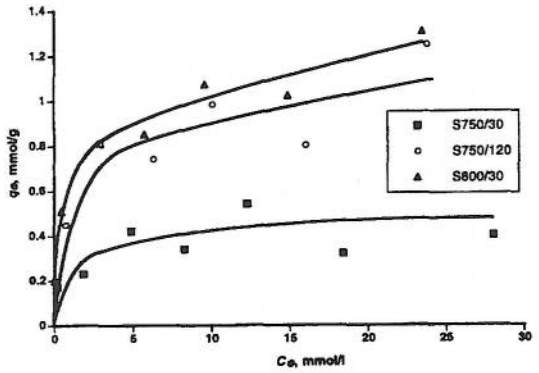


Fig. 4. Methylene blue adsorption isotherms.

coefficient r^2. For phenol and methylene blue adsorbates, the Freundlich model gave a slightly better fit than the Langmuir model, but with 4-nitrophenol the opposite was the case. The S750/30 carbon showed poor uptake of methylene blue, and its behaviour did not fit either the Langmuir or the Freundlich models well.

The substrate-specific surface apparent areas calculated from the Langmuir analysis and the Giles and Nakhwa method are shown in Table 2, compared with the specific surface areas previously calculated from N_2 adsorption isotherm analysis (Warhurst *et al.*, 1997). The Giles and Nakhwa method becomes less reliable as the intercept tends away from the horizontal, indicating that mesoporosity is involved in the adsorption. This affects the accuracy of the surface area calculations from the methylene blue and the phenol adsorption isotherms. For comparison, Giles and Nakhwa surface areas obtained from the phenol adsorption isotherms on two commercial carbons, Ceca Acticarbone TE and Eurocarb YAO, were 421 $m^2\ g^{-1}$ and 874 $m^2\ g^{-1}$, respectively (Pollard *et al.*, 1995).

Iodine numbers

The iodine numbers were found to be 703 mg g^{-1} for carbon S800/30, 718 mg g^{-1} for S750/120 and 552 mg g^{-1} for S750/30.

DISCUSSION

Properties of the carbon

The results published here and elsewhere (Warhurst *et al.*, 1997) demonstrate that a high quality activated carbon can be produced from the seed husks of *M. oleifera* by single-step steam pyrolysis. Carbons produced at 750 or 800°C have been shown to have a high surface area, and adsorb model adsorbates rapidly from solution.

These results show that alterations in the temperature and dwell time influence the extent and nature of pore development. Carbons S750/120 and S800/30 appear to have very similar pore structures, with similar 4-nitrophenol and methylene blue adsorption isotherms, and virtually identical phenol isotherms and iodine numbers (Figs 2–4, Table 1). Carbon S750/30 has a less developed pore structure, demonstrating that a 50°C difference in temperature, or a dwell time 90 min longer, have a significant bearing on the development of porosity within the microstructure of the product.

Additional information on the pore size distribution of the three carbons can be obtained by comparing the adsorption characteristics of the different adsorbates. The pores of activated carbons are by convention sub-divided into three groups: micropores of less than 2 nm in "pore width", mesopores of 2–50 nm and macropores of more than 50 nm (see, for example, Rouquerol *et al.*, 1994). Both N_2 and I_2 are small molecules, and so can penetrate into the smallest micropores. The results suggest that carbon S750/120 has slightly more micropore volume than S800/30, since both its iodine number, at 718 mg g^{-1}, and its BET surface area, 730 $m^2\ g^{-1}$, are slightly higher than those of S800/30, namely 703 mg g^{-1} and 710 $m^2\ g^{-1}$, respectively. Carbon S750/30 had both an iodine number and a BET surface area of under 600. The iodine number recommended as a minimum by the American Water Works Association for a carbon to be used in removal of low molecular weight compounds is 500 mg g^{-1} (Troxler *et al.*, 1988); all the carbons tested exceed this value, with carbons S750/120 and S800/30 having an iodine number 40% w/w higher.

Table 1. Summary of Freundlich and Langmuir adsorption isotherm results

		Langmuir			Freundlich		
Adsorbate	Carbon	Q_0 (mmol g^{-1})	b (l $mmol^{-1}$)	r^2	K_f (l g^{-1})	n	r^2
Phenol	S750/30	2.21	0.48	0.95	0.83	3.26	0.98
	S750/120	2.47	0.47	0.97	0.88	3.06	0.97
	S800/30	2.50	0.53	0.97	0.97	3.21	0.99
	N485/30, S850/5*	1.89	1.98	0.85	1.12	3.80	0.84
4-Nitrophenol	S750/30	1.96	0.38	0.99	0.61	2.67	0.84
	S750/120	2.38	0.32	1.00	0.66	2.56	0.90
	S800/30	2.37	0.49	0.96	0.81	2.82	0.83
Methylene blue	S750/30	0.44	0.66	0.60	0.24	5.62	0.68
	S750/120	0.99	1.16	0.87	0.59	5.85	0.93
	S800/30	1.06	2.15	0.91	0.66	5.46	0.99

*Carbonised under nitrogen at 485°C for 30 min, then activated at 850°C for 5 min in a nitrogen/steam atmosphere. Carbon acid-rinsed to remove ash (Pollard *et al.*, 1995).

Table 2. Summary of apparent "specific surface areas" (SSA) of carbons, derived using Giles and Nakhwa, Langmuir and BET methods

		Giles and Nakhwa		Langmuir
Adsorbate	Carbon	x_m (mmol g^{-1})	SSA (m^2 g^{-1})	SSA (m^2 g^{-1})
Phenol	S750/30	1.7	534	694
	S750/120	1.9	597	776
	S800/30	2.0	629	786
	N485/30, S850/5*	1.5	465	594
4-Nitrophenol	S750/30	1.6	506	620
	S750/120	1.9	601	751
	S800/30	2.1	664	749
Methylene blue	S750/30	0.4	94	139
	S750/120	0.8	188	312
	S800/30	0.9	211	334
		BET SSA (m^2 g^{-1})		
N_2 (Warhurst *et al.*, 1997)				
	S750/30	588		
	S750/120	730		
	S800/30	710		
	N485/30, S850/5*	734		

*Carbonised under nitrogen at 485°C for 30 min, then activated at 850°C for 5 min in a nitrogen/steam atmosphere. Carbon acid-rinsed to remove ash (Pollard *et al.*, 1995).

The model adsorbates phenol, 4-nitrophenol, and particularly methylene blue, are larger and so cannot penetrate the smallest micropores. For these adsorbates, slightly more is adsorbed on S800/30 than S750/120, suggesting that more of these larger micropores are present in S800/30. The methylene blue molecule has a minimum molecular cross-section of about 0.8 nm, and it has been estimated that the minimum pore diameter it can enter is 1.3 nm (Barton, 1987); so it can only enter the largest micropores, and much of its adsorbance is likely to be in mesopores. Methylene blue adsorption by S750/30 is particularly poor, probably due to an absence of the larger micropores. The 4-nitrophenol adsorbance has a very good fit with the Langmuir model, which assumes monolayer adsorbance, so suggesting that active site binding may also play a role in its uptake.

The apparent surface areas calculated using the Langmuir method are higher than those calculated by the Giles and Nakhwa method, but for phenol and 4-nitrophenol the Langmuir results are similar to those from the BET analysis (Table 2). The methylene blue surface area is substantially lower, since it is not able to penetrate most of the micropore volume.

When compared with the carbon produced by conventional carbonisation–activation (Pollard *et al.*, 1995), carbons S750/120 and S800/30 have similar BET surface areas, and higher phenol-specific surface areas (Table 2). This carbon was rinsed before testing, and so would be expected to have a higher adsorbance per unit mass than the carbons produced here, since up to 20% w/w of the mass of these carbons is ash that can be removed by rinsing in dilute acid (Warhurst *et al.*, 1997). If the carbons tested here were rinsed their adsorbance capacities per unit mass would probably rise by at least 20%, thus making them substantially more porous than the carbon produced by the conventional method.

The carbons produced here compare well with those produced by Gergova *et al.* (1994) from a variety of plant materials using steam pyrolysis activation for 2 h at 700°C. The *M. oleifera* carbon showed superior adsorbance to those produced from almond stones, cherry stones and grape seeds, though that produced from apricot stones was slightly superior, with a BET surface area of 820 m^2 g^{-1}, an iodine number of 895 mg g^{-1} (at a concentration of 0.5 mmol l^{-1}), and a methylene blue adsorbance of 0.89 mmol g^{-1}.

In the world as a whole, most activated carbon is used in a powdered form, though granular carbon is more popular in the U.S.A. and Europe, because of its improved handling and regeneration characteristics. Powdered carbon is usually defined as having a particle size distribution where at least 90% w/w of the particles are smaller than 50 μm (Haist-Gulde *et al.*, 1995). Powdered carbon can easily be added to treatment processes, and the dose can be varied with the extent of contamination. However, the powdered carbon is lost after use and cannot be regenerated. Granular carbon is usually used in columns or beds and can be regenerated, so reducing the quantity needed. Granular carbon is defined as that having a particle size of more than 180 μm (ASTM, 1991a), though many carbons have particle sizes of several millimetres. In this work the *M. oleifera* carbon has been ground and sieved to <250 μM, intermediate between powdered and granular. The maximum particle size of *M. oleifera* husk carbon is likely to be quite low, as the husk material is generally well divided and the carbon is not particularly strong. Therefore, any granular carbon produced from *M. oleifera* will probably have a particle size of several hundred micrometres, and so may be unsuitable for

some applications. Work is in progress to investigate the production and use of granular carbons from *M. oleifera*.

The carbon used in these experiments was not rinsed to remove ash material. Water-soluble ash typically makes up about 20% w/w of the mass of S800/30 (Warhurst *et al.*, 1997) and this plant ash will consist mainly of salts such as CaO, K_2O, Na_2O, MgO, SiO_2, Fe_2O_3 and P_2O_5 (Deglise and Magne, 1987) and so should have little impact on most uses. However, if the maximum adsorptive capacity per unit mass is needed, rinsing the carbon would be necessary; but rinsing and drying will require more equipment and some energy expenditure. In many circumstances unrinsed carbon will be the most economic option.

A pilot carbon production furnace is now under construction in Malawi, in association with The Polytechnic, The University of Malawi, Blantyre, Malawi, which should provide carbons for test applications with raw water supplies within Malawi and in the surrounding region, to demonstrate the feasibility of this low-cost production method. The supply of seeds will probably be seasonal, so it is likely that production of carbon will also be seasonal, unless the seeds are stored. However, there should be no problem storing the carbon so that it is available continuously. It is possible that once the production of activated carbon from *M. oleifera* is established, other local agricultural waste products may also emerge as good precursors for activated carbon, providing a more continuous feedstock for a full-scale steam pyrolysis plant.

Potential applications

There is a wide range of possible uses of the activated carbon from *M. oleifera*, particularly in the field of drinking water treatment. A major aesthetic problem with some drinking water is the presence of taste and odour contaminants (Wnorowski and Scott, 1992). These problems are caused by a wide range of chemical species, such as methylisoborneol and geosmin, some of which can be produced by algae. Powdered and granular activated carbons have been found to be very effective at removing these compounds, improving the acceptability of drinking water (see, for example, Lalezary-Craig *et al.*, 1988). In areas with particular taste and odour problems there might also be demand for activated carbon for rural domestic water treatment. Many communities have traditionally used plant ashes to treat foul-tasting water (Jahn, 1982). The carbons described here are likely to be competitive with commercial carbons for taste and odour removal, though their efficacy should be tested for each particular application. As with all uses of activated carbon, many factors affect carbon performance, particularly the presence of dissolved organic material.

Algal blooms can also produce toxins; both liver toxins, which are usually microcystins, and neurotoxins, such as anatoxin (Elder *et al.*, 1993). These toxins are found in water supplies throughout the world, including southern Africa (Scott, 1991). The microcystins are the main health concern from drinking water, since it has been suggested that chronic exposure to low levels may be associated with liver cancer (Lambert *et al.*, 1994). Activated carbon has been found to be an effective way of removing microcystins, though high mesoporosity is necessary (Donati *et al.*, 1994) since microcystins are large molecules, made up of a seven amino acid cyclic peptide (Lambert *et al.*, 1994). Carbons S750/120 and S800/30 do have some mesopore and macropore volume, 0.1 and 0.08 ml g^{-1}, respectively, though that of S800/60 carbon is higher, at 0.15 ml g^{-1}, but with a yield of only 8.8% w/w (Warhurst *et al.*, 1997). As noted above, the extent of methylene blue adsorption is related to the mesopore volume of a carbon; this creates the possibility that methylene blue adsorption might have some use in predicting microcystin adsorption, and so provide a simple method of screening carbons in situations where N_2 adsorption isotherms are unobtainable due to cost or lack of facilities. Further work is now underway to establish the effectiveness of *M. oleifera* carbons at removing microcystins from raw water.

Activated carbon can bind metal ions, and so it is used in both the extraction of gold and in the treatment of metal-contaminated industrial wastewaters (Reupke and Duff, 1992; Budinova *et al.*, 1994). It is effective in the removal of many organic chemicals, including textile dyes, which are a major pollution problem in both India and parts of Africa (Meyer *et al.*, 1992; Namasivayam and Kadirvelu, 1994). Carbon is also widely used in the food industry to decolourise sugar, and to remove off-tastes from a variety of products including vegetable oil (Reupke and Duff, 1992).

Benefits to communities

The cultivation of *M. oleifera* and the use of its products would have both economic and health benefits for rural communities. Communities could gain income from the sale of the seeds to companies or institutions processing them to produce oil, coagulant or carbon. In addition, rural household water treatment using the seed could be developed along the lines already pioneered in Sudan (Jahn, 1988). The leaves and young seed pods of *M. oleifera* are nutritious, being particularly rich in calcium, iron and vitamin C, and the oil pressed from the seeds has a composition similar to that of olive oil (Morton, 1991). There are also reported traditional medicinal uses of the tree, some of which are now being proven effective by modern medical science. For example, leaf extracts have abortifacient activity (Nath *et al.*, 1992) and contain hypotensive agents (Faizi *et al.*, 1994).

Local production of activated carbon by one-step steam pyrolysis has several environmental benefits:

1) no chemical inputs are required;
2) the single-step process requires much less energy than traditional processes involving two heating steps, frequently needing a higher temperature;
3) local production reduces the transportation required for the product;
4) local availability of low-cost carbon may encourage polluting industries to install waste treatment facilities; and
5) all the *M. oleifera* products—carbon, coagulant and oil—are renewable resources.

The only waste from this production process is the condensed liquor from the steam pyrolysis, which contains water, tarry material and other plant-derived chemicals. Analysis of steam pyrolysis volatiles derived from apricot stones and coconut husks has found that typical components included derivatives of phenol, guaicol, veratrol, syringol, resorcinol, free fatty acids and the esters of fatty acids (Razvigorova *et al.*, 1994). Currently there is no market for such material, but its plant origins suggest that it is likely to be easily biodegradable, and so disposal is unlikely to be a problem.

Barriers to use

Notwithstanding the substantial attractions of *M. oleifera* use, there are likely to be a number of practical and sociological barriers to the use of the carbons described in this research. The first is matching the scale of production to demand. Market demand will be contingent on the carbon product being produced continuously in reasonable quantities, but production will also be linked to the production of coagulant and oil from the *M. oleifera*. The success of these applications will probably determine the amount of *M. oleifera* planted, as they are likely to have a higher economic value than the carbon. Work is currently underway at the University of Leicester, as part of this research project, to formulate business plans for the development of *M. oleifera* production. One possible constraint that has been identified is that pressing the seeds for oil is more effective if some fibrous material is present, such as the husk. This, combined with the cost of dehusking, adds to the difficulty of evaluating production potential. However, the seed pod, currently a *bona fide* waste product, could possibly replace the husk in the oil pressing. In addition, work is underway to investigate the possibility of producing activated carbon from the pod.

The final barrier to use is the influence of conservatism and the desire to replicate the methods of richer countries. This barrier is a particular problem for the coagulant use of *M. oleifera*, where the technique must compete with conventional and heavily marketed chemical methods. The carbon has the advantage that, because of its high quality, it can be a direct replacement to commercial activated carbon, and can compete on technical grounds with commercial products by reference to the adsorption figures given here.

CONCLUSIONS

This research has shown that a simple production process can produce high quality activated carbon from the waste husks of *M. oleifera*. The activated carbon has many possible applications, as it is highly microporous with some mesoporosity and shows rapid uptake of pollutants.

Local production of this carbon could improve drinking water quality and palatability, whilst reducing importation and expenditure of foreign exchange, and contributing to improved local incomes. If the carbons were to be used in industrial wastewater treatment, river and lake quality could improve.

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Disclaimer—The opinions expressed in this work are those of the authors alone.

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Short communication

Adsorption of the cyanobacterial hepatotoxin microcystin-LR by a low-cost activated carbon from the seed husks of the pan-tropical tree, *Moringa oleifera*

A.M. Warhurst[a], S.L. Raggett[b], G.L. McConnachie[a], S.J.T. Pollard[c,*], V. Chipofya[d], G.A. Codd[b]

[a] *Department of Civil and Environmental Engineering, University of Edinburgh, The King's Buildings, West Mains Road, Edinburgh EH9 3JN, UK*
[b] *Department of Biological Sciences, University of Dundee, Dundee, DD1 4HN, UK*
[c] *Scottish Environment Protection Agency, Environmental Strategy Directorate, Erskine Court, The Castle Business Park, Stirling, FK9 4TR, UK*
[d] *Department of Civil Engineering, The Polytechnic, University of Malawi, Blantyre, Malawi*

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Abstract

A low-cost activated carbon from the pan-tropical multipurpose tree *Moringa oleifera* removes the cyanobacterial hepatotoxin microcystin-LR in quantitative amounts from water in batch adsorption trials. The potential of *M. oleifera* seed husk carbon for cyanobacterial toxin removal in drinking water treatment in tropical countries is discussed. © 1997 Elsevier Science B.V.

Keywords: Activated carbon; Algal toxins; Low-cost adsorbents; *Moringa oleifera*; Microcystin-LR

* Corresponding author.

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1. Introduction

Cyanobacteria (blue-green algae) present an increasing problem worldwide due to the production of excessive growths (blooms) as a consequence of increasing eutrophication in waterbodies used for drinking supplies. Besides filter blockage in water treatment and off-flavour and odour production, all of the cyanobacterial genera which commonly form blooms include toxin-producing species and strains (Codd et al., 1989; Carmichael, 1992; Codd, 1995). Cyanobacterial toxins present acute and chronic hazards to human health and include potent hepatotoxins (microcystins, nodularins) and neurotoxins. Waterborne microcystins have been implicated in cases of human liver damage and pulmonary consolidation (atypical pneumonia) via oral ingestion (Falconer, 1996) and, recently, in multiple human deaths in Brazil after haemodialysis using water containing microcystins (Barreto et al., 1996). Other human health effects associated with cyanobacterial toxins include gastrointestinal upsets and skin reactions (Bell and Codd, 1994; Ressom et al., 1994).

Increasing evidence of the adverse effects and widespread occurrence of cyanobacterial toxins is leading to the identification of environmental water quality criteria and guideline values (GV) for the toxins in drinking and recreational waters (Carmichael and Falconer, 1993; Bell and Codd, 1994). A GV of 1 μg/l for microcystins in drinking water can be derived from oral dosing studies with mice and pigs (e.g. Carmichael and Falconer, 1993). This GV is currently under consideration by the World Health Organization (WHO). Certain drinking water supplies in developed and developing countries require treatment to reduce microcystins levels below the GV. Water treatment works using conventional flocculation, coagulation and sand filtration unit processes are regarded as ineffective at removing cyanobacterial toxins, whilst activated carbon adsorption, with ozonation in some cases, is more effective (Falconer et al., 1989; Himberg et al., 1989; Lambert et al., 1996). Activated carbons with different physicochemical characteristics show distinct degrees of adsorption of microcystin-LR, with higher levels of mesoporosity (pore widths 2–50 nm) generally offering higher adsorption capacities for the cyclic heptapeptide toxin molecules (Donati et al., 1994).

A major disincentive against using activated carbon in water treatment, however, is its high cost, particularly to developing countries, where it is usually imported. There is considerable potential for activated carbons to be produced from agricultural and industrial wastes within these countries (Pollard et al., 1992, 1995). One carbon precursor, previously identified by related work, is the pan-tropical tree *Moringa oleifera* (the Drumstick or Horseradish tree), which grows rapidly in India, the Sudan and southern Africa and can be used as a food crop, a source of vegetable oil and as a coagulant and activated carbon in water treatment (Morton, 1991; McConnachie et al., 1994, 1996; Pollard et al., 1995). We have shown that a high quality, activated carbon can be prepared from *M. oleifera* seed husks by a simple one-step steam pyrolysis activation, a production method under current evaluation in Malawi, southern Africa (Warhurst et al., 1996). Solution phase isotherms using methylene blue as a 'molecular probe' previously indicated that sufficient mesoporosity was present within the material to trial *Moringa* carbon for microcystin uptake (Warhurst et al., 1997a). Here we report the removal of microcystin-LR from water by *M. oleifera* activated carbon in single batch adsorption trials.

2. Materials and methods

2.1. Materials

Microcystin-LR was purified to > 98% w/w purity from freeze-dried cells of the cyanobacterium *Microcystis* PCC 7813 as previously detailed (Lawton et al., 1994). The toxin was stored in dried form at − 20°C and dissolved in high-performance liquid chromatography (HPLC)-grade methanol for subsequent dilution in de-ionised water. Activated carbon was produced by single-step pyrolysis of *Moringa oleifera* husks, heated to 800°C for 30 min in a steam atmosphere, then ground to a diameter < 250 μm and stored under desiccation

(Warhurst et al., 1996). The detailed physicochemical characteristics of this material are described in full elsewhere (Warhurst et al., 1997b). The representative pore structure is illustrated in the scanning electron micrograph presented in Fig. 1.

2.2. Single point batch adsorption experiments and microcystin analysis

Pyrex borosilicate glass beakers (1 l) containing 1 l of de-ionised water, were dosed with 20 μg microcystin and a known amount of *M. oleifera* carbon (0, 10 or 50 mg). The contents were stirred at 100 rpm for 24 h using a Stuart Scientific Flocculator SW1. The resultant suspensions were then filtered through Whatman No. 542 filter paper. Microcystin-LR in the filtrate was recovered for analysis by passage of the filtrate through Isolute C_{18}-trifunctional, end-capped solid phase cartridges (1 g in a 3-ml syringe body; International Sorbent Technology, Hengoed, Wales) (Lawton et al., 1994). Subsequent recovery and quantification of microcystin-LR was by HPLC with diode array detection (DAD) (Lawton et al., 1994).

3. Results and discussion

Preliminary trials indicated that the activated carbon did not release components which interfered with the HPLC-DAD analysis of microcystins (data not shown). Water was spiked with microcystin-LR to give a starting concentration of 20 μg/l since concentrations of approximately this level have been detected in untreated potable waters (Edwards et al., 1994) and such concentrations would additionally require action for microcystin removal/destruction for health protection. In the absence of activated carbon, > 90% w/w of the microcystin-LR was recovered from the water sample using the C_{18} Isolute cartridges (Table 1). A dose of 10 mg *M. oleifera* carbon/l reduced the initial microcystin-LR concentration of 20 μg/l by 93 to 98% w/w and 50 mg carbon/l removed the toxin to levels below the practical detection limit of the HPLC-DAD procedure (< 0.08 μg/l) indicating quantitative adsorption of microcystin-LR from the aqueous phase.

These results show that *M. oleifera* seed husk activated carbon is potentially capable of reducing microcystin-LR concentrations to below the

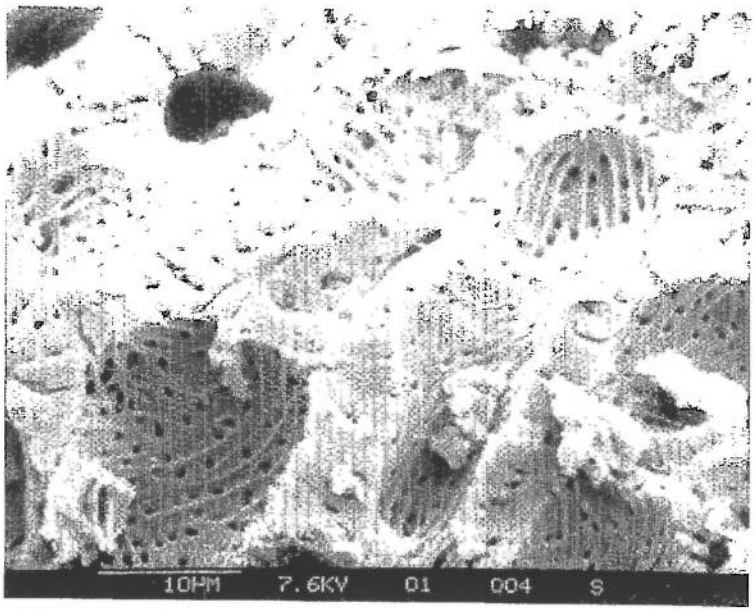


Fig. 1. Representative S.E.M. micrograph of *Moringa* carbon pore structure (1000 ×).

Table 1
Removal of microcystin-LR by *Moringa oleifera* activated carbon in batch adsorption trials

Carbon dose (mg/l)	Final microcystin-LR % concentration (μg/l)	Removal of microcystin-LR by carbon (w/w)
0 (control)	19.02	—
0 (control)	18.06	—
10	1.24	93.8
10	0.46	97.7
50	< 0.08	> 99.6
50	< 0.08	> 99.6

All trials performed at initial microcystin-LR concentration of 20 μg/l. Microcystin-LR analysed by HPLC-DAD; individual toxin concentrations are the means of duplicate determinations.

proposed GV for drinking water. The presence of other substances, particularly other dissolved organic carbon species, would be expected to reduce the efficiency of the *Moringa* carbon for cyanobacterial toxin removal, due to competition for binding sites. For this reason, further investigations into the applicability of this material for cyanobacterial toxin removal in *M. oleifera* producer countries should involve evaluating the efficacy of the carbon with the authentic waters to be treated with attention being focused on the effect of competing/interfering adsorbates and the effect of suspended solids on microcystin uptake. Activated carbon can be used in water treatment in two forms: granular (GAC) in columns or beds; and powdered (PAC), which is added by mixing, then removed by coagulation, sedimentation or filtering. Both methods have been found to be effective at removing microcystins using certain commercially-available carbons (Falconer et al., 1989; Himberg et al., 1989; Lambert et al., 1996). Previous work on *Moringa* carbon has shown that it can be produced either in a powdered form, as used here, or as small granules (e.g. 400–600 mm diameter) although the latter are sensitive to attrition (Warhurst et al., 1996, 1997a). A complementary advantage of treating water supplies with activated carbon is its potential ability to remove cyanobacterial and algal taste and odour compounds (Suffet et al., 1996). *M. oleifera* carbon also merits evaluation for this purpose.

Many lakes and reservoirs in southern Africa are prone to cyanobacterial bloom development. Microcystins, including microcystin-LR have been identified in southern Africa (Scott, 1991) and *Microcystis aeruginosa* blooms in a water supply reservoir were previously implicated in repeated outbreaks of gastroenteritis in Harare, Zimbabwe (Zilberg, 1966). As more research is carried out on the health implications of chronic exposure to low concentrations of cyanobacterial toxins, it is likely that treatment of drinking water to remove these compounds will become more important (Bell and Codd, 1994; Falconer, 1996), as will the economics of treatment. We believe that the preliminary results presented here, combined with our existing knowledge on the performance characteristics of *Moringa* carbon and its ease of production, demonstrate the potential that *M. oleifera* seed husk carbon has for the treatment of microcystin-contaminated drinking waters in tropical regions.

Acknowledgements

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PORE STRUCTURE AND ADSORPTION CHARACTERISTICS OF STEAM PYROLYSIS CARBONS FROM *MORINGA OLEIFERA*

A. M. WARHURST,[a] G. D. FOWLER,[b] G. L. MCCONNACHIE[c] and S. J. T. POLLARD[d,*]
[a]Bio-Logic Remediation Works Ltd, Festival Business Centre, 150 Brand Street, Glasgow, G51 1DH, U.K.
[b]Centre for Environmental Control and Waste Management, Civil Engineering Department, Imperial College of Science, Technology and Medicine, South Kensington, London, SW7 2BU, U.K.
[c]Department of Civil and Environmental Engineering, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, EH9 3JJ, U.K.
[d]Scottish Environment Protection Agency, Environmental Strategy Directorate, Erskine Court, The Castle Business Park, Stirling, FK9 4TR, U.K.

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Abstract—A series of activated carbons has been prepared from the waste seed husks of the tropical multi-purpose tree *Moringa oleifera*, using a single-stage steam pyrolysis activation. Carbons were characterised by N_2 adsorption, CHN analysis and scanning electron microscopy. Nitrogen adsorption isotherms were analysed by the BET, t-plot and Horváth and Kawazoe methods. All the carbons were microporous, with those activated at 750°C for 120 minutes (750/120) and 800°C for 30 or 60 minutes having the highest BET surface areas, of 730, 713 and 774 $m^2 g^{-1}$, respectively. A simple acid rinse of the 800°C/30 minutes carbon increased the surface area to 932 $m^2 g^{-1}$. The 800/60 carbon had the highest mesopore and macropore surface area, 135.7 $m^2 g^{-1}$, compared to 92.7 $m^2 g^{-1}$ for the 800/30 carbon. Scanning electron micrographs of the 800/30 carbon showed a lignocellulosic macropore structure, cleaned by the steam pyrolysis.

These results show that it is possible to produce a high quality microporous activated carbon from *M. oleifera* husks using a simple single-stage steam pyrolysis activation. © 1997 Elsevier Science Ltd

Key Words—A. Activated carbon, B. pyrolysis, C. adsorption, D. porosity.

1. INTRODUCTION

The characterisation of carbonaceous porous solids (active carbons, chars and composites) produced from agricultural by-products has been an established and productive field within carbon research for many years [1–4]. Our recent efforts have focused on the preparation of activated carbon from the tree *Moringa oleifera* for water treatment in those developing countries where the plant is grown [5–7].

Moringa oleifera is a perfect example of a so-called "multipurpose tree"; it grows quickly in dry conditions, its green pods are edible ("Drumstick" in India), its seeds both contain a good-quality vegetable oil, and can be used as a coagulant to replace conventional coagulants in drinking water treatment [8,9]. In addition, many parts of the plant have traditional medicinal uses [8]. The seed husks and pods left over from the production of the vegetable oil and coagulant are currently waste products, but we have demonstrated that steam activation of the husk material can produce a high quality, microporous carbon [5]. Our initial research used a two-stage production process, carbonisation under N_2 at 485°C, followed by physical activation under steam at 850°C. We now report an improved preparative strategy aimed at a much cheaper activated carbon product, and one that avoids the expense of excessive heating.

Previous workers [1] have reported that a single-stage steam pyrolysis activation procedure can yield high quality carbons, and our initial research on the production of carbon from *M. oleifera* by this method has also shown promising results [6,7]. The work described in this paper examines the physico-chemical characteristics of carbons produced under steam at 700, 750 and 800°C, with a view to identifying the optimum process characteristics for production of low-cost activated carbon. The adsorption of chemicals from aqueous solution by these carbons is described elsewhere [7].

*Corresponding author.

2. MATERIALS AND METHODS

2.1 *Materials*

M. oleifera husks were obtained from Malawi, where they had been produced as a waste product from the production of *M. oleifera* seed. Because of the nature of the seed–husk separation process, this husk material also contained a small amount of seed material, and was not of an even particle size, varying between powder and particles several mm in dimensions.

2.2 *Carbonisation/activation of husks*

Carbonisation of *M. oleifera* husks was performed in a Carbolite 12/65 tube furnace, containing a purpose-made quartz tube (Multi-Lab, Newcastle, U.K.), connected to Quickfit connections at one end, and a ball and cup joint at the other, allowing flow-through of steam [7]. Charges of 30 g of *M. oleifera* husks were placed in a quartz boat positioned in the centre of the furnace, and were heated at a fixed rate of approximately 20°C min^{-1} to the appropriate temperature, and held at this temperature (±10°C) for the time specified, e.g. carbon S800/30 was heated to 800°C for 30 minutes under steam. After the furnace had cooled to between 200 and 300°C, the carbonised husks were removed, allowed to cool in air for a few minutes and then weighed to determine the yield. The carbon was then moved to a desiccator for storage. Carbons, duplicated for each set of temperature and time, were later mixed, homogenised and sieved to $<250\ \mu m$, dried in an oven at 110°C overnight, then stored in a desiccator over silica gel.

Carbons were not rinsed to remove ash, except in the case of S800/30r ("r", denoting rinsed). Rinsing of S800/30r was done after sieving; the carbon was mixed with 100 cm^3 of 1M HCl, stirred for 15 minutes, then filtered off using Whatman No. 542 filter paper, on which it was washed with 500 cm^3 of distilled water, then dried in an oven at 110°C overnight. The mass of the carbon was recorded before and after rinsing.

2.3 *CHN microanalysis*

CHN microanalysis was performed using a Perkin–Elmer 2400 CHN Elemental Analyzer with standards of cyclohexanone-2,4-dinitrophenylhydrazone (Elemental Microanalysis Ltd, U.K.) and acetanilide (Fisons, U.K.).

2.4 *N_2 – gaseous adsorption analysis of carbons*

Adsorption/desorption isotherms were determined for the activated carbons using an Omnisorp 100 (Coulter Electronics Ltd, Northwell Drive, Luton) with nitrogen (N_2) as the adsorbate at liquid nitrogen temperatures. Representative samples (typically 0.25 g) were degassed to a residual pressure of 2×10^{-5} Torr by heating at 250°C for eight hours. This degassing protocol has been established as appropriate for the preparation of reproducible gas adsorption isotherms from carbon samples, based upon literature information [10,11] and extensive carbonaceous sample analysis work within the Centre for Environmental Control and Waste Management.

The Omnisorp can be operated in either "continuous mode" or "static mode", the advantages and disadvantages of each mode have been discussed elsewhere [12]. The traditional "static mode" allows equilibrium to become established before further addition of N_2. In "continuous mode", which was originally developed for gravimetric adsorption techniques by Rouquerol and co-workers [13] the rate of N_2 entry into the sample holder is regulated by a mass flow controller and it is assumed that this rate of adsorbate flow is sufficiently slow that quasi-equilibrium always exists between the adsorbate and adsorbent, enabling the rapid collection of up to 2000 data points per adsorption–desorption isotherm, the principles, development and validity of this technique have been discussed elsewhere [14,15]. For the analyses reported in this paper, the continuous mode of operation was used with a calibrated flow rate of ≈ 0.27 ml min^{-1} with an adsorption cut-off p/p^0 of 0.95.

The adsorption–desorption isotherms measured were interpreted by application of the well-established BET method for surface area calculation [16], using a nitrogen molecule surface area of 0.162 nm^2. The micropore volume and surface area attributable to the meso and macropores were calculated by application of the t-plot method of Lippens and de Boer to the adsorption data [17]. The micropore-size distribution for the carbons was established by the method of Horváth and Kawazoe [18]. The theory and application of these interpretative methods used in this research have been discussed elsewhere [19–22]. Isotherms were already available for a commercial steam-activated peat-based carbon, Norit SA4, and a carbon produced from *M. oleifera* husk by a two-stage carbonisation–activation process [23]. These isotherms were re-analysed for this work.

2.5 *Scanning electron microscopy*

Oven-dried carbon samples were scattered on adhesive carbon disks, which were then mounted on aluminium microstubs. The samples were gold sputter coated for 5 minutes (Emscope, U.K.), then examined at various magnifications on a Cambridge Stereoscan 250 scanning electron microscope, operating at 7.5 kV. Representative portions of the surface were photographed on monochrome paper.

3. RESULTS AND DISCUSSION

3.1 *Yield and CHN analysis*

Our results demonstrated steam pyrolysis activation to be a reproducible process, with little variation in yields between experimental runs (Table 1). As expected, as temperature and dwell times were increased, yields were reduced [24]; an attempt was made to make an S800/120 carbon, but only ash was produced.

The results of the CHN analysis (Table 1) show that all the steam pyrolysed carbons were enriched in carbon as compared with the raw husks. The C/H quotient can tentatively be used as a measure of the "aromaticity" of the carbon, which would be expected to increase as burn-off increases. However, interpretation of the quotient is difficult due to the increasing percentage of non-CHN components as burn-off increases, to a maximum of 41% w/w in the S800/60 carbon. This component is mainly ash, but

Table 1. Results from CHN analysis

Sample	Overall yield (%w/w) (±s.d., *n*)	C(%w/w)	H (%w/w)	N (%w/w)	Not CHN (%w/w)	C/H quotient
S700/120	17.3 (±0.4, 2)	73.8	1.3	2.6	22.3	55.9
S750/30	16.6 (±0.2, 7)	75.7	1.3	2.3	20.7	60.6
S750/60	15.1 (±0.1, 2)	71.8	1.3	2.0	24.8	55.3
S750/120	11.9 (±0.4, 9)	65.4	1.0	1.6	32.0	66.1
S800/30	12.2 (±0.2, 11)	67.4	1.0	1.5	30.1	65.4
S800/30r	9.0	87.3	1.3	1.9	9.5	68.2
S800/60	9.0 (±0.3, 5)	56.8	1.2	1.0	41.1	48.5
Results below from [5]						
Raw husk	–	46.9	7.1	3.0	43.1	6.6
Carbonised 485/30	27.6	75.2	2.9	1.4	20.5	25.7
Activated S850/5	9.6	82.4	1.5	14.6	1.6	56.8

will also include any O in the carbon. Most of this ash is removable by acid washing, as is shown by both the analysis of S800/30r, and the activated S850/5 carbon from the earlier work, which was also acid washed [5].

3.2 N_2 *adsorption*

The adsorption–desorption isotherms for the *M. oleifera* samples and Norit SA4 are shown in Fig. 1. The isotherm changes from a type I with a characteristic H4 hysteresis loop for carbon S700/120 to a

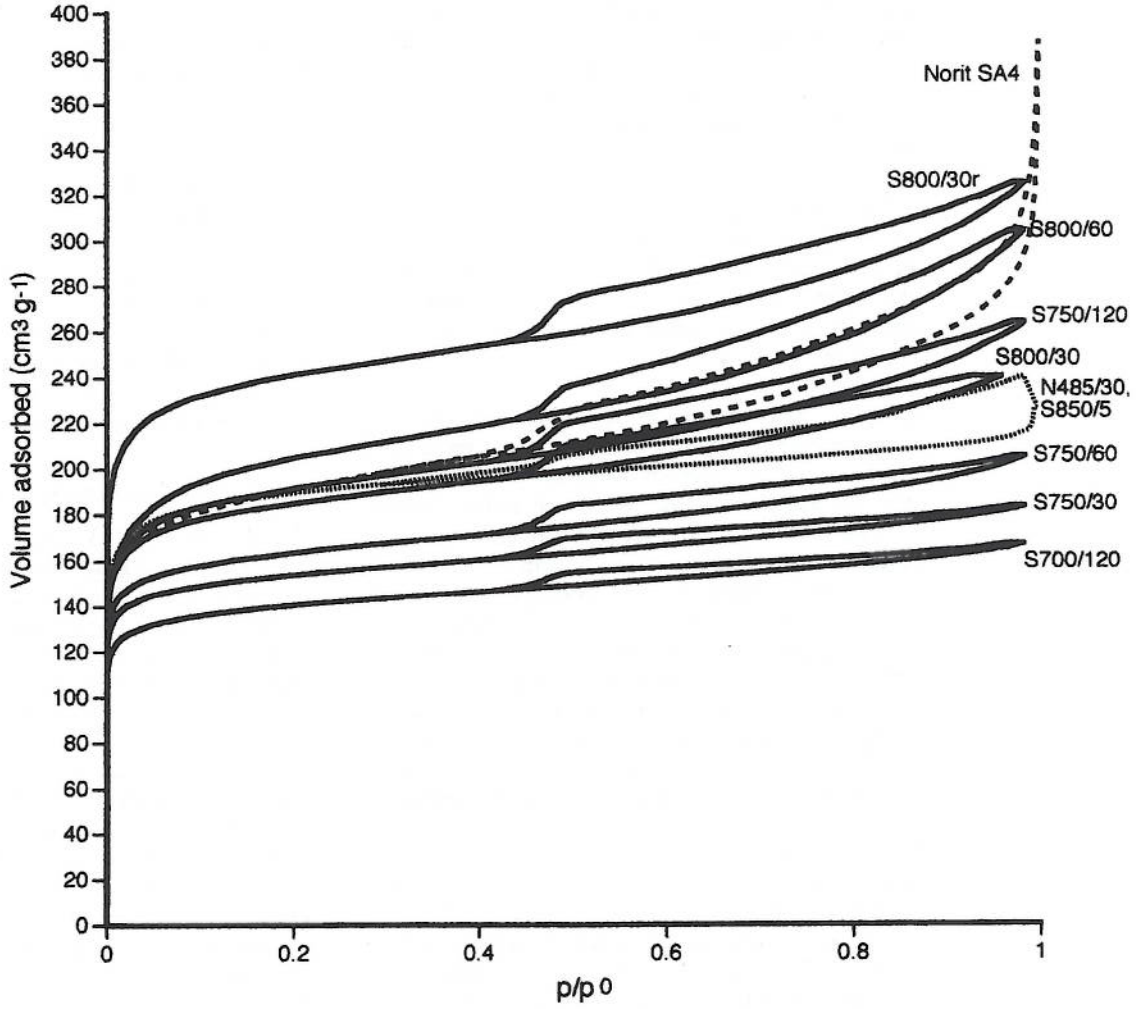


Fig. 1. Adsorption isotherms for N_2 on the steam activated *M. oleifera* husk carbons.

Table 2. Results from N_2 isothermal analysis

Sample	BET p/p^0 range	BET surface area ($m^2\ g^{-1}$)	Mesopore and macropore surface area ($m^2\ g^{-1}$)(t-plot)	BET "c" value	BET r^2	Micropore volume ($cm^3\ g^{-1}$)
S700/120	0.005–0.06	549	55	3100	1.00	0.20
S750/30	0.005–0.05	605	62	2830	1.00	0.21
S750/60	0.005–0.07	637	76	2790	1.00	0.22
S750/120	0.005–0.1	730	112	1920	0.99	0.25
S800/30	0.004–0.08	713	93	1740	1.00	0.25
S800/30r	0.005–0.08	932	119	1470	1.00	0.33
S800/60	0.005–0.1	774	136	800	1.00	0.26
N_2 485/30,S850/5 [1]	0.005–0.074	739	42	2270	1.00	0.29
Norit SA4 [5]	0.005–0.11	716	126	1600	0.99	0.25

type IV isotherm exhibiting a borderline type H3/H4 hysteresis loop for carbon S800/30r. However, given the observed microporous nature of all the *M. oleifera* carbons (Table 2), the later isotherms are probably of the mixed type I/type IV as discussed by Sing [25]. The commercial carbon, Norit SA4, exhibits a classical type IV isotherm with H3 hysteresis loop and has the highest pore volume of all the samples up to the $p/p^0 = 0.95$ cut-off point. The extent of the hysteresis loop suggests that this carbon possesses a greater volume of mesopores than the *M. oleifera* carbons, but the nature of this loop (H3) does not make it amenable to a Kelvin equation based mesopores size distribution analysis [26]. The acid rinsed sample S800/30r possessed the highest microporous surface area and volume of all the *M. oleifera* carbons, mainly because the removal of the ash component reduces the mass of non-adsorptive material. It is also notable that the BET linear p/p^0 range for the *M. oleifera* carbons is very short (Table 1) which is further evidence for the presence of microporosity. The BET c value is often quoted as providing a suitable guide to the applicability of the BET method with values greater than 150, as in this case, implying that the method is not wholly reliable [20,26,27]. The decrease in the c value with burn-off (compare Tables 1 and 2) and the simultaneous broadening of the "knee" of the isotherms both imply a reduction in the micropore distribution of the samples with greater activation [28].

The t-plot data (Table 2), demonstrates increasing mesoporosity and macroporosity with increasing burn-off, with a maximum of 136 $m^2\ g^{-1}$ in S800/60. This method, however, relies on the BET equation [20] so is probably not entirely reliable in this case.

Figure 2 shows the micropore size distribution of the carbons determined by the Horváth and Kawazoe method. The S700/120 sample has the highest distribution function of all the samples ($dW/dr = 16$ at 0.61 nm pore diameter) and the N485/30, S850/5 sample [5] has the lowest dW/dr value (≈ 7.0 centred at a pore diameter of ≈ 0.54 nm). The 750°C samples (Fig. 2(a)) show clearly the effect of increased residence time upon the pore distributions, with a steady fall in the value of the dW/dr value from 14 to 10 with increased burn-off. The higher activation temperature used for these samples has also resulted in a decrease in the effective pore diameter, corresponding to the change in position of the dW/dr maximum. The S800/30 and S750/120 samples exhibit almost identical micropore size distributions (Fig. 2(b)), but the acid rinsed S800/30r shows an increase in the intensity of the dW/dr value from 10 to 11 and a shift in its effective pore diameter to approximately 0.61 nm when compared to the unwashed sample. This suggests that the observed narrowing of the micropores with increase temperature and residence time may be partially due to the formation of ash and activation residues in the pores. This conclusion is further supported by the increased micropore surface area and micropore volume in sample S800/30r compared to S800/30 (Table 2) and our inability to prepare sample S800/120, which only produced an ash residue.

The Horváth and Kawazoe method is only valid for micropores of width between 0.35–1.4 nm, and has been described as idealised and simplistic, but nevertheless it is useful for micropore analysis, as the physical validity of the more traditional Kelvin equation based model breaks down at pore radii of 3.6 nm [11,29]. It is, however, disconcerting that the model tends to produce distributions which clusters in a relatively narrow pore width range, between 0.54 and 0.7 nm [21,29,30], as in this work.

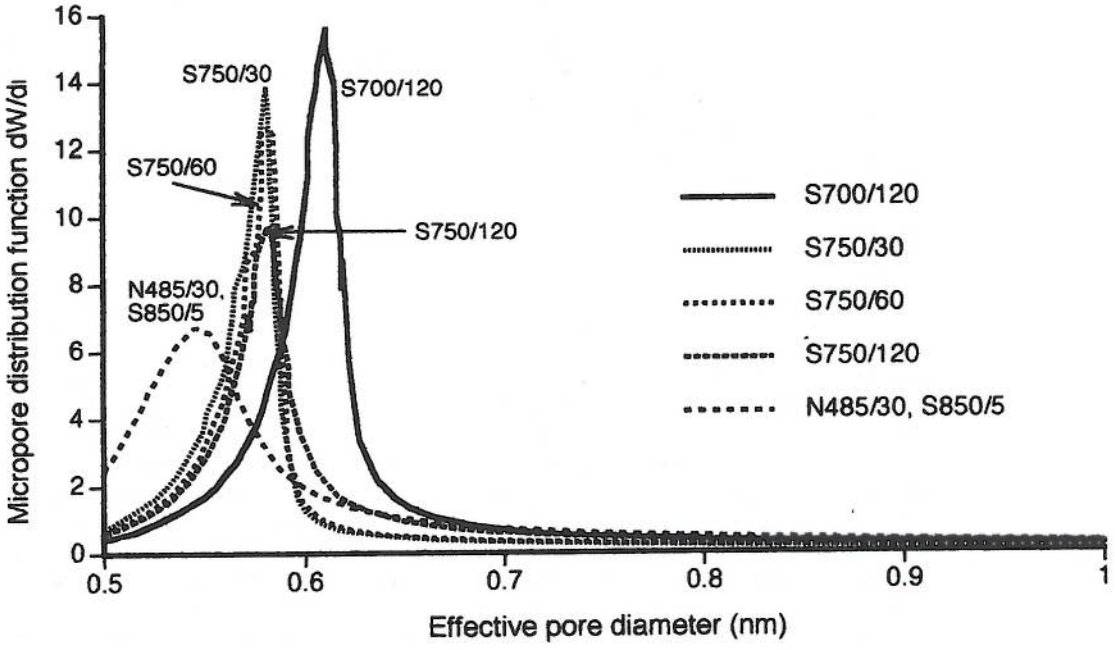
In spite of the deficiencies of the models used in analysing the N_2 adsorption data, the results clearly mirror the burn-off and chemical composition data, and are a useful method of comparing the porous characteristics of the different *M. oleifera* carbons.

3.3 *Scanning electron microscopy*

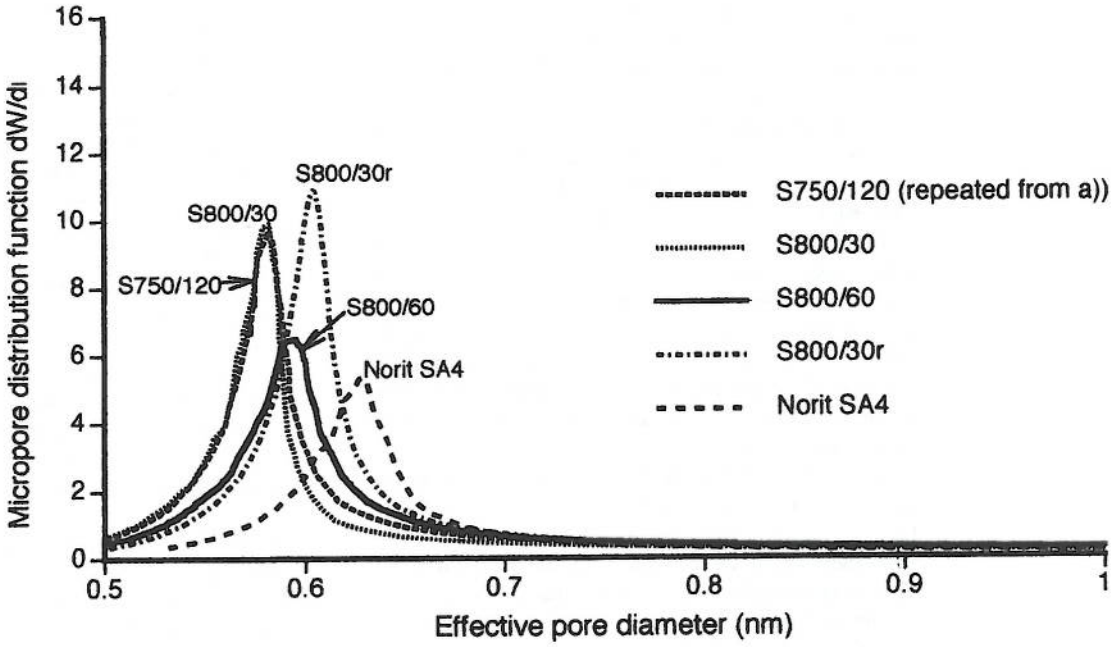
The scanning electron micrographs of carbon S800/30 suggest a very open, ordered macropore structure, presumably derived from the lignocellulosic structure of the husk material (Figs 3(a) and (b)). Previous work has shown that the shape and distribution of carbon pores is very dependent upon the structural characteristics of the precursor material, and tends to be unaffected by the thermal processing, only really undergoing a contraction and twisting as carbonisation occurs [25,31,32].

3.4 *Practical relevance*

It is clear from these results that the S800 carbons have the optimum surface areas for the minimum



a) Carbons with low burn off, and the carbon from the previous work [5]



b) Carbons with high burn off, and Norit SA4

Fig. 2. Horváth-Kawazoe plots of the micropore distribution in the *M. oleifera* carbons.

energy expenditure, provided it is reasonably assumed that less energy is expended heating the husks to 800°C for 30 minutes than 750°C for 120 minutes. The S800/30 carbon is produced with a 40% w/w higher yield than the S800/60 carbon, whilst only having a slightly lower micropore volume, so the S800/30 carbon is probably the best for use in applications where adsorption of small molecules is important. However, the S800/60 carbon has a much higher mesopore and macropore surface area than

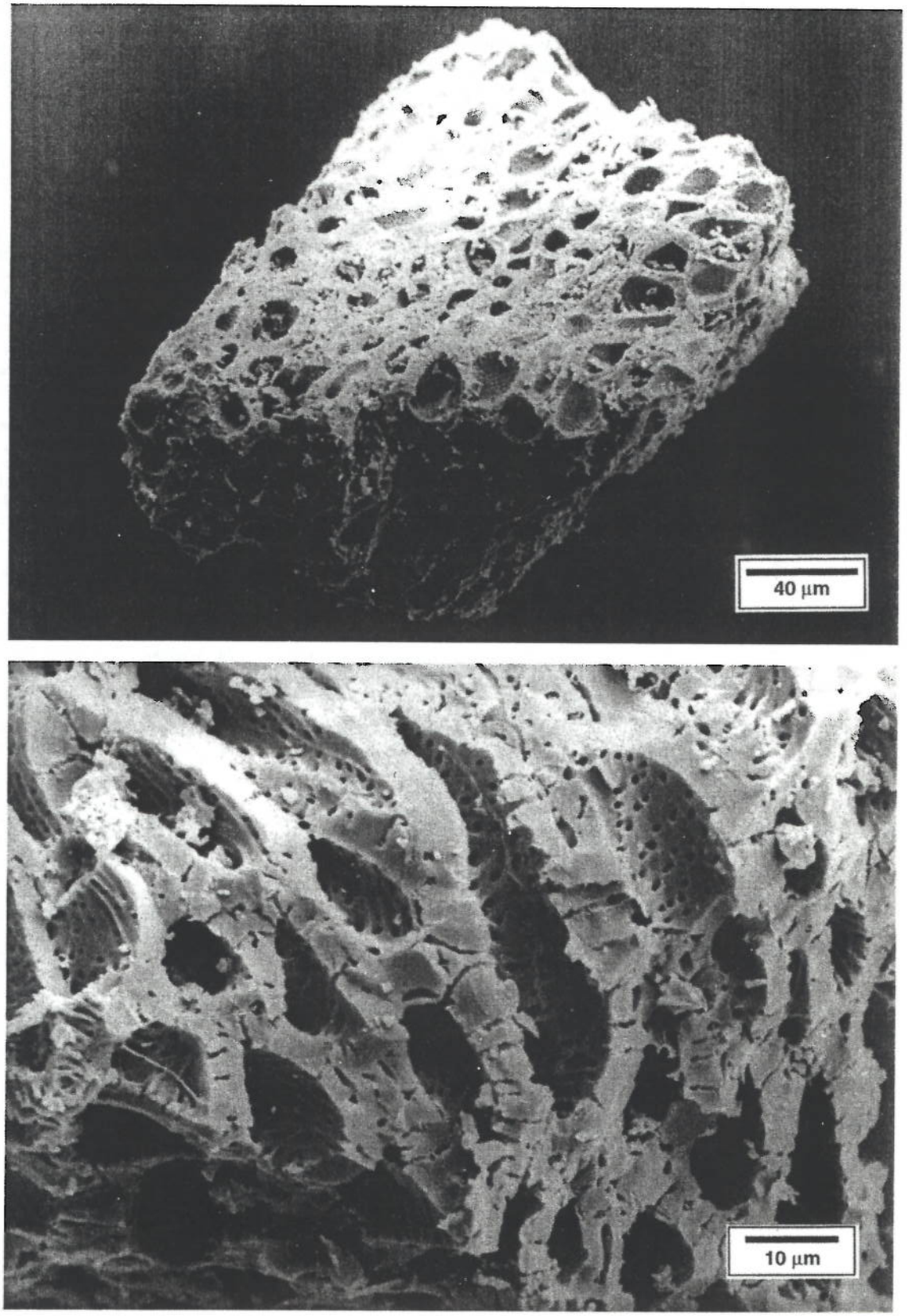


Fig. 3. Scanning electron micrographs of a representative particle of carbon S800/30.

the S800/30 carbon, so could be substantially better in applications where the removal of larger dimension species is important, such as the removal of microcystin algal toxins from water supplies, which requires adsorbents with high mesopore volume [33].

4. CONCLUSIONS

The single-stage steam pyrolysis process is clearly an effective way of creating activated carbons. It has been shown that the structure of lignocellulosic materials is the main factor determining the nature of the activated carbon produced from them [34,35], and the results given here demonstrate that the structure of *M. oleifera* husks is well suited to the production of highly microporous activated carbons, with surface areas of between 549 and 931 $m^2 g^{-1}$, comparable to the peat-based, steam activated commercial carbon Norit SA4. In addition, the open pore structure of this carbon will allow maximum penetration of adsorbates, providing easy transport to the mesopores and micropores.

We are now developing production of this carbon in Malawi in conjunction with the University of Malawi, and, in association with the University of Leicester, U.K., business plans for the growth and utilisation of *Moringa oleifera* are being developed.

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Review

Organic compounds in the cement-based stabilisation/solidification of hazardous mixed wastes—Mechanistic and process considerations

S.J.T. Pollard, D.M. Montgomery, C.J. Sollars and R. Perry

Imperial College Centre for Toxic Waste Management, Imperial College of Science, Technology and Medicine, London SW7 2BU (Great Britain)

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Abstract

The pretreatment of hazardous wastes by cement-based stabilisation/solidification is of increasing importance as an alternative to the direct landfill of toxic materials. Inorganic and organic compounds are known to have a range of beneficial or harmful effects on cement hydration and their presence within construction materials has been strictly controlled. This paper reviews cement and pozzolanic hydration and the use of organic admixtures as a prerequisite to a discussion of the effects of organic wastes in cement. The pre-adsorption of organic contaminants is reviewed and presented as a potential extension of existing solidification processes for the successful treatment of mixed organic/inorganic wastes.

Introduction

Cement-based stabilisation/solidification (S/S) is a chemical treatment process which aims to either bind or complex the components of a hazardous waste stream into a stable insoluble form (stabilisation) or to entrap the waste within a solid cementitious matrix (solidification [1]). Hazardous industrial wastes, however, often contain constituents which may interfere with the hydration reactions of cement or pozzolanic materials, and certain organic compounds are among the known inhibitors of cement set [2, 3]. Whilst chemical stabilisation/solidification of hazardous wastes prior to disposal is of increasing importance, only a limited research effort has been directed towards elucidating the effects of specific waste components on the containment and physical properties of the final waste–cement product.

Within the construction industry, a wide range of organic materials has been employed to improve the performance and workability of cement blends [4, 5]. Such admixtures are routinely introduced in order to retard set during transport, lower heat production, increase water resistance and develop ulti-

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mate cement strength. Consequently, experience with a variety of organic additives has resulted in the identification of organics as either inhibitors or accelerators of cement set [6], and care has been taken accordingly to ensure that aggregates or other components do not contain deleterious materials.

The complexity of hydration reactions, variations in processing parameters and differences in waste-cement formulations have precluded an accurate prediction of the effects of organics in S/S processes. The results of single-component organic additions to the cement mix are, in general, poorly understood. Consequently, forecasting the outcome of complex and variable compositions, such as those found in many mixed organic/inorganic waste streams, is extremely difficult. Further fundamental research on the behaviour of organic compounds in cement-based S/S is therefore clearly essential. From a processing perspective, however, several researchers have attempted to counteract the problems of set inhibition by using adsorbents to isolate the organic fraction of these wastes prior to cement fixation [7–9]. Whilst the majority of these studies to date have been performed at the laboratory or pilot scale, the results have indicated that this could form the basis of a successful approach to the solidification of organically contaminated wastes.

Cementitious reactions

Hydration of cement

The ultimate properties of cement-based S/S products depend largely on the characteristic behaviour of the cement additives and how they react with the wastes. An extensive literature exists on the chemical and physical processes occuring during the hydration of ordinary portland cement [10, 11] and this information provides a sound foundation for an understanding of cement hydration in the presence of organics.

Ordinary portland cement (OPC) is an hydraulic cement; it sets, hardens and does not disintegrate in water [12]. Anhydrous OPC consists of angular particles (~ 20 μm in diameter) and is typically comprised of the following major constituents [13]:

tricalcium silicate	(C_3S)	54% (w/w)
dicalcium silicate	(C_2S)	17
tricalcium aluminate	(C_3A)	11
alumino-ferrite	(C_4AF)	9
gypsum	(CSH_2)	4

where $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $\bar{S} = SO_3$ and $H = H_2O$ in cement chemists nomenclature. The hydration of C_3S is the dominant mechanism in the overall hydration and hardening process of OPC. The general hydration reaction can be written as:

$$C_3S + (1.3+x)H = C_{1.7}SH_x + 1.3CH \quad (1)$$

where $C_{1.7}SH_x$ is calcium silicate hydrate and CH is calcium hydroxide (portlandite [13]). Calcium silicate hydrate (CSH) is an ill-defined, poorly crystalline solid, which in hardened cement pastes accounts for ~70% of the hydrated material [14] and is principally responsible for strength development.

Several distinct stages in the hydration of C_3S have been identified [15–17]. Initially, when OPC is dispersed in water (Stage I, Fig. 1), calcium ions are rapidly leached from the solids to form a solution of mainly CH [15], leaving behind silica-rich cement grains. The aqueous CH is thought to react with silicic acids on the surface of the cement to form a gelatinous semi-permeable membrane of CSH around the cement particles [18–20]. This semi-permeable membrane causes a dormant phase in the hydration process as the osmotic pressure within steadily increases. This pressure eventually causes the membrane to rupture (Stage II, Fig. 1) with the development of new CSH radiating out from the anhydrous grain. Breaching of the gelatinous membrane is now believed to occur by a scaling (exfoliation) process [10] whereas previously, rupture was thought to occur via an "osmotic pumping" mechanism [14] which formed radial tubules of CSH. These "tubules" have subsequently been associated with the hydration of C_3A and C_4AF in the presence of gypsum [21]. Stage III of the hydration process is also characterised by initial CH crystallisation [22] and the transformation of CSH gel which exposes additional surface area of the anhydrous particles. The hydration of C_3A, whilst not critical to initial strength development, is essential in determining setting times and the characteristics of early hydration stages [23]. In the absence of sulphate, the hydration of C_3A can be represented as:

$$2C_3A + 21H = \underset{\substack{\text{metastable hexagonal}\\ \text{hydrates}}}{C_4AH_{13} + C_2AH_8} = \underset{\text{stable hydrates}}{2C_3AH_6} + 9H \quad (2)$$

Most OPCs contain small quantities of sulphate in the form of gypsum (calcium sulphate) to prevent flash setting of the cement due to the reaction of C_3A (eq. 2). This modifies the hydration of C_3A to:

$$C_3A + 3CS\cdot H_2 + 26H = \underset{\text{ettringite}}{C_3A\cdot 3CS\cdot H_{32}} \quad (3)$$

$$\underset{\text{ettringite}}{C_3A\cdot 3CSH_{32}} + 2C_3A + 4H = 3\underset{\text{monosulphoaluminate}}{(C_3A\cdot CSH_{12})} \quad (4)$$

The formation of ettringite (Eq. 3) slows the hydration of C_3A by precipitation onto its surface. Ettringite forms both long prismatic crystals with hexagonal cross-sections, and amorphous layers. Its formation brings a volume increase, which, if ettringite is formed after initial set, disrupts the structure causing an increase in permeability and a concomitant loss in strength [24]. In time, the ettringite may react with dicalcium aluminate (Eq. 4) and produce monosul-

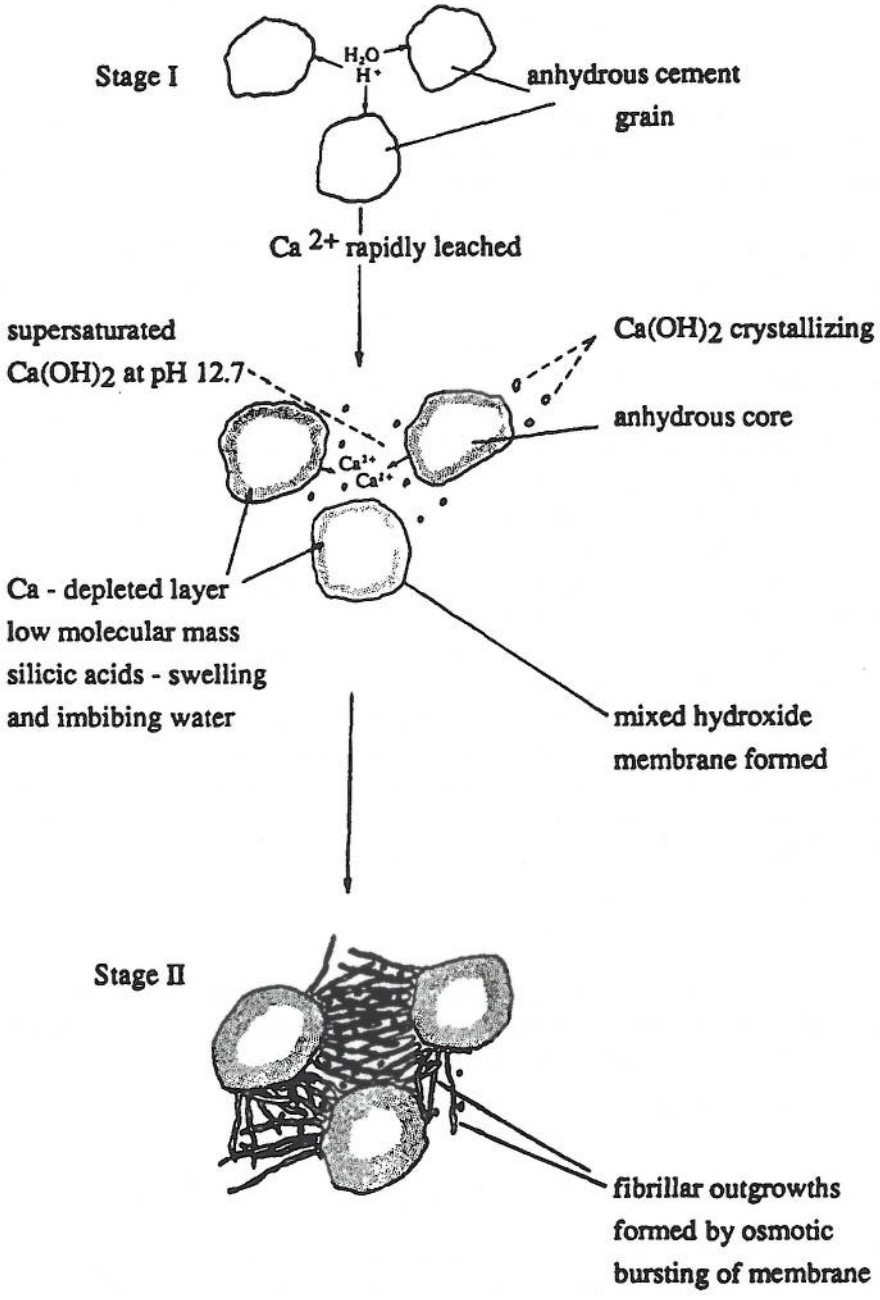


Fig. 1. Schematic model for the hydration and setting of portland cement [15].

phoaluminate. Monosulphoaluminate provides 15–20 % (v/v) of hydrated OPC and is the primary constituent vulnerable to sulphate attack.

Hydration of pozzolanic materials

The term "pozzolana" is used to describe a range of materials which react with lime, set and develop strength in the presence of water [13, 25]. Pozzolana principally consist of reactive (amorphous) silica and alumina and these include materials such as volcanic glass, calcined clays, fly ash and metallurgical slags. The use of blended portland–pozzolana cements generally brings about improved durability, sulphate resistance and obvious economic benefits. At present, the main pozzolanas in commercial use are pulverised fuel (fly) ash (PFA) and ground, granulated blast furnace slag (GGBFS [26]). Both materials have received extensive attention in the cement literature and PFA in particular has been used for many years in cement-based S/S processes [1].

The reaction products of pozzolan hydration are similar to those of OPC, the major difference being that in contrast to cements, pozzolans consume lime rather than produce it. This is an important factor in sulphate corrosion resistance and is also relevant to differences between the two systems with regards buffering capacities and the effect of additives. Hydraulic blast furnace slags, for example, react with lime and water to produce identical hydrates to OPC i.e. CSH and hydrated aluminates [27]. Similarly, a study of eight U.S. fly ashes and their reactions with hydrated lime over periods of up to 32 weeks [28] led to the following set of proposed reactions and resultant products:

$$CH+S+H = C_xS_yH_z \quad \text{(CSH of varying stoichiometry)}$$
$$CH+A+H = C_xA_yH_z \quad \text{(hexagonal/cubic aluminate hydrates)}$$
$$CH+A+S+H = C_xA_yS_zH_w \quad \text{(hydrogarnet)}$$
$$CH+S+A+H = C_xA_y(CS)_zH_w \quad \text{(ettringite and derivatives)}$$

Pozzolanic reactions, therefore, are similar to the hydration reactions of portland cement although generally they take place more slowly, with times to final set being measured in days rather than hours. In both cases, the strength of the final product results essentially from the formation of hydrated calcium silicates (CSH) and thus organic compounds which inhibit this process can be expected to affect cement and pozzolanic systems alike.

Organic compounds as additives in cement products

The properties of concrete in both fresh and hardened states can be modified by the addition of specific compounds, many of which are organic in nature [2]. The use of such admixtures in the concrete industry has been regularly reviewed [28–31]. An understanding of the role played by organic admixtures during cement hydration can provide a basis for assessing the possible effects

of organic waste constituents in cement-based S/S. Admixtures have been broadly sub-divided into three categories depending on their interaction or function within the cement–water system [2]:

(a) *Surfactants* affect the cement–water system immediately upon addition by influencing the surface tension of the water and by adsorbing onto cement grain surfaces.

(b) *Set-controlling* materials are capable of dissociation in water, ionise and affect the chemical reactions between the cement and surrounding hydration water after a time lapse of between several minutes or even hours.

(c) Finely-ground, *mineral additives* affect the rheology of the fresh concrete formulation, but their chemical effects are generally less important and manifest themselves only after several days or even months.

The major function of organic-based admixtures is for water reduction and as plasticisers. By reducing the interparticulate attraction between cement grains, surfactants prevent the agglomeration of particles and facilitate better dispersion, thus reducing the amount of hydration water for a required workability [32]. Water-reducers can also be used to increase slump, hence improving ease of placement [33] and to obtain higher strengths by the use of lower water/cement ratios. They include organic compounds such as lignosulphonic acids (and their salts), citric acid and gluconic acid. Detailed studies on the effect of superplasticisers on the different stages of cement hydration have also been performed. Recognised superplasticisers, which have a far greater effect than conventional plasticisers, include naphthalene compounds, melamine and sulphonated hydrocarbons. Such compounds have been shown to retard set without affecting the total heat of hydration [34] and superplasticisers derived from gluconate and lignosulphonate have been observed to stabilise the formation of ettringite by inhibiting its subsequent conversion to monosulphate in the presence of lime [35].

Air-entrainment admixtures are used in cement blends to increase entrapped air, enhance durability and reduce the potential frost damage of concretes [36]. Typically, these are organic surfactants which possess a non-polar hydrocarbon "tail" with an anionic polar group attached at one end of the molecule. The surfactant molecules are capable of coating the surface of small air bubbles and preventing them from coalescing or separating from the mixture during blending. In addition, they may also neutralise the charged surface of cement grains causing them to become hydrophobic, thus resulting in a lower rate of hydration and a subsequently delayed set [2].

The third major use of organic admixtures is to intentionally retard set in order to allow prolonged workability and thus facilitate transport of the liquid concrete [37]. Superplasticisers can be used as retarders due to their ability to delay bond formation between hydration products and so delay crystallisation [38, 39]. More commonly used retarding admixtures, however, contain carboxylic acids. These are thought to interfere with hydration by strongly ad-

sorbing on to the cement particle surface in their ionised carboxylate forms [40]. Citric acid has been found to be particularly effective [41] at high concentrations whilst acting as an accelerator at low levels of addition [42]. Sugars are well established set retarders with the retarding action again being described in terms of the adsorption onto and the poisoning of hydrating surfaces. Sucrose and raffinose in particular have been attributed with the ability to solubilise cement constituents giving rise to dramatic increases in the amount of silica present in solution [43].

Cement–organic interactions

The variables associated with the use of admixtures in concrete production are numerous and increase accordingly when a hazardous mixed waste is being considered for cement-based stabilisation/solidification.

An example of the complexity surrounding the interactions of organics with cement matrices is the effect of phenol and its substituted analogues on hydrating cement paste [44]. In one such study [44], several phenols with varying substituent groups were solidified with types I and III portland cement. The solidified products were examined intermittently at selected cure times using water and solvent extraction (leach testing), optical and electron microscopy, X-ray diffraction and NMR spectroscopy. Whilst in each case the phenol substrate was readily leached from the cement matrix, significant differences in physical characteristics (e.g. setting times and compressive strengths), matrix morphology and phase composition were observed. The authors thus concluded that even subtle alterations in the chemical structure of the interfering organic may result in major differences in the nature of the cement–organic interaction.

The effects of low concentrations of some organic compounds on cement strength and hydration are well documented [28, 45–48]. In an attempt to elucidate the mechanisms of chemical interference by waste components during cement-based fixation, much research is now being directed towards investigating interactions between single organic components and OPC. Phenol, for example, has been found to have an adverse effect on long-term strength development at concentrations as low as 0.2 % (v/v) [49] and 3-chlorophenol was observed to inhibit cement hydration by stabilising ettringite formation, retarding its conversion to monosulphate [50]. Trichlorobenzene was shown to reduce the mean pore diameter of cement pastes in which it was incorporated [51] but without leaching significantly from the hardened product. An examination of the effect of three common organic wastes on the microstructure of the cement matrix [52] demonstrated that whilst methanol and phenol inhibited ettringite formation, trichloroethylene appeared to stimulate it.

A significant contribution to data on the microstructural behaviour of cement in the presence of organics has come from workers at Louisiana State

University, Baton Rouge, LA [53–59] who examined the effects of ethylene glycol, *p*-bromophenol and *p*-chlorophenol on cement hydration using a wide range of microstructural, and some macrostructural techniques. Ethylene glycol was shown to have a retarding effect upon cement and occupied three distinct sites in the hydrated cement matrix. The microstructure was also altered, producing grainy nodular surfaces which lacked crystallinity. It was postulated [59] that ethylene glycol was small enough to substitute for water molecules during hydration and thus cause product deformation. Parabromophenol was observed to react with CSH gel which then underwent phase separation forming a concentrated crystalline phase. Although *p*-bromophenol had no overall effect on the hydration products, the chlorinated analogue was found to cause morphological changes in the hydration products and shown to be both closely associated with the CSH gel as well as homogeneously distributed within it.

Conduction calorimetry is being used increasingly to classify the effect of organic compounds on the hydration of cement paste. Initial studies performed by Taplin [60] identified hydrocarboxylic groups as particularly effective retarders of cement set. Recent developments in the technique have facilitated its use on a quantitative basis for surveying a wide range of organic admixtures [61], the retarding efficiency of which have been generally found to increase with molecular weight. In a further study, the most effective retarders were also found to inhibit the precipitation of CH from aqueous solution and this has led to the derivation of a "retardation index" for inhibiting organics [62].

Close examination of the functional groups responsible for retardation of cement set has led to a variety of conceptual models being proposed to explain the interference mechanisms of organics on cement and pozzolan hydration. These mechanisms include adsorption, nucleation, complexation and precipitation [28,39] and have recently been thoroughly reviewed by Jones [2].

Stabilisation/solidification of organic wastes

Conventional cement-based S/S processes are designed to bind or complex soluble metal ions present in an inorganic waste stream by firstly neutralising the waste to precipitate them as insoluble metal hydroxides. Addition of OPC follows to produce a solid cementitious matrix. Structural integrity of the resultant solidified mix is provided by the cementitious and pozzolanic reactions of OPC, PFA, kiln dust or other pozzolans added with water during the process. These conventional processes are generally unsuitable for the treatment of wastes containing organic compounds [63] due to the interfering effects of contaminating organics on the various hydration reactions. Consequently, the treatment of mixed organic/inorganic waste by such processes has often been problematic in the past. In an attempt to overcome this problem, several authors have adapted or extended existing S/S processes using proprietary binders and/or industrial adsorbents to isolate the organic content of these wastes prior to solidification.

Pre-adsorption of organics in cement-based S/S processes

A range of commercial industrial adsorbents including activated carbon, quaternary ammonium exchanged clays and zeolites have been evaluated for the adsorption of retarding organics in mixed waste streams prior to cement-based solidification. A survey of adsorbents intended for use in the cement-based S/S of oily wastes, for example, showed that each of the materials examined was capable of adsorbing up to 30% (w/w) of the oily waste prior to successful solidification with OPC [64]. In an extension of the Soliroc® process [7], acidic organic wastes arising from the manufacture of fine chemicals were treated with and without the inclusion of powdered activated carbon. In the latter case, the wastes were mixed with reactive silicates to form silicic acids, neutralised to precipitate the silica gel polymer and then, following the addition of activated carbon (1–10% w/w), final cementation was achieved by the addition of hydraulic cement.

Claimed reductions in the COD (chemical oxygen demand) of leach test filtrates were in the order of 70–90% (w/w) compared to 20–50% (w/w) for the process without the inclusion of carbon. Kyles et al. [65] screened a range of conventional and novel processes for the S/S of four wastes including an electroplating filter cake contaminated with chlorinated solvents, an acidic tar residue from petroleum refining, a mixed waste containing an array of dyes and pigments and an oil filter cake, again from petroleum refining. The study compared S/S with kiln dust, PFA, calcium oxide and activated carbon and found that whilst most of the techniques examined produced solid products, carbon adsorption prior to fixation proved the only effective means of immobilising the organic constituents such that they were less vulnerable to leaching. In a third study [8], decolourising charcoal and quaternary ammonium exchanged clay were utilised for the cement-based fixation of aqueous phenol, 3-chlorophenol and 2,3-dichlorophenol solutions (100–2000 ppm). The charcoal (1–2% by weight) displayed rapid adsorption of the phenolics and effective stabilisation of organics in the solidified products. In addition, charcoal was observed to aid cement hydration and increase compressive strength.

Exchanged clays have also received considerable attention as potential adsorbents for the S/S of organically contaminated wastes. In such a system, the organophilic nature of the quaternary ammonium salt (QAS) exchanged clay enhances the clay's capacity to adsorb organic compounds from aqueous media [66]. In two similar studies [8, 67] tetra-alkylammonium substituted bentonite clays were employed as pre-stabilisation adsorbents for phenol, 3-chlorophenol and 2,3-dichlorophenol before being incorporated into a range of cementitious matrices. Both studies reported a clear trend between the degree of polarity for the substituted phenols and their ability to be adsorbed by the QAS-clays. Leachability and physical strength measurements performed on the solidified phenol solutions confirmed pre-adsorption as a potential pre-treatment requirement of mixed waste solidification. Patent adsorbents con-

taining sodium magnesium fluorolithosilicate and QAS-exchanged sodium bentonite have been used in a similar fashion to immobilise and successfully solidify a wide range of organic containing wastes [68].

Unexchanged and thermally treated clays have also been utilised for the pre-adsorption of organics in mixed waste streams. Escher and Newton [69] used an OPC/bentonite clay mix to solidify three wastes contaminated with cyanide and phenol. In a novel development, spent clay from the edible oil industry was converted to a low-cost clay-carbon adsorbent by the chemical activation of residual oil on the mineral surface. Activated spent bleaching earth was then evaluated for the cement-based S/S of an organically contaminated pickling acid waste and its performance compared with a typical water treatment carbon [9]. The effects of adding activated spent clay at 10% (w/w) to the mix reflected the bifunctional properties of the clay–carbon material. Reductions in leachable TOC (total organic carbon) of up to 37% (w/w) were observed as a consequence of the adsorptive nature of the carbon char, whilst the fired clay support imparted 240–300% increases in compressive strength as a result of its pozzolanic activity.

Proprietary and pozzolanic systems for the treatment of organic wastes

In recent years a number of bench scale and pilot studies have been reported on wastes containing significant concentrations of organic compounds. In addition to utilising a range of industrial adsorbents, some of these studies have presented the use of proprietary trade name products, the contents and structures of which, unfortunately, are not reported. Two such studies examined the treatment of a mixed, liquid organic waste and a contaminated soil using an identical commercial process with varying degrees of success [70, 71]. Whilst the liquid waste produced a hardened solidified form, the authors were still able to leach >87% (w/w) of the organic contaminants from the product, using distilled-deionized water. In contrast, the PCB contaminated soil was successfully solidified with negligible volatile and leachable TOC in leach test filtrates. Cement only and proprietary cement-based processes have also been used to treat PCB contaminated dredge material [72]. Three S/S processes were evaluated in this study and the OPC treatment found to be the most effective for the containment of PCBs.

The detailed effects of organic waste components in pozzolanic S/S systems have not been widely investigated [2]. A number of workers have proposed that unpyrolised organics are capable of adsorbing onto the reactive sites of fly ash and preventing cementation reactions between certain constituents [73–76]. Pozzolans have been shown to solidify clay soil with an organic content of 11.4% (w/w) [76] and the addition of 5% (w/w) lignite fly ash in this case was demonstrated to increase compressive strength by 40%. The organics in this study were added up to 8.5% (w/w) of dry reagents and ranged in chemical structure from simple alcohols to substituted aromatics and in aqueous

solubility from highly soluble to virtually insoluble. From investigations of cement strength it was inferred that aliphatic and dicarboxylic acids neutralised lime and therefore interfered with pozzolanic hydration. Methanol, xylene and benzene acted initially as set retarders without, however, affecting ultimate strength. Examinations of hardened pastes using scanning electron microscopy (SEM) indicated that the presence of interfering organics altered the morphological structure of the pozzolanic hydration products at concentration levels as low as 6.1% (w/w).

In conclusion, it is generally recognised [1, 2, 77] that a significant correlation exists between cementitious and pozzolanic hydration reactions, and therefore, under this hypothesis, the mechanistic details of chemical interference by a range of organics should be applicable to both systems.

Conclusions

Although cement-based S/S processes are attracting increasing attention for the treatment of hazardous wastes prior to landfill, a number of research studies have shown that the organic constituents of mixed waste streams can have a detrimental effect on the hydration of cementitious and pozzolanic materials. Whilst the inhibiting effect of organics on cement set have been utilised to advantage in the construction materials industry for many years, the distinct mechanisms of cement/organic interaction are still poorly understood despite the postulation of several interference models. It is evident, however, that even at low concentrations, organics can produce significant micro- and macrostructural changes to the properties of hydrating cement and that chemical functionality plays an important role in determining the relative extent of inhibition.

Research on pure organic/cement pastes has shown that, in general, non-polar organics do not hinder strength development in cementitious or pozzolanic systems. Further study of chlorinated hydrocarbons, however, which comprise a large section of these compounds and are prolific in mixed waste streams, is still required. Organic waste constituents containing hydroxy (sugars, alcohols), carboxylate (acids) and possibly amine functionalities can be expected to inhibit or even prevent cement/pozzolanic hydration altogether. These functionalities are commonly found in biological sludges, paint residues and many solvent wastes [1].

On the basis of research on organic/cement interactions to date, it is dear that conventional cement-based S/S processes must be applied with strict caution to the treatment of inorganic wastes which may contain additional organic contaminants. Industrial adsorbents such as activated carbon and organophilic clays have shown promise as pre-solidification agents for organic waste components but their use beyond the pilot scale has yet to be validated, as have the long term effects of weathering on the final waste forms. Adsorbents have,

nevertheless, been used commercially in the US but documentation is poor and the composition of many such materials is subject to commercial confidentiality thus hindering a rigorous assessment of their mode of action. They are, in addition, often expensive and their use would undoubtedly incur a cost penalty to the S/S process, although this may become of limited importance in an era of rising costs for all waste disposal options. The search for low-cost alternatives is therefore an area requiring further investigation.

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PRELIMINARY EXAMINATIONS OF MECHANISTIC CONTROL IN THE SOLIDIFICATION OF FLUE GAS DESULPHURISATION SLUDGE AND PULVERISED FUEL ASH

SIMON J.T. POLLARD[1#*], COLIN D. HILLS[2] AND JANE KENNEDY[1]

[1]Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, Scotland, EH9 3JJ, UK
[2]Environmental Geoscience Group, Geomaterials Unit, School of Engineering, Queen Mary and Westfield College, London E1 4NS, UK

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ABSTRACT

Cement-based solidification of pulverised fuel ash and flue gas desulphurisation waste is examined using mix designs adapted from a commercial process. Monoliths augmented with up to 3.75%^{w}/w Portland cement exhibited dimensional stability and unconfined compressive strengths exceeding 2 MPa at 84 days set. Total aqueous-extractable metals of 0.1-1.7 mg l^{-1}, determined using rapid dynamic leach tests, indicated minimal, but progressive removal of cationic species from solidified waste forms at 7, 28 and 84 days. Distinction between the mechanistic processes of solidification and cation fixation is evidenced by microstructural investigations suggesting that well-developed ettringite crystallites, formed in the presence of available sulphate, are instrumental in controlling the leachability of metals from waste matrices.

Key words: Solidification/stabilisation, pulverised fuel ash, flue gas desulphurisation, waste, sulphates

INTRODUCTION

Cement-based stabilisation/solidification (S/S) refers to a range of physico-chemical treatment processes that utilise pozzolanic agents or binders such as silicates, ordinary Portland cement (OPC), pulverised fuel ash (PFA) and ground granulated blast furnace slag (GGBFS) for the pre-treatment of inorganic waste sludges prior to landfill disposal (1). These processes have an established record of application in Europe and the USA, albeit a controversial one due to incidents in which treated wastes have failed to 'set' into their intended monolithic masses (2,3).

Central to a rational understanding of the chemistry of S/S processes is the ability to distinguish, at both the microstructural and molecular levels, between the mechanistically distinct processes of stabilisation and solidification. 'Stabilisation' refers to the *chemical* complexation of waste constituents within the cementitious form whereas 'solidification' infers the *physical* entrapment of wastes within the set monolithic mass. Waste components that are not both stabilised *and* solidified within the processed matrix may become mobilised in time and pose a threat to groundwater quality. With the recent tightening of international regulations on landfill practice and a developing focus on leachate composition and control, S/S systems are now being applied to a wide range of wastes that may otherwise have received disposal without pre-treatment. These include mixed organic/inorganic industrial wastes, soils contaminated with toxic metals and organic constituents, incinerator residues and bulk wastes from the power generation industry (4,5). In certain cases, this diversification has highlighted process difficulties associated with specific types of waste. A re-evaluation of the fundamental technical and scientific viability of

Currently Senior Environmental Chemist, Aspinwall & Company, 31 Rutland Square, Edinburgh, EH1 2BW, UK.

S/S treatment has therefore been initiated in the research literature (6-8).

Residues from power generation and flue gas emission control are not strictly regarded as hazardous. The rationale for their treatment by S/S is a desire to chemically fix potentially leachable metals in these wastes prior to direct landfill or conversion into constructed mounds. Combined disposal of flue-gas desulphurisation (FGD) sludges and unmarketable PFA either direct to landfill, or as gypsum/PFA/cement blocks for artificial marine reef construction is currently practised. In the US, for example, the proprietary "Poz-O-Tec" process is in widespread use and typically involves addition of 0.5-1.0 part PFA to 1 part FGD sludge with ≤ 4%^{w}/w lime (for pozzolanic activity in low-lime PFA). In the UK, an adaptation of this process for the conversion of PFA and FGD wastes to monoliths suitable for marine reef construction is reported by Billinge *et al.* (9). The latter system involves augmentation of the matrix with 5-10%^{w}/w OPC for strength enhancement and resistance to attrition and sea water exposure once in place.

Research studies into the S/S of PFA and FGD sludges suggest that well-designed and quality controlled formulations can produce monoliths with suitable geotechnical characteristics for landfill, though abrasion resistance and long-term stability considerations remain unaddressed. Examination of the bulk structural properties of sludges solidified with PFA (5) showed improved density and order of magnitude reductions in permeability with cure time. Replication of commercial mix designs (10) demonstrated negligible leaching of metals from solidified model wastes over an initial 30-day period. Many studies, however, fail to account for the void structure inherent to gypsum and PFA, differential hydration rates between primary constituents or the documented attack of high levels of available SO_4^{2-} on OPC, any of which could have significant implications for the long-term stability and fixation properties of solidified wastes.

In acknowledgement of the documented capacity of metals to leach from fly ash (11, 12) and the incompatibility of SO_4^{2-} with OPC concrete (13), the following study presents initial results on the underlying chemistry of the combined disposal process, using authentic mix designs, with the objective of examining the relationship between structural integrity of solidified products and the microstructural interactions occurring during and following hydration.

EXPERIMENTAL

Materials

Representative portions of BS 3892 Class 2 PFA were sampled from the precipitator at Cockenzie power station, Prestonpans, East Lothian. Fresh, dry OPC was obtained from Blue Circle Industries and kept airtight prior to use. Simulated FGD sludge was prepared as required using 1:1 $CaSO_4 \cdot {}^{1}/_{2}H_2O$ (BDH, UK) and deionised water (MilliRO; mean resistivity 18 MΩ), mixed for 20 secs in a rotary mixer. All remaining reagents were supplied by at analytical grade unless specified otherwise. Glassware was acid-washed in 10%^{v}/v HNO_3, 10%^{v}/v surfactant and deionised water prior to use. Low-iron sand (FSA) (40-100 mesh) was used as an inert filler as required.

Materials were analysed by X-ray fluorescence using a Phillips PW1480 XRF spectrophotometer at 50-80 kV and tungsten filament at 30-50 mA current. PFA was further analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) for the detailed analysis of acid-extractable (HCl/HNO_3) metals. The composition of the primary oxide constituents and extracatble metals is detailed in Table 1. Discrepancies between XRF and ICP-OES determinations of PFA metal content are reflective of sample preparation, with acid-digestable metal contents (ICP-OES) consistently reporting higher than concentrations determined directly form the solid matrix by XRF.

Mix Design

The mix design, adapted from the optimised formulations reported by Bishop *et al.* (10), is depicted in Figure 1. Cement mixes utilise a minimum OPC contribution to achieve desired compressive strength of > 350 kPa. PFA and lime contributions were kept constant at 22.5 %^{w}/w and 2.5 %^{w}/w, respectively, throughout. Mixes 3,4,5,6 and 11 represent decreasing amounts of OPC (5, 3.75, 2.5, 1.25 and 0 %^{w}/w) added to the matrix with the series repeated for sand in mixes 7,8,9,10 and 11. Controls 1, 2 and 11 represent mixes without $CaSO_4 \cdot {}^{1}/_{2}H_2O$, PFA and OPC, respectively. All mixes were made up to 50 %^{w}/w in total water and were 50 %^{w}/w in total inorganic solids content. Cement mixes 3-6 had water/cement ratios of 10.0, 13.3, 20.0 and 40.0:1.0, respectively.

Table 1. Major oxide and trace metal composition of reagents (after 9, 11).

component (%w/w)	UK range (XRF)	PFA (XRF)	PFA (ICP†)	Sludge (XRF)	OPC (XRF)	Sand (XRF)
SiO_2	47-52	36.6			20.5	
Al_2O_3	27-32	27.4			5.0	
Fe_2O_3	7-14	7.1			3.3	
MgO	1.5-5.0	0.8			2.8	
CaO	1.0-2.0	1.7			63.8	
Na_2O	1.0-2.0	0.1			0.0	
K_2O	0.5-1.5	0.6			0.6	
TiO_2	0.8-1.2	1.2			0.2	
MnO		0.05			0.1	
P_2O_5		0.8			0.1	
($\mu g\ kg^{-1}$)						
Cr	113	172±5	32.59	<DL	53±5	<DL
V		425±5		30±5	92±5	<DL
Cu	163	274±10		<DL	43±10	<DL
Zn	173	904±1	501	5±1	80±1	1±1
Sr		1836±1		1202±1	1422±1	<DL
Rb		32±1		<DL	28±1	1±1
Zr		320±1		15±1	75±1	23±1
Nb		22±0.5		<DL	3.9±0.5	0.3±0.5
Ba		1261±10		31±10	276±10	16±10
Pb	133	839±1	474	1±1	37±1	<DL
La		130±5		<DL	19±5	<DL
Ce		273±5		14±5	40±5	6±5
Nd		137±5		<DL	17±5	<DL
Y		104±1		<DL	16±1	<DL
Mo	17	14±1	10.7	1±1	4±1	<DL
Ni		341±5	149	<DL	52±5	<DL
Cd	7		3.92			

†HCl/HNO_3 extractable; <DL below detection limit

Required amounts of sand, PFA and free water were added to simulated FGD sludge and the constituents homogenised using a rotary mixer for 4 minutes. Monoliths for unconfined compressive strength testing, leaching studies and microstructural examination were prepared from 2.0 kg batches in 9 170 cm^3 polycarbonate moulds (66 mm height x 57 mm o.d.) pretreated with PTFE mould release to aid removal. Following initial set, moulds were sealed in polythene bags and left to cure in a relative humidity of 100% prior to microstructural examination. Moisture contents and mix densities were recorded at 7, 28 and 84 days cure.

Unconfined Compressive Strength

Initial set was determined up to 7 days using a hand-held pocket penetrometer (ELE International). Unconfined compressive strength (UCS) measurements were performed on cylinders in triplicate at 7, 28 and 84 days curing (100% RH, 20±2°C) using a calibrated Avery W&T compression apparatus (Model 7104DC) fitted with a 200 kN load cell on its most sensitive setting. Loads were recorded at the point of fracture and converted to kPa for the 57 mm cylinders.

Leaching Procedure and Metals Analysis

A distilled water-shake extraction procedure was adapted from the ASTM Leaching of Waste Materials Test, Method A (14). This rapid dynamic test is designed to determine the immediate surface washing and time-dependent, diffusion-controlled contributions to leaching. The procedure is not vigorous and involves only gentle contact of the leachant with the sub-sample. Mixes were evaluated in triplicate on

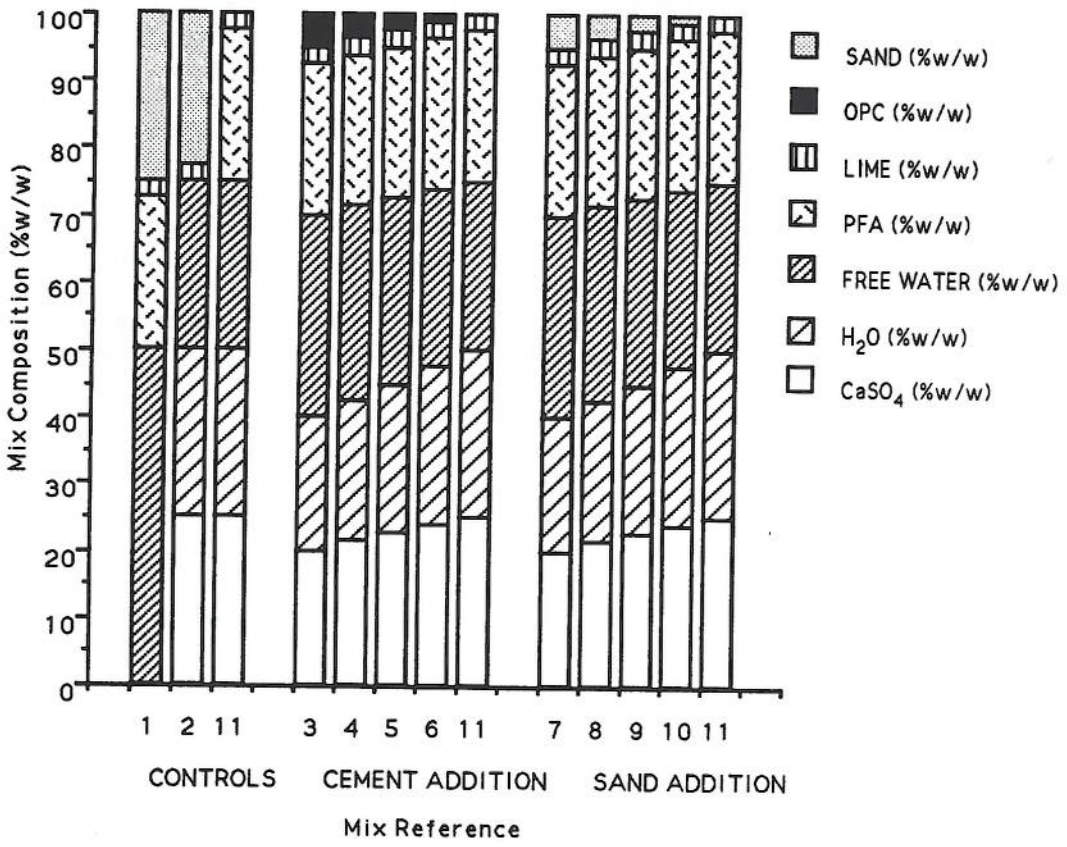


Figure 1. Mix design for study of the combined disposal of FGD and PFA.

account of a reduced sample size. Three 20.0 g sub-samples of each mix were placed in separate 150 cm^3 conical flasks. 80 cm^3 of deionised water was added, the flasks covered with parafilm, capped with aluminium foil and then shaken simultaneously at 20±2°C for 24 hrs. at 65 one-inch strokes per minute on a shaker bath (Grant Instruments, Model SS40-2). Aqueous leachates were vacuum filtered through a 45μm cellulose nitrate membrane, the pH monitored and leachates analysed in quadruplicate by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a calibrated Thermo-Jarrel Ash instrument (Model ICAP 61E) with a flush time between samples of 20 secs.

Microstructural Analysis

Thin plane sections (1-2 mm) of solidified pastes cured for 7 and 28 days respectively, were prepared between the cleaned surfaces of PTFE-lubricated microslides. At 84 days cure, representative fractions were taken from the centre of solidified monoliths, avoiding edge effects. Fractured (crushed) and plane surfaces of cured pastes were presented on areas of double-sided adhesive tape (0.5 cm x 0.5 cm), mounted on the methanol-cleaned surface of a aluminium microstub. Stubs were gold coated for 5 minutes (Emscope, UK) and examined by SEM at selected magnifications to enable examination and characterisation of various hydration features using a Cambridge Stereoscan S250 instrument under an operating voltage of 10 kV. Representative sections of surface were recorded and developed on monochrome paper (Ilford FP4).

Finely ground (<150 μm) portions of cured paste at 7, 28 and 84 days were examined by XRD for crystallographic composition. 10 g of each sample was dried, a 2 g sub-sample packed into an X-ray slide and then scanned using Cu-Kα radiation between 2θ of 3-65° at 1° min^{-1} on a Phillips PW1730/10 powder diffractometer using an generating voltage of 50kV (25 mA).

RESULTS AND DISCUSSION

Initial Matrix Set

Figure 2 illustrates initial set for control mixes 1,2 and 11. Clearly the bulk of initial strength is provided by rapid set of the simulated FGD sludge as evidenced by the improved strengths of controls 2 and 11 compared with matrix 1 without sludge. The accepted mechanism is the expansive and exothermic hydration of hemihydrate ($CaSO_4 \cdot {}^1/_2\ H_2O$) to form the crystalline gypsum ($CaSO_4 \cdot 2\ H_2O$) matrix. The structure is reportedly cleaved with ease by rupture of intermolecular hydrogen bonds between adjacent waters of crystallisation (15). As a consequence, the aqueous phase SO_4^{2-} concentration plays a key role in controlling metal solubility along with OH^- from evolved portlandite as in conventional cement-based stabilisation.

Addition of OPC to the matrix has the effect of improving the mid-term UCS, as evidenced in Figure 3. Seven and 28 day UCS values are

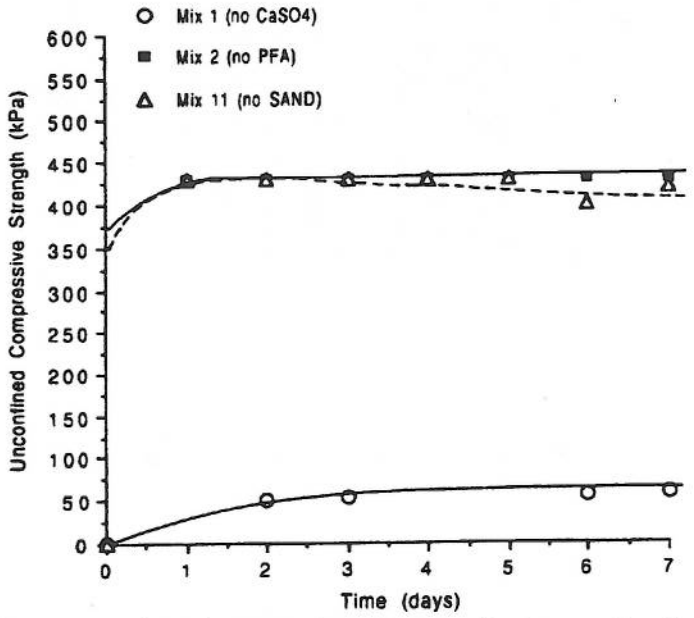


Figure 2. Initial set 0-7 days for control mixes 1, 2 and 11.

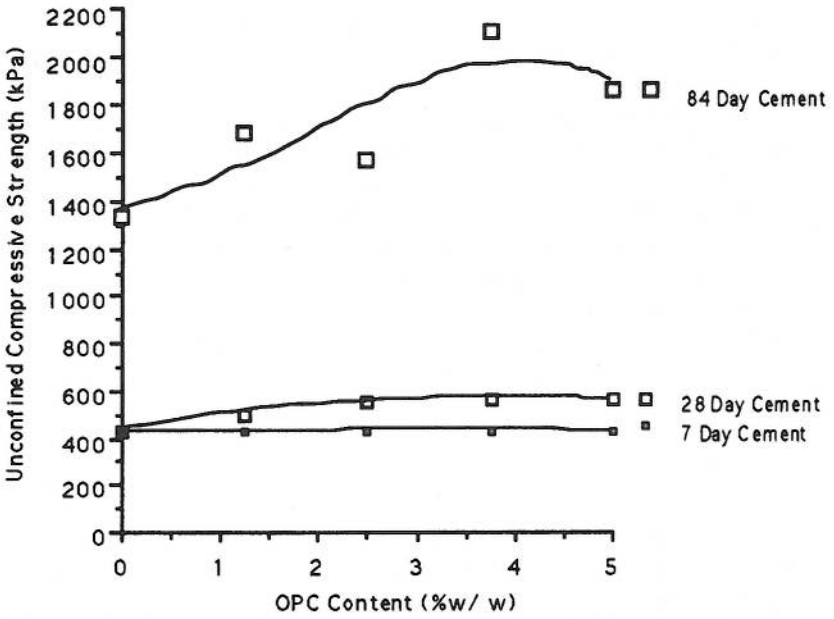


Figure 3. Relationship between OPC content (mixes 3-6 and 11) and UCS at 7, 28 and 84 days.

comparable to those obtained by Bishop *et al.* (10) and exceed the suggested, though modest, strength criterion of >350 kPa (10, 16) inferring geotechnical suitability of monoliths for landfill. UCS values at 84 days (Figure 4a-c) exceed the criteria for both the cement and sand (inert filler) series suggesting that sufficient strength is attained by gypsum and pozzolanic PFA/lime reactions alone, with OPC providing > 2-fold improved UCS (> 2MPa) at the 3.75 %^{w}/w addition. Further addition of OPC (Figure 3) at 5 %^{w}/w resulted in a slight decrease in UCS and may be related to expansive ettringite formation following product hardening as discussed below.

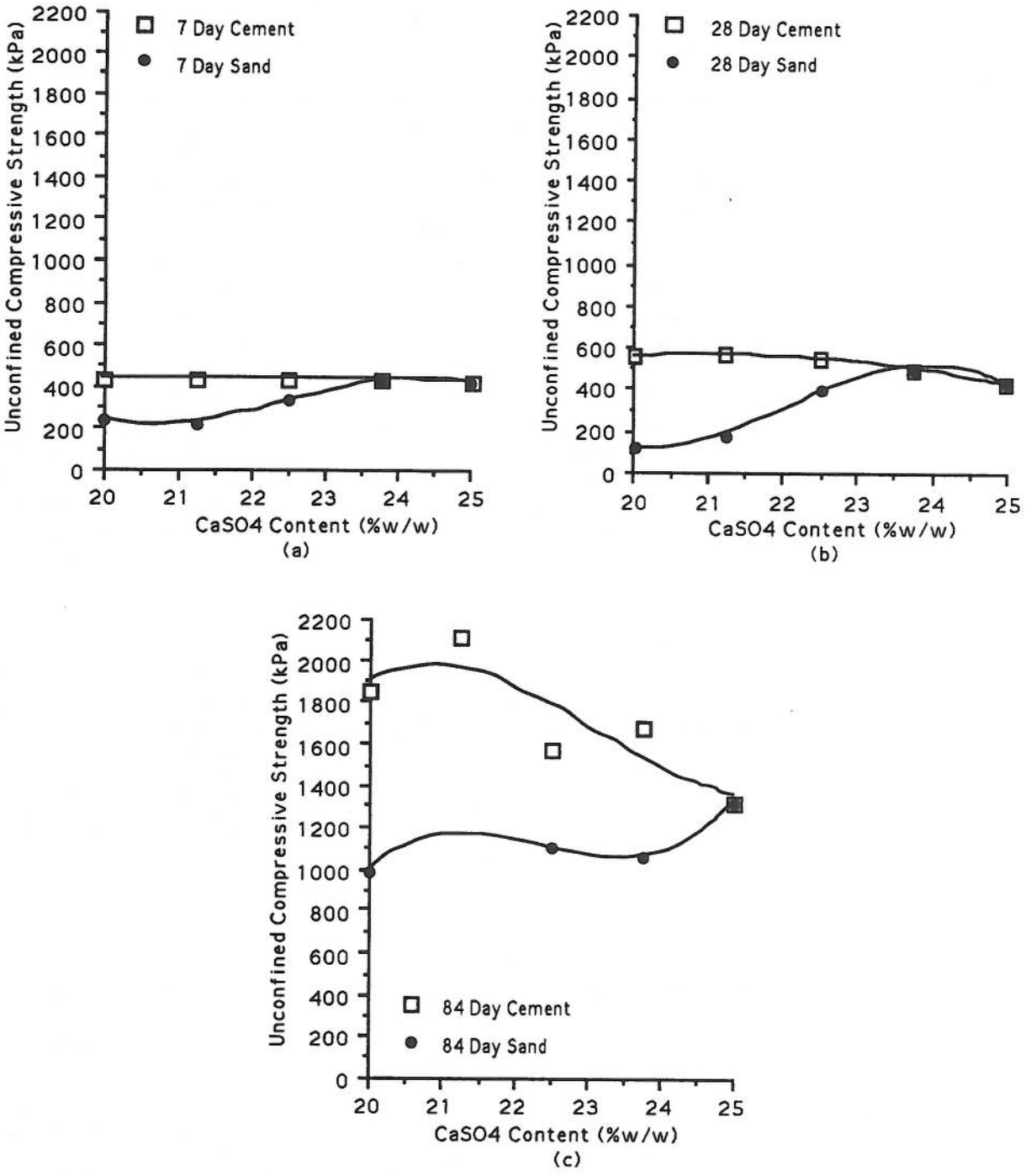


Figure 4. Relationship between FGD sludge content and UCS for OPC and sand mix sets at (a) 7; (b) 28; and (c) 84 days set.

Metal Leaching

Initial inspection of the leachable metals (Figure 5a-c) and monolith density data (Table 2) demonstrates a distinction between the mechanistic processes of physical solidification and cation stabilization occurring within set waste forms. Total metal concentrations in leachates isolated from cement-augmented mixes are < 1.7 mg l^{-1} indicating that set monoliths can be regarded *at the initial point of set* as effectively 'inert'. However, extractable metal concentrations increase with time of set rather than decreasing as would be expected, indicating that fixation is not accomplished despite monoliths exhibiting dimensional strength. Figures 5a-c show leachable metals removed from set matrices at 7, 28 and 84 days, respectively. A review of Table 1 shows PFA to be the main source term of metals in the matrix. Significant contributions of Cr, V, Cu, Zn, Sr, Ba, Ce and Ni can come from OPC, though in the proportions used in this study the primary metals source remains PFA. Clearly, metals are leached from PFA in this rapid leaching procedure, as evidenced by the Ba contributions in Mix 1 leachates (no FGD sludge; Figure 5a).

Gypsum has an aqueous solubility at pH 7 of 2100 mg l^{-1} and supersaturation is well-recognised. In a sulphate-dominated system under equilibrium conditions, one would expect $SO_4^{2-}{}_{(aq)}$ to be instrumental in the precipitation of free cations with solubility products lower that that of $CaSO_4 \cdot 2\ H_2O$ (-log K_{sp} = 4.6). This includes most metals and is evidenced by the reduction in Ba concentrations on addition of hemihydrate to the mix design (Figure 5a; Mix 1 vs. Mix 11). For matrices in which portlandite is formed, $OH^-{}_{(aq)}$ increases in importance as a counter ion. Free cations are precipitated as their metal hydroxides, where appropriate, providing the pH is maintained at the solubility minimum. In general, metal hydroxides have log K_{sp} much lower than the corresponding sulphates and would be expected to precipitate preferentially in the presence of $OH^-{}_{(aq)}$ and $SO_4^{2-}{}_{(aq)}$. However, pH depression can occur in solidifying waste forms (Table 2) enabling the leaching of cationic species over time.

In this study, the ability of metals to leach from monoliths exhibiting dimensional stability is of significance to the long term environmental impact of solidified matrices once in place. This is particularly acute for waste streams that contain much higher concentrations of metal components than in this study. The significance of Mo, Se and As to the leachate profiles in this study is noteworthy because under alkaline conditions, this group of metals occur as their polyoxy anionic molybdates (MoO_4^{2-}), selenates (SeO_4^{2-}) and arsenates

Table 2. Moisture content, density of monoliths and leachate pH at 7, 28 and 84 days.

Mix Reference	Moisture content (%w/w)	Monolith density 10^{-3} (kg m^{-3})	Leachate pH
Days	7 28 84	7 28 84	7 28 84
1	ND	ND	10.20, 10.50, 10.20
2 CONTROLS	38.9, 36.2, 31.4	1.57, 1.57, 1.40	10.22, 10.05, 7.90
11	47.3, 45.1, 42.1	1.43, 1.44, 1.28	10.20, 10.49, 8.20
3	46.0, 44.2, 39.2	1.42, 1.44, 1.23	10.05, 10.40, 9.10
4	46.8, 44.6, 40.1	1.41, 1.43, 1.27	10.25, 10.40, 8.80
5 CEMENT MIXES	48.4, 43.6, 38.7	1.44, 1.44, 1.29	10.35, 10.40, 8.70
6	44.6, 44.5, 39.9	1.41, 1.43, 1.28	10.32, 10.36, 8.50
11	47.3, 45.1, 42.1	1.43, 1.44, 1.28	10.20, 10.49, 8.20
7	45.6, 46.6, 41.6	1.41, 1.42, 1.27	10.02, 10.41, 8.50
8	46.0, 48.2, 42.5	1.39, 1.40, 1.27	10.27, 10.46, 8.55
9 SAND MIXES	45.5, 44.7, 41.2	1.43, 1.42, 1.28	10.10, 10.40, 8.60
10	49.9, 44.6, 41.2	1.42, 1.42, 1.27	10.25, 10.42, 8.90
11	47.3, 45.1, 42.1	1.43, 1.44, 1.28	10.20, 10.49, 8.20

ND; not determined

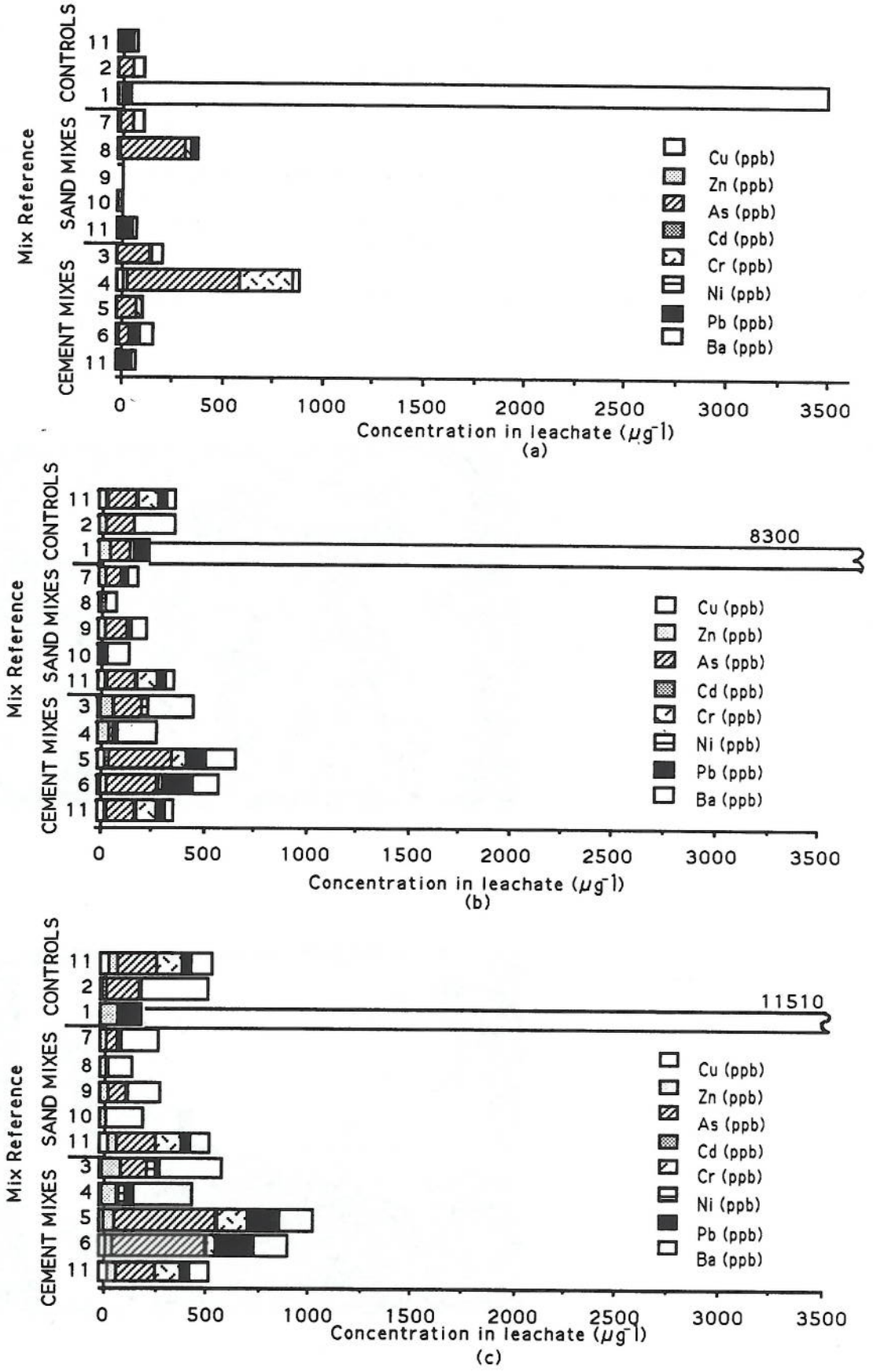


Figure 5. Leachate metal concentration profiles for controls, sand and OPC mix sets at (a) 7; (b) 28; and (c) 84 days set.

(AsO_4^{3-}) and by experience are poorly stabilised in the presence of OPC. These species are likely to become more easily mobilised with time.

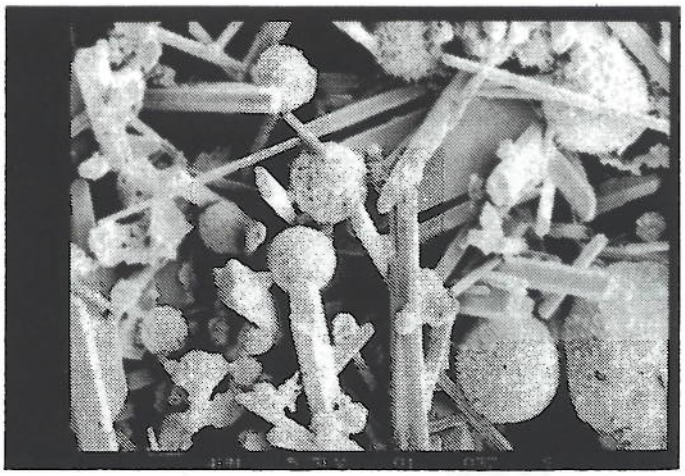
Microstructural Analysis

Illustrative micrographs of solidified pastes are given in Figures 6-8. The principle strength forming mechanism under study is the hydration of hemihydrate to gypsum [1] (Figure 6a), which is in equilibrium with the recrystallisation of gypsum from pore solution [2].

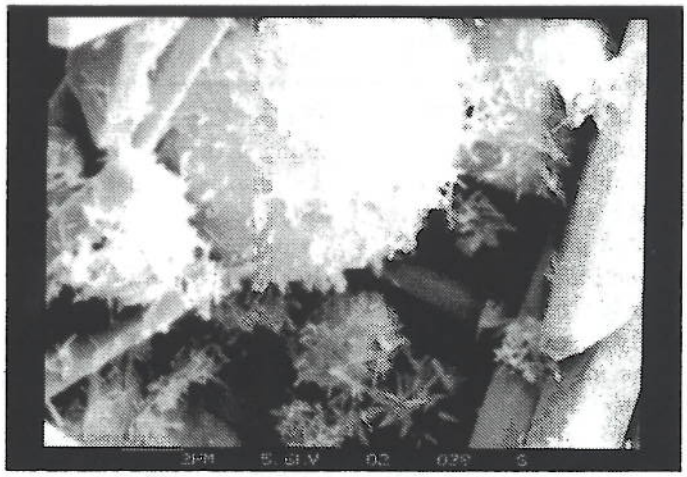
$$CaSO_4 \cdot {}^1/_2H_2O + {}^3/_2H_2O \rightarrow CaSO_4 \cdot 2\,H_2O \quad (\equiv C\,\overline{S} \cdot H_2) \qquad [1]$$

$$Ca^{2+} + SO_4^{2-} + 2\,H_2O \rightarrow C\,\overline{S} \cdot H_2 \qquad [2]$$

On addition of PFA and lime, this reaction is further supplemented by the formation of ettringite [3,4] and, where appropriate, CH [5]. The surface of PFA cenospheres act as sites for topochemical reactions such as nucleation (Figure 6a, b), the precipitation of gypsum (17, [2]) and for adsorption of metal species (18). PFA can also improve the early age physical properties of mixes when OPC hydration is



(a)



(b)

Figure 6. SEM micrograph of hydrated matrix for Mix 11 at (a) 7 days; and (b) 28 days set.

retarded or 'poisoned' by acting as a bulking agent and filler.

$$C_3A + 3\,C\overline{S}\bullet H_2 + 26\,H \rightarrow C_3A\bullet(C\overline{S})_3\bullet H_{32} \quad [3]$$

$$6\,Ca2+ + 2\,Al(OH)_4- + 4\,OH^- + 3\,SO_4{}^{2-} + 26\,H \rightarrow C_3A\bullet(C\overline{S})_3\bullet H_{32} \quad [4]$$

$$2\,C_3S + 6\,H \rightarrow C_3S_2H_3\,(\equiv \text{C-S-H}) + 3\,CH \quad [5]$$

As a general comment on the cement-augmented matrices, the marked increases in UCS resulting from the addition of OPC to FGD sludge / PFA mixes are not endorsed by visual signs of 'normal hydration'. Other processes, most notably enhanced ettringite development (Figures 7a-c) appear to play a key role and this is consistent with ettringite crystallisation [4] which progresses whilst sulphate remains available in the solution phase. This situation is analogous to massive ettringite formation in supersulphated cements and type K expansive cements [6] with PFA providing the additional source of Al_2O_3 (13).

$$C_4A_3\,\overline{S} + 8\,C\overline{S}\bullet H_2 + 6\,CH + 74\,H \rightarrow 3\,C_3A\bullet(C\overline{S})_3\bullet H_{32} \quad [6]$$

Figures 7a, b of Mix 3 taken at 7 and 28 days, shows PFA surrounded by small ettringites and euhedral gypsum crystals forming the interlocking matrix. Normal products of OPC hydration are clearly absent. In Mix 11, the control without OPC but with PFA (Figure 6b), ettringite development has progressed to a lesser extent as would be expected.

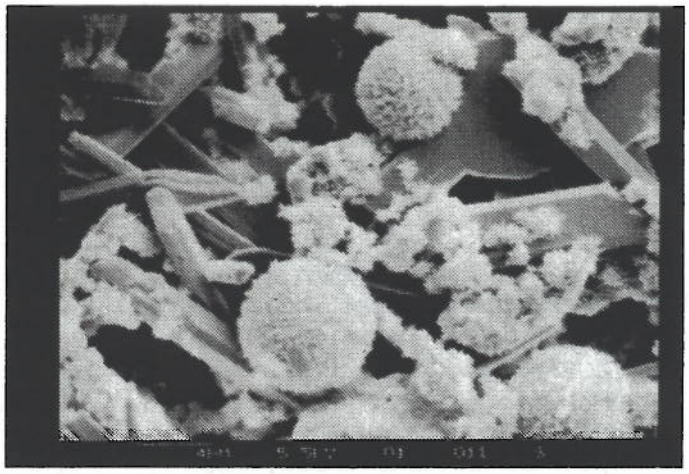
OPC contributes to the specific area available for nucleation and also to localised changes in pore solution chemistry via CH evolution. Initially Al_2O_3 dissolution from the anhydrous aluminate containing phases ($C_4A_3\overline{S}$) may be enhanced by localised pH conditions [4]. As the formation of ettringites continues on the surfaces of the cement grain, they may restrict further hydration because they develop as a thin solid, relatively impermeable, surface layer (19) and this may explain the absence of 'normal' hydration products in hydrated pastes.

The topochemical reactions identified in this work are known to be Al^{3+} concentration dependent and kinetically controlled. As a result, the sites of reactions may shift from one phase to another as illustrated in Figures 7a and 7b where the site of nucleation shows a clear shift from being gypsum dominated to being PFA based. Furthermore, the type of ettringite formed is also dependent on the pH of the nucleation surface. 'Small' ettringites (Figure 7a, b) form at pH greater than 10.7 (19). Over time, CH and $C\overline{S}\bullet H_2$ dissolve and $OH^-_{(aq)}$ is consumed resulting in localised regions of reduced pH (Table 2) with the concomitant growth and re-growth of ettringite [4,6] on cement grain surfaces producing elongated ettringite crystallites (Figure 7c). These conditions may eventually contribute to cation desorption and enhanced metal mobility.

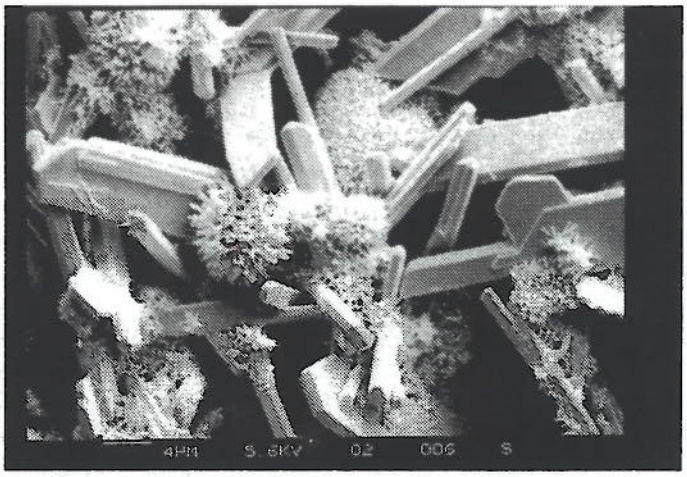
Kinetic factors are also of significance to the potential stability of FGD products solidified without OPC. Figures 8a and 8b, taken of Mix 10 at 28 and 84 days respectively, show dissolution of gypsum and renewed growth of ettringite. XRD reflections obtained for this mix (omitted for brevity) confirmed this observation with lowered intensities for CH and increased intensities for ettringite being recorded at later ages. Continued formation of significant quantities of ettringite after product hardening could, if the conditions are right, be expansive in both OPC and FGD-PFA systems and cause loss of strength and disruption of microstructure as implied by the strength data obtained from 5 $\%^w$/w OPC additions at 84 days (Figure 3).

An additional potential expansive reaction in authentic FGD wastes, not covered to date by this work, is the oxidation of sulphite in non-regenerable FGD residues to sulphate. Percentage conversions of sulphite to sulphate in non-regenerable lime and limestone wet scrubbing FGD processes range from almost 0-40% with typical conversions of 25% (20) hence the reactivity, morphology and fate of unoxidised sulphite clearly warrants investigation.

Our results are consistent with recently proposed mechanisms for interference of OPC hydration (2, 21). These can be classified into early and medium/long term effects. Early age effects limit immediate development of conventional hydration products whereas medium/long term effects result in phase changes that influence the temporal stability of the limited hydration products that do form. Mechanisms of interference include: (a) formation and stabilisation of expansive phases such as ettringite ($C_3A\bullet(C\overline{S})_3\bullet H_{32}$) and gypsum ($C\overline{S}\bullet H_2$) by certain organic waste components; (b) inhibition of portlandite (CH) precipitation by certain organic constituents; (c) 'poisoning' of gel products (C-S-H / CH solid phase) by certain inorganic species e.g. Zn^{2+}, CN^-, rendering the gel impermeable to normal hydration reactions; and (d) formation of 'false set' products such as precipitated salts that may dissociate during subsequent changes in matrix porewater chemistry/pH conditions.



(a)

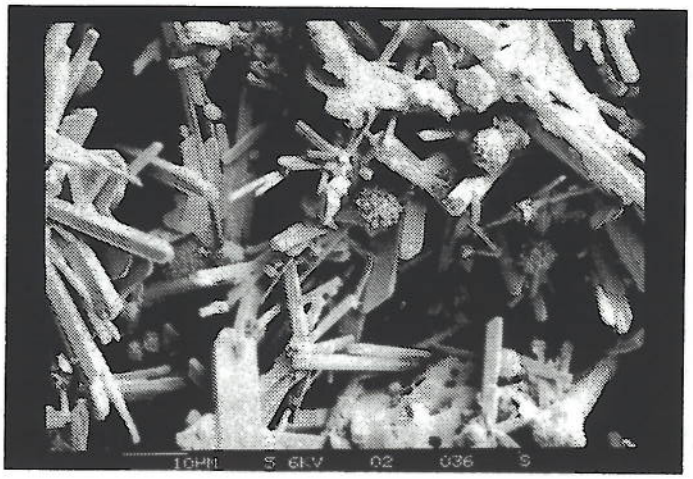


(b)



(c)

Figure 7. SEM micrograph of hydrated matrix for Mix 3 at (a) 7 days; (b) 28 days; and (c) 84 days set.



(a)



(b)

Figure 8. SEM micrograph of hydrated matrix for Mix 10 at (a) 28 days; and (b) 84 days set.

CONCLUSIONS

Combined disposal of PFA and FGD wastes using up to 5%^{w}/w Portland cement can produce monoliths with suitable geotechnical characteristics for landfill. However, examination of leachable metals from cement-augmented waste forms revealed that whilst dimensional stability was achieved, low concentrations of metals leached progressively from waste forms over time. This clearly demonstrates the distinct nature of stabilisation and solidification processes at the microstructural level.

The central role of pH, available SO_4^{2-} and the specific types of ettringite prevailing within the solidified matrix may explain observed differences in the leaching behaviour of individual cations, although a more detailed investigation is warranted. 'Small' ettringites adsorb significant quantities of water on their surfaces. Not only are these types the most expansive (22), but their crystalline surfaces offer preferential sites for cation substitution (23). 'Larger', more developed ettringites are produced over time where aqueous SO_4^{2-} and Al^{3+} concentrations are higher and these have a lower surface area, adsorb less water and prefer lower pH conditions. Hence, metals substituted in small ettringites may become liberated with ettringite development and concomitant pH depression. This initial findings underscore the

need for pH control and monitoring during the processing and placement of solidified monoliths. Future work will now focus on formation of metal-substituted ettringites and their solubility behaviour as a function of pH.

ACKNOWLEDGEMENTS

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NOMENCLATURE

C_3A:	tricalcium aluminate
$C_3A \bullet (C\bar{S})_3 \bullet H_{32}$:	ettringite
C_3S:	tricalcium silicate, 'alite'
$C_4A_3\bar{S}$:	anhydrous aluminate
$CaSO_4 \bullet 1/2\ H_2O$:	hemihydrate
$C\bar{S} \bullet H_2$:	$CaSO_4 \bullet 2\ H_2O$, gypsum
CH:	$Ca(OH)_2$, portlandite
C-S-H:	calcium silicate hydrate
H:	H_2O, water
S:	SiO_2
$\bar{S}$:	SO_3

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The influence of interference effects on the mechanical, microstructural and fixation characteristics of cement-solidified hazardous waste forms

Colin D. Hills [a,*], Simon J.T. Pollard [b]

[a] *Research Fellow in Cementitious Systems, Concrete Durability Group, Department of Civil Engineering, Imperial College of Science, Technology and Medicine, London SW7 2BU, UK*

[b] *Senior Environmental Chemist, Aspinwall and Company, Consultants in Environmental Management, 13 Melville Street, Edinburgh EH3 7PE, UK*

Abstract

The hydration behaviour of ordinary Portland cement (OPC) and other hydraulic binder systems in the presence of industrial wastes considered "suitable" for cement-based solidification is not always consistent. Waste-binder interference effects can significantly alter the short and long term mechanical, microstructural and binding characteristics of solidified waste forms containing materials from a wide variety of waste streams. In general, the mechanisms of interference can be explained and this lends support to the need for a critical evaluation of current waste form quality control procedures and the development of additional pre-treatment/alternative treatment methods. Future research studies including the in-situ examination of waste forms together with an in-depth quantitative analysis of the effects of waste species on the short- and long-term properties of solidified products is warranted. © 1997 Elsevier Science B.V.

Keywords: Cement-solidified waste; Waste–binder interference

1. Introduction

1.1. Background

Cement-based stabilisation/solidification (S/S) technology is one of several treatment technologies for industrial residues and contaminated land [1–3] and is widely

* Corresponding author.

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used in North America in this respect [4,5]. Ordinary Portland cement (OPC) is often used as the binding agent on its own, or in combination with cement replacement materials [6], which may be hydraulic (cement kiln dust) or pozzolanic (pulverised fuel ash, slag etc.) in nature. Initially designed for the chemical fixation and encapsulation of electroplating sludges and radionuclide wastes, S/S systems are now being applied to a wide range of wastes that may previously have received disposal without pre-treatment. These include mixed organic/inorganic industrial wastes, soils contaminated with toxic metals and organic constituents, incinerator residues and bulk wastes from the power generation industries [7,8]. In many cases this diversification from the origins of the technology has highlighted the process difficulties associated with specific waste types. A fundamental re-evaluation of the evidence from the research literature [9–12] has on occasions conflicted with the claims of commercial S/S operators.

Central to a rational understanding of the chemistry of S/S processes is the ability to distinguish, at both the microstructural and molecular levels, between the mechanistically distinct processes of stabilisation and solidification, and to place research data in the context of field application [3,11].

1.2. Performance monitoring

The test methods used to assess cement-solidified wastes vary [12] but are generally based upon setting and strength development (solidification) and the application of a leaching test to assess the extent of fixation (or stabilisation) of waste-borne elements. Common test methods have been evaluated and reviewed elsewhere [13,14]. Leach tests are invariably accelerated examinations of waste stability and are usually aggressive in an attempt to compensate for their short duration and thus provide conservative assessments of leaching performance that are protective of environment. Leachants such as distilled, de-ionised water and dilute acids are used for this purpose and the results obtained provide an assessment of the extent of waste stabilisation effected during processing and the capacity of binding agents to "neutralise" aggressive leachants. However, because they are accelerated tests, leach tests rarely relate to actual ground conditions at the intended site of disposal, and should instead be regarded as comparative performance tests under standardised conditions. This is a critical factor for consideration when assessing the long-term stability of waste forms from short term tests [15,16]. Furthermore, these mass balance assessments of stabilised waste forms rarely account for the effect of proton activity (pH) on the speciation of inorganic components, some of which may exhibit wide variations in behaviour between valence states (e.g. As(V) As(III), Cr(VI), Cr(III) or ionised forms (NH_4^+ vs. NH_3, CN^- vs. HCN), for example [17].

Effective containment of a waste involves an interaction of both physical and chemical mechanisms. Whilst effective physical containment is regarded as an essential pre-requisite of any process, and a significant factor governing leaching and long-term performance also relies heavily on the chemical fixation of encapsulated species. When cement is used, for example, these include, sorption, precipitation and lattice inclusion [16]. Where binders are employed, a direct relationship exists between a binding agent and the immobilisation mechanisms at work and this criteria should govern the choice of

a binder on technical grounds. Factors such as adsorption, absorption etc. are of importance as are the availability and cost of materials and the perceived public acceptability of OPC-type binders, together with the reported ability of OPC to hydrate in the presence of a variety of inorganic waste species. These factors have made hydraulic binder systems based on OPC a popular choice and are reviewed on a scientific basis by Macphee and Glasser [18].

The continuing need to develop economic and improved waste management techniques has increased the potential importance of solidification technology throughout the world. This has been supported by increased research particularly from within the nuclear industry (for example, Wilding [19]). As a result, there is an increasing amount of information available that suggests that there are limitations on the suitability of hydraulic binders for this application (for example [11,20,21]). This appears to result from complex interactions with certain common waste-contained species and to the degree to which these interactions may influence the long-term field performance of solidified wastes.

The often loose relationship between the research literature and field application of the technology has been a perennial problem of the S/S. This is often in strict contrast to other remedial technologies such as bioremediation that appear to have developed effective means of translating research efforts into modifications in the field and vice-versa. In contrast, several authors have reported the inappropriate use of S/S for wastes with high organic contents on the grounds of hydration inhibition, yet oil-soaked sludges, petroleum wastes and organic solvents (see Malone and Lundquist for a review [5]) continue to be solidified with varying degrees of success. Such discrepancies between the laboratory and field work require urgent resolution if credibility for the S/S technology is to be sustained.

2. Process research

Portland cement-bound wastes have been examined in the laboratory by a number of workers. Importantly, few have clearly demonstrated that "normal" hydration reactions are taking place in waste–OPC mixtures. Another approach has been to add single compounds, or simple mixtures to OPC and examine the results. There is the tendency to over extrapolate these results to the solidification of real wastes. There is a major problem with this approach as:

1. Real wastes are invariably complex mixtures of compounds with often contrasting physical and chemical properties that are difficult to characterise;
2. The synergistic or antagonistic effects of multiple component mixtures significantly influence both hydraulic and pozzolanic reactivity, and these effects difficult to predict at the present time.

It is, therefore, inappropriate to assume that a compound will behave similarly on its own as in an admixture with other compounds. When cement-bound waste forms are setting and undergoing strength development, "normal" reaction mechanisms may not be taking place. This is a particularly important factor since "false set" reactions have been shown to be capable of producing rigidity in solidified products. This can be

mistaken for normal binder activity in cement-based systems with and without certain pozzolanic additions [10].

The following work describes selected results from a series of recent laboratory investigations in the use of hydraulic systems to solidify real waste materials using calorimetric, microstructural and mechanical methods of analysis. The objective of these studies has, in each case, been to bridge the divide between single component studies and real wastes and provide robust analyses of the mechanistic control in genuine S/S systems.

2.1. Structural development during solidification

The structural development of cement-based solidified wastes is claimed to result from complex hydration reactions that stiffen and densify the product and impart structural integrity [6]. The hydration reactions of OPC have been widely studied and are described in detail by Taylor [22]. The four main anhydrous phases, namely alite (C_3S) belite (C_2S), tricalcium aluminate (C_3A) and ferrite (C_4AF) hydrate at different rates. [1]

The dominant hydration phases under normal conditions are C–S–H, a gel of variable stoichiometry, and calcium hydroxide (CH) which together form some 90% w/w of the solid hydration products of an OPC paste [23] as discrete phases or as an intimate mixture. The remaining solid products are hexacalcium aluminoferrite trisulphate ''ettringite'' type phases (AFt) and tetracalcium aluminate monosulphate ''monosulphate''-(AFm)/C_4AH_{13} solid solution phase which may be accompanied by C_4AH_{13} or similar phases.

Bonen and Diamond [24] have shown that the composition of C–S–H is distinctive between that derived ''in situ'' from larger cement grains to that formed by smaller grains which infills porosity as amorphic or skeletal groundmass (mean gross Ca/Si ratios of 2.1, 2.3 and 2.8, respectively). Intimate C–S–H and CH mixtures are characterised by Ca/Si ratios of 1.7 to 1.8 and as both ettringite and monosulphate components may be associated similarly, the composition of this phase may appear to change wildly. This is an important factor for consideration when assessing the interactions of C–S–H with waste contained species.

In practice, the amount of cement used during commercial solidification may vary considerably depending on waste type, success at the pilot scale and cost. For example, cement contents varying from 5% to 20% w/w may be routinely used to solidify. The lower levels of cement addition cannot always be adequate enough to physically coat all the individual waste particles present in the solidifying mixture, but nevertheless, treated products tend to set and develop rigidity. This is generally assumed to be the result of physical changes induced by normal ''hydration processes'' despite the ability of ''false set'' mechanisms, such as the precipitation of salts like gypsum, to impart ''adequate'' strength [10,11]. These mechanisms also appear to be supplemented, in certain cases, by the results of atmospheric carbonation which hitherto has received only limited attention. This enhanced strength, however, must not be interpreted as effective solidification

[1] Nomenclature used in this work: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O.

Table 1
Strength development for increasing zinc plating waste additions

UCS (kPa)	Waste addition (% w/w as solids)		
	1	2	3
7 day	5196	2788	39
28 day	5837	4417	69

despite the fact that in certain cases, carbonation may prove to be beneficial in nature [25].

The strength requirements for solidified products in the UK, for example, are governed by the issue of a waste management licence by the controlling Waste Regulation Authority (WRA). A 28 day strength of 700 kPa is typical of that considered acceptable but criteria may be as low as 350 kPa depending on the circumstances of testing. For materials that may contain a cement content of 20% w/w, these strength requirements are surprisingly low despite the limiting effects of relatively high water/cement ratios. Even so, it is known that these strengths may not always be achieved and that solidified products sometimes require reprocessing before the required strength is met.

As a considerable number of chemical species are known to interfere with, or even completely disrupt OPC hydration, a reliance upon physical parameters alone to indicate

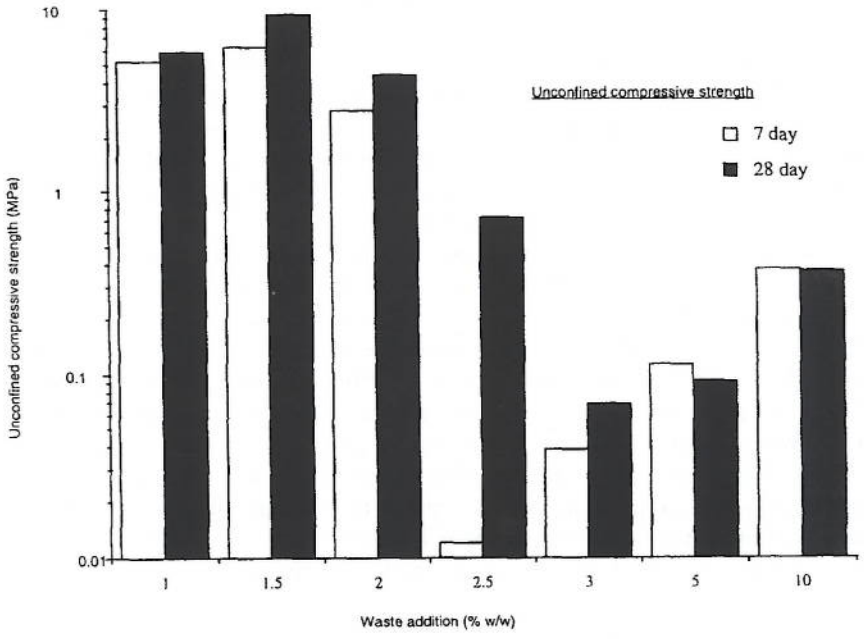


Fig. 1. Strength development for waste additons to OPC.

"normal" binder activity should be treated with suspicion. Indeed, as solidified products are expected to harden over a 2–5 day period [6] waste/binder interference and retardation effects must be a commonly accepted phenomenon.

A simple way of examining the effects of waste is by adding progressive quantities to OPC. Apart from the strength loss gained by dilution effects, the influence of waste on the development of physical and other parameters can be established. As seen during previous work [10], a severe strength loss could be observed at very low additions. For example, Table 1 shows 28-day strength development of Portland cement paste with increasing additions of a zinc-containing metal plating waste. At 3% addition (w/w total solids) a reduction in strength of approximately 99% of the OPC paste control was observed. Fig. 1 shows the general effect of increasing waste additions, as typified by a zinc/chromium plating residue on unconfined compressive strength (UCS). Fig. 2 shows the effects on setting, as defined by cone penetrometry, of waste forms containing increasing proportions of a commercially blended inorganic waste product produced from a variety of waste streams.

Nevertheless, the development of "short term" structural stability must also not be considered as a guarantee of long-term waste form properties. The potential for diverse and adverse chemical interactions between waste components and matrix may cause dimensional instability [26] resulting from the encapsulation of reactive metals, ion-exchange resins or potential expansive phases.

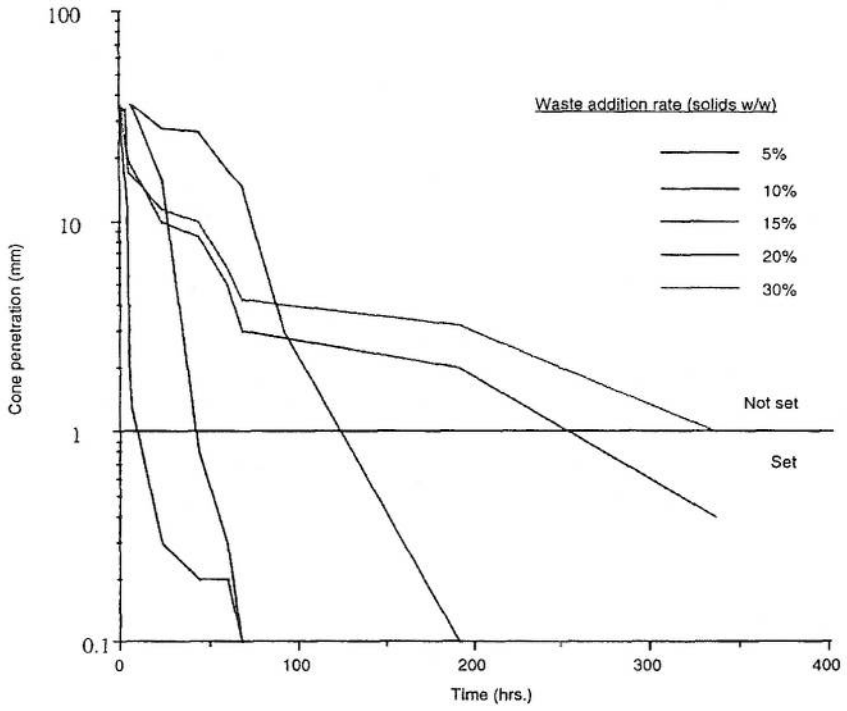


Fig. 2. Setting curves for waste addition to OPC.

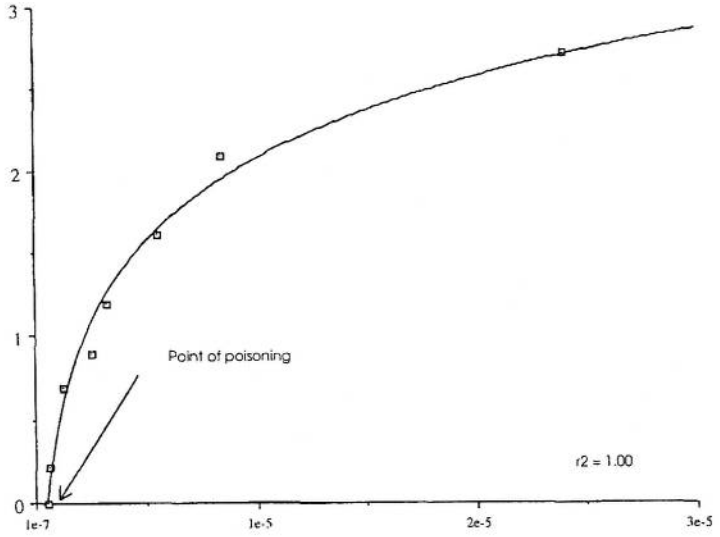


Fig. 3. Poisoning of hydration by waste additions.

2.2. Hydration of hydraulic binder systems

The hydration of OPC is exothermic and can be examined by isothermal conduction calorimetry. As hydration proceeds, a characteristic rate of heat is produced that is a function of composition, hydration efficiency of the system, temperature and other effects [27,28]. In general, however, the heat of hydration curve for OPC closely resembles that produced by C_3S and can be correlated to the amount of CH evolved [22].

Waste/OPC mixes tend to produce heat of hydration curves that are dissimilar to the pure hydraulic or blended binder systems. Often, as the waste content of a system increases, the main exotherm becomes less pronounced and broadens. At waste/binder ratios typically used during commercial operations, the main hydration exotherm may be absent and normal hydration is therefore indefinitely retarded. Fig. 3 illustrates these poisoning effects for a commercially blended waste stream containing materials derived from, for example, metal plating and finishing operations and laboratory residues containing a range of heavy metals. Here, the maximum rate of heat evolved, as defined by the gradient of the hydration curve, for incremental additions up to 30% w/w (solids) are plotted against time (in reciprocal seconds) taken for the maximum amount of heat to be evolved. Table 2 gives typical total heats recorded for a zinc and chromium

Table 2
Total heat of evolved at 120 h for increasing zinc plating waste additions

Waste addition (% solids w/w)	0	0.25	0.5	1.0	1.5	2.0	2.5
Total heat evolved ($kJ\,kg^{-1}$ solids)	291	302	285 [a]	280 [a]	182	144	20

[a] Extrapolated values.

containing plating waste during calorimetric analysis up to 120 h after mixing. The point of poisoning, where the main period of heat evolution is absent and indefinitely retarded, is also given in Fig. 3. This point, which corresponds to a particular waste addition, provides a convenient reference point to measure and compare the total heat produced by different waste products.

It appears normal to find that despite the drastic reduction in the total heat of hydration produced by poisoned solidified products a small, but measurable, rate of heat (0.02–0.04 $W\,kg^{-1}$ solids) can often be recorded indicating that limited reactions which are probably diffusion controlled may continue. A comparison between the total heats given in Table 2 for the 2 and 2.5% w/w waste additions can be used as an illustration. For OPC, for example, a typical heat of hydration of approximately 400 $kJ\,kg^{-1}$ can be realised at 28 days age where values of $< 70\ kJ\,kg^{-1}$ are typical for poisoned binder systems. It is worth noting here that the heat of hydration characteristics of poisoned systems can be largely reproduced in the laboratory by employing simple mixtures of, for example, heavy metal hydroxides [29].

2.3. Microstructural development of solidified waste forms

The microstructural development of solidified products results directly from the hydration of the binders used. Hydration processes cause densification, a reduction in permeability and can improve the ability of the product to combat aggressive conditions after disposal. On examination, cement-solidified wastes should ideally be expected to clearly display the products of hydration, but results may vary considerably contingent on the waste and binder used.

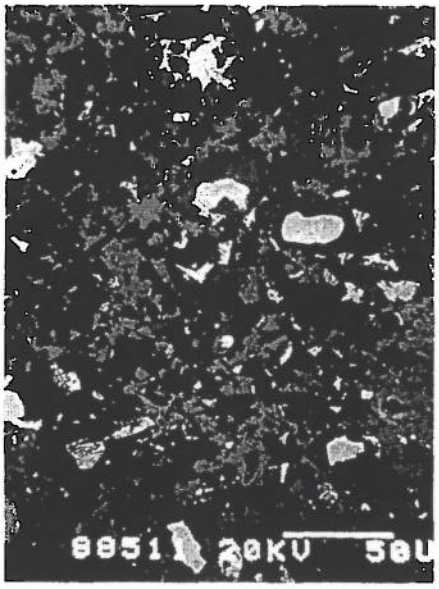


Fig. 4. Micrograph of solidified waste form (BSE image).

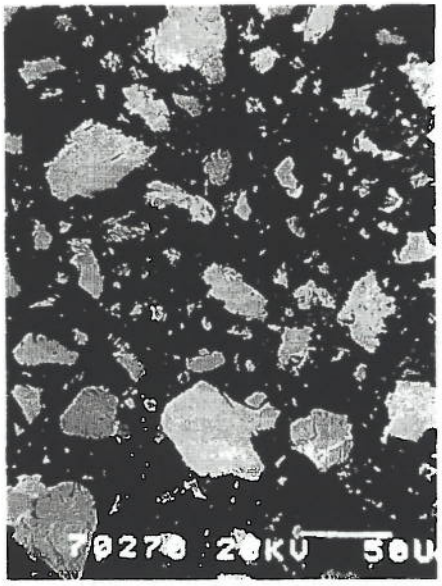


Fig. 5. Micrograph of waste form with hydration interference (BSE image).

The solid phase of hydrated cement paste is dominated by C–S–H gel which can be difficult to characterise by electron microscopic techniques. Other phases such as CH, AFt and CS are more crystalline. When present in solidified products, they are often found associated with voids owing to the relatively higher water contents of these materials.

By way of illustration, Fig. 4 shows a backscattered electron (BSI) micrograph of an OPC-solidified product containing a small quantity (0.25% w/w total solids) of a chromium plating waste. Porosity appears black, CH, infilling porosity as light grey, amorphic and skeletal C–S–H as dark grey and larger cement phenograins display characteristic white coloured unhydrated cores enveloped by a "shell of hydration product" [30]. In this instance, the product is characterised by an intimate mixture of waste enveloped by hydration products. Fig. 5, however, also shows a BSI image of a waste form containing a zinc/chromium plating filter cake and OPC from the same batch of cement at 56 days of age. Here, in the authors opinion, the overall degree of hydration, as defined by the average depth of hydration shells on larger phenograins was less as a result of interference effects. In addition, the degree of porosity occupied by C–S–H groundmass was also reduced, although some growth of AFt (not evident in this micrograph), owing to limited reactivity of the aluminate/ferrite cement phases, was observed [31].

It should be noted that in the study undertaken by Diamond and Bonen [30] the relative degree of hydration of adjacent cement grains in concrete at normal water/cement ratios was found to vary wildly. Nevertheless, solidified wastes which are affected by retardation and interference effects can display phenograins with an overall lower degree of hydration typified by reduced hydration shell thickness and a more open

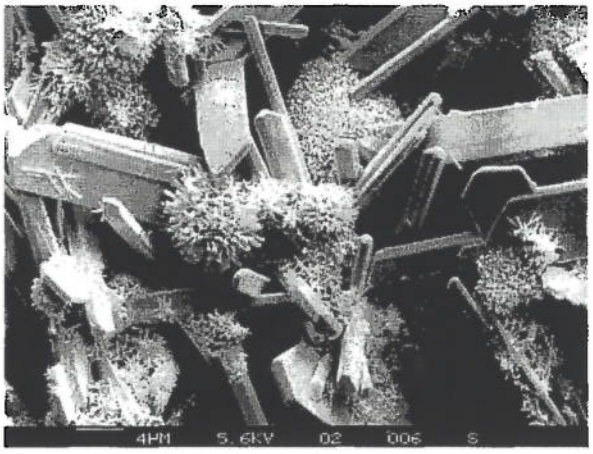


Fig. 6. Solidified FGD waste showing ettringite and euhedral gypsum development.

microstructure characterised by sparse and discontinuous skeletal and amorphic C–S–H gel distribution. These waste forms also have a lower than expected compressive strength, extended setting times and reduced total heats of hydration.

An additional example of waste specific effects is shown in Fig. 6. Here we illustrate the hydration products observed in stabilised (synthetic) flue gas desulphurisation (FGD) waste augmented with OPC [11]. Products of OPC hydration such as CH and C–S–H, as described above, are clearly absent and instead we see small ettringite and euhedral gypsum crystals surrounding PFA and forming an interlocking matrix. Here then, alternative enhanced ettringite development appears to play a key role in strength development consistent with ettringite crystallisation which occurs when sulphate from the FGD waste remains available in the solution phase.

X-ray diffraction techniques can be used to chart the progress of hydration of waste/binder mixes. CH, AFt, monosulphate and the original cement clinker phases can all be readily detected, although sometimes crystalline components of the waste may significantly complicate the diffraction patterns obtained. For example, during increasing addition to OPC of a mixed metal plating waste (zinc and chromium) known to poison hydration, the intensity of portlandite reflections obtained (d-spacing at 4.90 Å) decreased until resolution was no longer possible. At the same time, the intensity of peaks obtained for AFt decreased dramatically whereas the intensity of the reflections for C_2S (2.80 Å) and C_3S (2.76 Å) increased markedly indicating that the relative proportion of the anhydrous cement phases increased, as hydration became retarded, despite dilution effects. Fig. 7 illustrates this effect with reference to a solidified product containing material from the blended, commercially solidified, waste stream previously described. Fig. 8, however, further illustrates this effect in a plot of comparative X-ray intensities recorded for portlandite (CH) against 7 day UCS for a number of waste forms containing incremental additions of this waste material.

The mineralogy of laboratory-produced, OPC-based waste forms in which hydration has been indefinitely retarded is often characterised by the presence of AFt/AFm

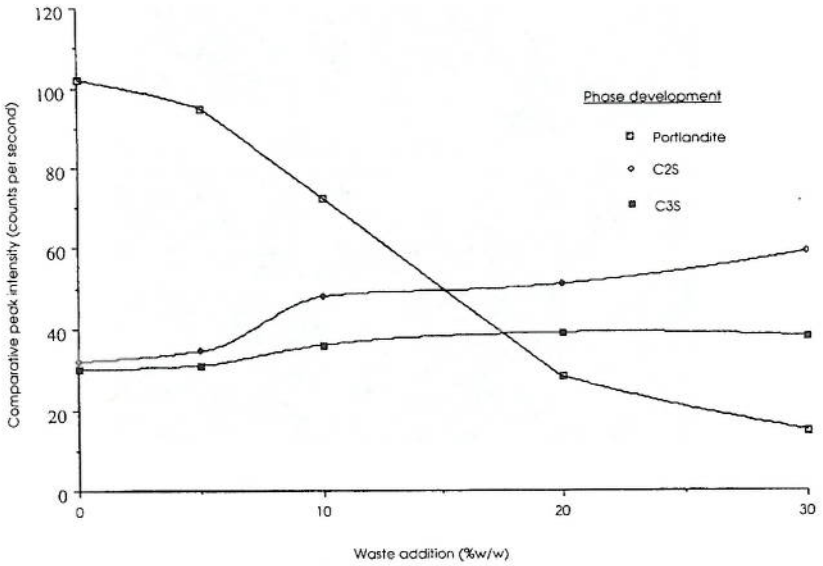


Fig. 7. Effect of blended waste additions on X-ray intensity for portlandite, C_2S and C_3S.

phases. In the absence of other phases, early age development ettringite "type" mineralogy may be largely responsible for the waste form properties at this age. At later ages, however, other phases of importance may result from diffusion-controlled reactions discussed above.

Therefore, inhibition of hydration by waste specific effects is of primary concern as it

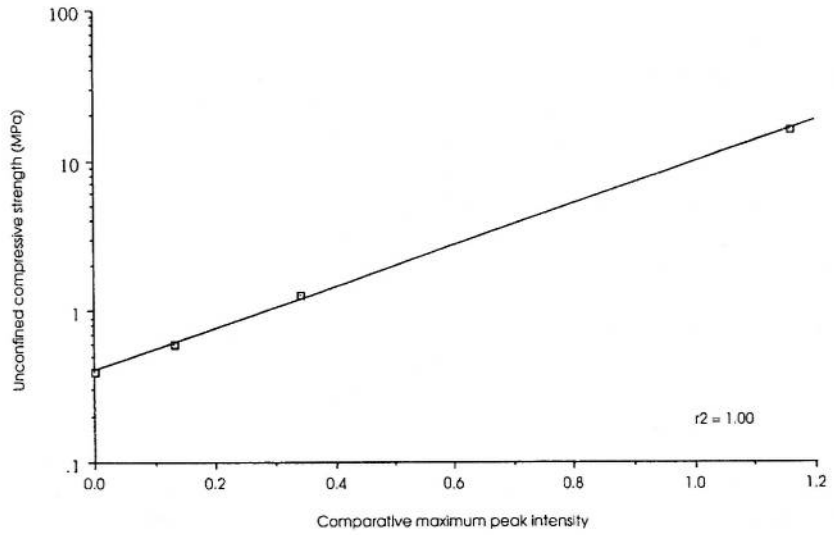


Fig. 8. Relationship between portlandite X-ray intensity and 7-day UCS.

can result in significantly impaired physical and leaching performance (e.g. such as that reported with copper and chromium sludges by Shin et al. [32]). It should also be noted that waste-dependent time effects have also been identified elsewhere [33] and that longer term changes in the microstructure and fixation capability in waste forms do occur; thereby reinforcing the view that current testing protocols cannot be used to reliably predict the longer-term properties and performance of waste forms.

2.4. Effect of carbonation of solidified waste forms

The influence of carbonation on the properties of solidified wastes has hitherto been largely neglected. Carbonation is capable of inducing setting and strength development in waste forms where hydration is significantly retarded. In addition, susceptibility of waste forms to carbonate may explain why, for example, some wastes may be more easily processed during summer months when warm temperatures and drying winds can facilitate carbonation. A similar effect may also explain why, in the authors experience, samples of cement-bound wastes sealed in plastic bags often appear not to set whereas companion samples exposed to laboratory conditions develop strength within a few days. Analysis by X-ray diffraction can be used to examine the enhanced development of carbonation but it should be pointed out, however, that alternative reasons for this phenomenon may also apply.

The process by which carbonation proceeds may also be different for different wastes and also dependent upon the severity of retardation of hydration. In general, the carbonation reaction may be expected to involve AFt/AFm, C–S–H gel and CH. The carbonation reaction undertaken by ettringite may be represented in Eq. (1) [34], whereas Eq. (2) shows that for CH. In Eq. (1), aluminium is not shown as transforming to gibbsite as might be expected. This probably represents the authors uncertainty as to whether the pure phase was formed. The carbonation of C–S–H may be expected to result in the production of silica gel and $CaCO_3$, which for the latter, could form in the sequence: vaterite, aragonite and calcite particularly if the degree of cement hydration is low [35].

Carbonation reactions for ettringite

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 3CO_2 \Rightarrow 3CaCO_3 + 3(CaSO_4 \cdot 2H_2O) + Al_2O_3 \cdot xH_2O + 20 - xH_2O \quad (1)$$

Carbonation of portlandite

$$Ca(OH)_2 + CO_2 \Rightarrow CaCO_3 + H_2O \quad (2)$$

The changes induced by carbonation can be expected to affect both microstructure and fixation characteristics of disposed waste forms. The pH and redox conditions within a waste form can expected to be significantly altered as carbonation proceeds. This could result in phase changes within the waste/binder system and in the extreme, changes in the fixation characteristics of the waste form which may result in the selective release of specific waste components [36]. Carbonation can also be expected to be a factor for consideration in waste forms disposed in open or partially buried environments, although

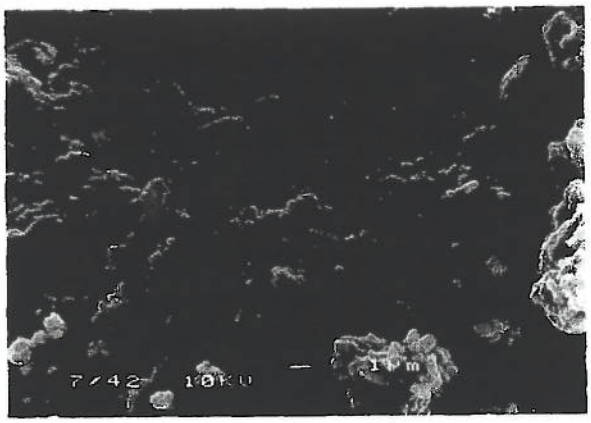


Fig. 9. Alite (C_3S) "rich" OPC displaying "gel" dominated microstructure.

the latter much less so. The influence of seasonal variations in groundwater levels and the possibility of CO_2 gas generation from both organic (e.g. from an adjacent sanitary landfill) and inorganic processes (waste/binder interactions) augmented by the effects of acidic ground conditions may yet prove to be important factors for consideration.

2.5. Binder chemistry and waste form properties

One cannot assume the mere presence of a hydraulic cement within a process formulation will provide adequate strength and fixation. Different cement and pozzolan systems may exhibit a wide variety of chemistries and even relatively minor changes in the anhydrous nature of binder systems can have significant effects upon the microstructural development of waste forms. For example, the alite content of Portland cement falls within the general range 50–70% w/w (Bogue analysis), aluminate and ferrite between 10 and 30% w/w with belite making up the balance. The micrographs, Figs. 9 and 10, show waste forms bound by "modified" OPC. Here, the aluminate and ferrite compositions were fixed and the alite and belite components were "adjusted" to vary between 24 and 50% w/w and 70 and 10% w/w, respectively. The micrographs clearly show major differences in the microstructure observed for the end members of the series at the same waste loading of 40% w/w.

Fig. 11 shows how cement type can influence early age properties of waste forms. Here contrasting shaped curves have been produced from plotting strength development against setting time for blended OPC and high alumina cement (HAC) for a range of waste additions (0–40% w/w) of a commercially blended waste stream. The products were produced with a fixed solids content of 55% w/w and examined for mechanical, microstructural and leaching properties. With the OPC-based binder, an increasing waste/binder ratio resulted in extended setting times and lowered strength. For HAC, however, as strength decreased with increasing waste additions, setting times which were defined by cone penetrometry were found to decrease markedly.

Shin et al. [32] have shown that the leaching properties of waste forms containing

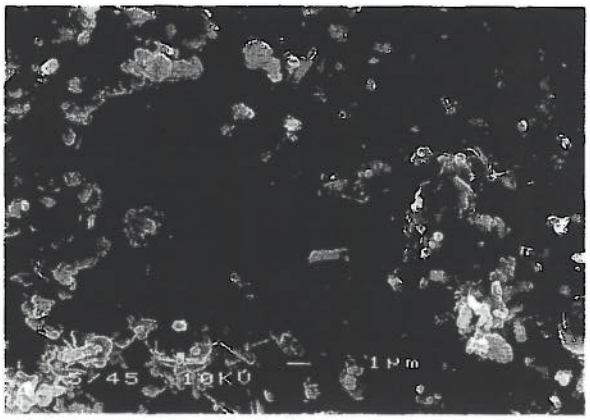


Fig. 10. Belite (C_2S) "rich" OPC displaying crystalline microstructure with gypsum.

heavy metals can be significantly influenced by binder choice. Fig. 12 illustrates the effect of binder choice on the amount of leachable chromium determined on waste forms containing commercially blended inorganic wastes at a fixed waste/binder ratio. The five binders shown consisted of a 1:10 blend of metakaolin with OPC, rapid hardening Portland cement, sulphate-resisting Portland cement, white Portland cement and a calcium aluminate cement. The waste forms, which were treated similarly, were subject to a single leaching test procedure. The estimated standard deviation indicated on the

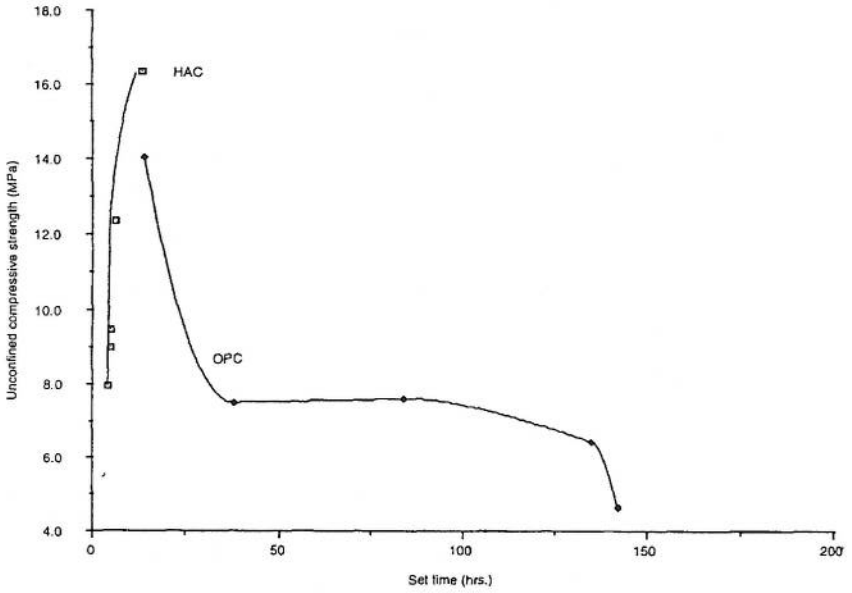
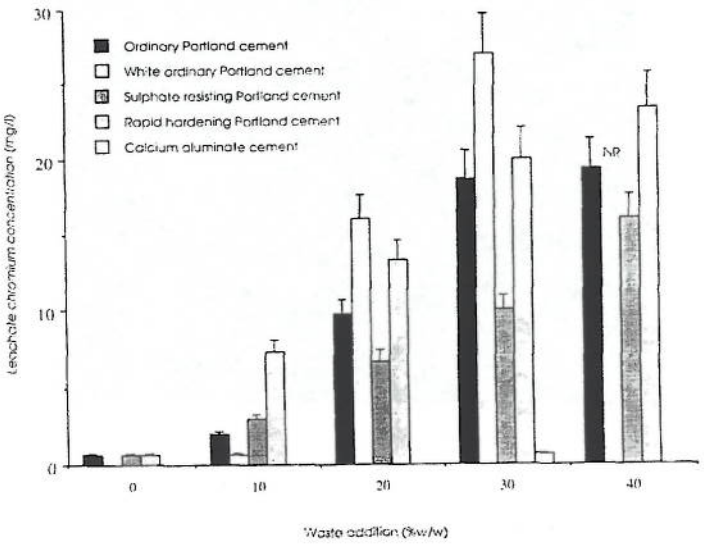


Fig. 11. Influence of binder type on waste form setting and strength characteristics.



NR = no result available.

Error bars = estimated standard deviation.

Fig. 12. Leachate chromium concentration from metakaoline–cement blended binders. (NR = no result available. Error bars = estimated standard deviation.)

figure as error bars was calculated from control samples of known composition. The results clearly indicate that, in this instance, the differences in the leaching performance resulted from the binder systems employed. Nevertheless, the careful selection and proportioning of hydraulic binders can be augmented by pre-treatment steps to minimise the effects of variability within waste [26].

In addition to phase composition, kinetic factors are of significance to the potential stability of solidified waste forms. For a series of pozzolan solidified flue gas desulphurisation wastes examined at 28 days and 84 days respectively, dissolution of gypsum and renewed growth of ettringite was demonstrated by microstructural analysis. Continued formation of significant quantities of ettringite in these matrices over time and subsequent to product hardening could potentially be expansive in both OPC and PFA-FGD systems and cause loss of strength, disruption of microstructure as implied by the strength data obtained in this study [11].

3. Implications for field application

The process of solidification is entirely contingent upon the formation of stable hydration products that bind waste components and provide a solidified product with strength and dimensional stability. A number of intimately linked components are responsible for the properties of the hardened cementitious system [16] and can be described as: crystalline, amorphous phases, aqueous phase; and porosity.

Table 3
Classification of interference effects for waste additions to OPC leading to indefinite retardation (poisoning) of hydration

Reaction	Waste type (process)	Initial phase (prior to poisoning)	Final phase (after poisoning)	Total heat (evolved to P [a])
Initial	Zn Ni, Zn, Cr	e.g. C_3AH_6	AFt	Low (40 $kJ\,kg^{-1}$ [b]) > 50% > 24 h
Initial	Zn Ni, Cr, Cu	AFt	AFt	Moderate (50 $kJ\,kg^{-1}$) < 50% < 24 h
Initial/ intermediate	Numerous (blended) [c]	AFt	AFt	High (70 $kJ\,kg^{-1}$) < 60% < 120h

[a] P denotes the point of poisoning (the waste addition at which indefinite retardation occurs).
[b] Total heat of hydration for OPC is taken as 400 $kJ\,kg^{-1}$ for comparison purposes.
[c] Commercially neutralised, blended and solidified product.

If any of these components is compromised, then others will be adversely affected [16]. For example, where OPC is concerned, C–S–H dominates the solid phase of the hydrated product and contains most of the gel pores. These pores have a high surface area and largely control the sorption potential of the cement. In addition the relationship between C–S–H and CH [37] significantly influences microstructural development and the buffering capacity of a cementitious product. Interference from a waste with either of these phases, for example, will have an important effect and properties such as durability performance may be adversely affected.

3.1. Classification of hydration interference

The disruption of hydration processes can be clearly seen reflected in the calorimetric, mechanical and microstructural properties of solidified products [30]. In spite of significant interference with hydration, a variety of metal plating and finishing wastes produced waste forms where the early age, < 120 h reactivity of alumina-containing phases, was of importance (Table 2). In this case, phase development could be related to the heat of hydration. From this work, which involved an examination of solidified products containing increasing waste additions, a tentative classification system of interference effects was produced, and is summarised in Table 3. The resultant waste specific nature of hydration curves obtained from waste OPC mixtures of differing proportions, as shown in this work may place a requirement on calorimetry to be incorporated in future performance assessment criteria.

3.2. Mechanisms of interference

Solidified waste forms are very different from laboratory-prepared cement pastes in which many observations concerning hydration behaviour have been recorded. Nevertheless, it is logical to consider that hydration must proceed in manner that is predictable to a certain degree even though the field hydration environment may be hostile. In the author's opinion, the very fact that a limited but measurable degree of heat of hydration

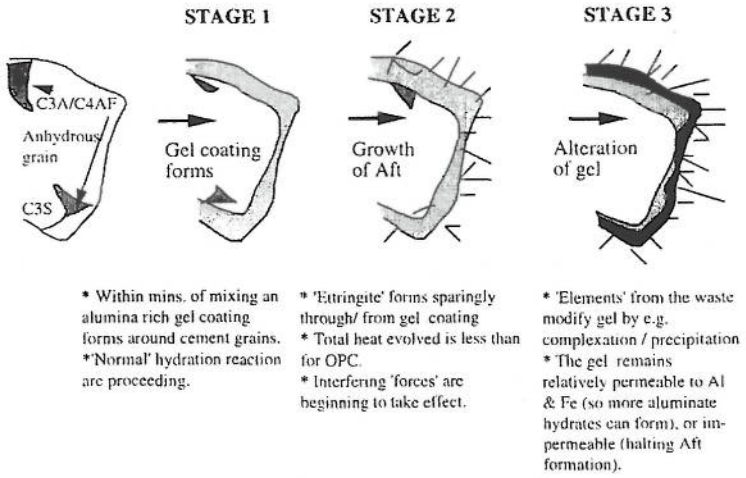


Fig. 13. Generalised mechanism for interference with hydration of OPC.

occurs in affected waste forms suggests that "normal" hydration reactions are likely to be stifled by the interference effects from waste-borne agents.

From hydration studies on OPC [38], it is known that the aluminate phases are capable of producing AFt within < 10 min of mixing cement with water. Within a short time, a gelatinous layer can be observed to form and, at the end of the induction period, further products of hydration "burst" through. The formation of the gel coating around cement particles is an important reaction rate determining step and when modified by waste contained species, as observed for admixtures [39,40], it could easily explain interference with normal hydraulic activity and the consequent low heats of hydration recorded [31].

Modification of the gel coating described may be achieved through complexation or precipitation effects rendering it essentially impermeable, e.g. complexation and removal of calcium at the surface of hydrating cement grains by anionic or cationic agents will limit the production of both CH and C–S–H and, where appropriate, alter the chemistry of these phases (e.g. gel Ca/Si ratio during progressive hydration) by, for example, the removal of calcium through precipitation effects. Subtle but selective differences in the interference mechanisms operating on a gel coating may also explain why some products show minor AFt development whereas others do not. By way of illustration, Fig. 13 gives a schematic representation of the effects of interference on the progress of hydration of a cement grain. It should be noted, however, that other mechanisms may also be in operation during poisoning of hydration. Fig. 14 shows a micrograph of a waste particle partially enveloped by AFt. This particular waste form contained an OPC-based solidified zinc metal plating residue derived from a cyanide-based process and was largely devoid of this phase with the exception shown. This clearly illustrates that selective mechanisms were in operation, were influenced by localised physico-chemical effects and that the spatial distribution and microstructure of phases important to the fixation of toxic species may be discontinuous within a solidified waste form.

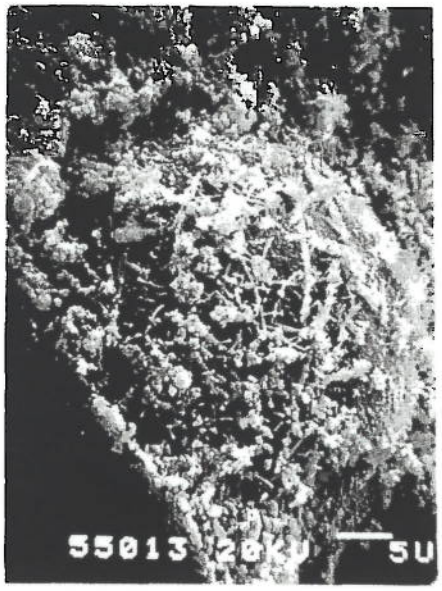


Fig. 14. AFt enveloping metal plating waste particle as a result of selective physico-chemical effects.

In general, it can be concluded that the evidence available form microstructural, calorimetric and other techniques suggests that the hydration of OPC and tricalcium silicate are essentially similar [22]. The main difference appears to surround the nucleation and growth of C-S-H during hydration. It should be of no surprise, therefore, that a correlation exists between the results from studies employing these techniques in respect of the effects of waste/binder interference effects and this is of fundamental importance.

The addition of complex chemical admixtures, such as waste, to cement-based and pozzolanic systems significantly influences the way in which the cement subsequently behaves. The effects at work may be the result of opposing accelerating and retarding forces which are controlled by soluble species present within the admixture. Subtle variations in the way in which interference takes place implies that the balance of forces in action can be changed, whether intentional or not. Macphee and Glasser [18] discussed the immobilisation science behind cement-based systems and concluded that the interactions of a certain metallic species were controlled by various mechanisms including pH-driven precipitation and transient forces. It may, therefore, be possible at some future time to use admixtures in a controlled way to prevent destructive interference of hydration. However, this would depend on the development of a detailed understanding of the complex chemical and physical processes that take place during solidification and, in this respect, there is a considerable quantity of work still to be done.

The fact that wastes routinely interfere with hydration processes during solidification appears to have had little influence on the widespread use of this management technique at the present time, particularly as solidified wastes clearly pass current, though often

incomplete, quality acceptance criteria that render them "suitable" for disposal. There is, however, a fundamental lack of field data relating to the performance of solidified products thereafter. This is now being recognised [18,20,41,42] as a major problem because the satisfactory field service of these materials is of the utmost importance to operators and land owners alike, and should be clearly demonstrable. If field data highlights significant differences between the performance of those products that contain hydrated binding agents as against those that do not, then the situation may change. Already this may be happening as reports of failed solidified wastes within the UK [43,44] are available and they suggest that in fact "unsuitable" inorganic materials have been widely processed with little regard to longer term properties and field performance.

4. Summary and conclusions

The above studies using a combination of systems and genuine waste additions show that the mechanical, microstructural and calorimetric properties developed by solidified wastes are largely controlled by the nature of the waste being treated. These effects are particularly evident and of acute significance at the binder levels used commercially.

If hydration reactions are being commonly compromised, as this work suggests, then the basis for using OPC to solidify wastes is undermined because the reactions claimed responsible for physical and chemical encapsulation of waste species are not always present. Even when strength criteria are being met, it is possible that false set reactions involving not only the rapid, limited, development of ettringite and precipitation of salts are responsible. This means that normal hydration reactions may appear to be present when they actually are not.

For cement-based solidification processes to be optimised the hydration behaviour of binders should be monitored and should be used in the assessment of solidified product quality. Those wastes found capable of poisoning hydraulic and pozzolanic binder hydration should be considered for additional pre-treatments or treated by other means to ensure optimum disposal is achieved.

The time dependent nature of ageing processes that may occur in or at the interface of S/S deposits and ground water are complicated by waste form chemistry, local geology and hydrology and the potential mechanisms of degradation of both organic constituents and inorganic toxic species. These interactions, which cannot be evaluated at this time, may be predicted by future techniques incorporating novel modelling systems and advanced materials testing protocols. Nevertheless, certain changes to the way solidified wastes are currently assessed are technically possible and could lead to improvements in solidified product quality.

Not withstanding the outcome of our work there is a considerable amount of information available to suggest that stabilisation/solidification technology is suitable for inorganic and organic waste materials and this illustrates the gap between academic research and industrial experience. The potential of this form of waste management is in part, reliant upon these differences being reconciled by detailed research work, and studies are urgently required that establish the physico-chemical reasons for field "successes" as well as failures. In this respect, the research community now looks to

the technology operators to relay the successes back to the laboratory for mechanistic interrogation. Future studies should therefore embrace both parties in combined processes and product testing programmes that allow the in-situ examination of waste forms together with an in-depth quantitative analysis of the effects of waste species on the short- and long-term properties of solidified wastes.

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BIOREMEDIATION OF PETROLEUM- AND CREOSOTE-CONTAMINATED SOILS: A REVIEW OF CONSTRAINTS

Simon J. T. Pollard*[1], Steve E. Hrudey*[2] and Phillip M. Fedorak†

** Environmental Health Program, Department of Health Services Administration and Community Medicine and † Department of Microbiology, University of Alberta, Edmonton, Alberta, Canada, T6G 2G3.*

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The evaluation and selection of technologies for the effective remediation of hydrocarbon-contaminated sites requires careful consideration of the waste/site/soil characteristics that determine their ultimate success. The presence of weathered hydrocarbon wastes and sub-optimal environmental conditions places technical restraints on the bioremediation of polynuclear aromatic hydrocarbon-contaminated soils. A brief overview of applicable bioremediation technologies is followed by an in-depth critical evaluation of limiting factors that can influence the efficacy of bio-treatment options, including waste composition, temperature, substrate, bioavailability, accompanying toxicants and soil structure.

Key Words—Creosote wood-preserving wastes, petroleum wastes, polynuclear aromatic hydrocarbons, bioremediation, constraints, weathered composition, bioavailability, salinity, toxic metals, soil texture, climatic conditions.

1. Introduction

Contaminated land resulting from previous industrial activity is now widely recognized as a potential threat to environmental health and its continual discovery over recent years has led to international efforts to restore contaminated soils and aquifers (Smith 1988, Hrudey & Pollard 1993). Current strategies for site clean-up emhasize on-site/*in-situ* treatment technologies that can be linked together in a process train of physico-chemical and/or biological methods capable of tackling a range of multi-media contamination (Sims 1990). This approach recognizes that application of a single technology alone is usually insufficient for effective site remediation.

Bioremediation is one component of the process train approach finding increasing application for hydrocarbon-contaminated soils. This process option has generated growing interest because of its reported cost-effectiveness. Bioremediation has been successfully applied at a number of coal-tar, petroleum and creosote hazardous waste sites in Europe (Bewley *et al.* 1990, Ellis *et al.* 1991) and North America (Piontek 1989, McGinnis *et al.* 1991, Hinchee *et al.* 1991). The presence of hydrocarbon contamination alone, however, is insufficient justification for the application of bioremediation.

Soil contamination at petroleum and wood-preserving sites has received increasing attention across Canada (CCREM 1988, CCME 1991*a,b*) because the contaminants

[1] Currently, Lecturer, Environmental Chemistry, Chemistry Department, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK.
[2] Author to whom correspondence should be addressed.

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frequently identified include polynuclear aromatic hydrocarbons (PAHs), BTEX compounds (benzene, toluene, ethylbenzene and xylenes), biocidal organics (pentachlorophenol, 2,4,6-trichlorophenol) and a range of toxic metals associated with refining and wood treatment operations (e.g. As, Cr, Cu, Pb and Ni). An exhaustive review of the bioremediation literature (Pollard & Hrudey 1992), coupled with an examination of waste/site/soil characteristics at several sites in Alberta (Pollard *et al.*1992, 1993) has highlighted a number of constraints that may reduce treatment efficacy at sites chronically exposed to hydrocarbon contamination. The purpose of this paper is to present a critical evaluation of the potential constraints on bioremediation technologies at petroleum and creosote wood-preserving facilities such that remediation specialists may be aware of these factors and design treatment process trains that can incorporate them accordingly.

The application and ultimate success of remedial measures is determined by a multitude of waste/site/soil characteristics and the interactions among them. These factors demand that evaluation of the potential applicability of treatment technologies is made on an individual site basis. Our discussion is largely focused on PAH bioremediation because the documented carcinogenicity of certain compounds in this group has resulted in relatively demanding clean-up criteria (Moen 1988, ATSDR 1990, CCME 1991*b*). Furthermore, the persistence of these compounds in the soil environment has been demonstrated consistently (Edwards 1983, Jones *et al.* 1989*a,b*, Wild *et al.* 1991).

2. Overview of bioremediation technologies

Biological treatment methods for the reclamation of contaminated land may be classed into four categories: *in situ* bioremediation; enhanced land treatment; slurry bioreactors; and bioventing. The first three technologies are applicable to the remediation of PAH-contaminated soils, while the last is limited to volatile organic compounds amenable to aerobic biotransformation (Long 1992). Here, we present a brief overview of these technologies, but this is a rapidly developing research field and biological soil treatment technologies are continually under refinement. For greater detail, the reader is referred to the many excellent reviews on the fundamental technical and microbiological aspects of bioremediation strategies (Lee *et al.* 1988, Morgan & Watkinson 1989*a,b*, Sims *et al.* 1990, Grady 1990, Madsen 1991, Ryan & Loehr 1991).

2.1 In situ *bioremediation*

The objective of *in situ* bioremediation is to stimulate the activity of the hydrocarbon-degrading microbial population in the subsurface vadose and saturated zones. This is achieved through the addition and management of oxygen and nutrients in a controlled, closed-loop system (Hopper 1989). Amendments (nutrients, electron acceptor and primary substrate) used to aid stimulation and maintenance of biological activity, are introduced up-gradient of the contaminated zone using wells, infiltration galleries or natural fractures in the underlying strata. Soluble transformation by-products, mobilized contaminant and unused nutrients are transported by diffusion and advection down-gradient to the recovery system. At the surface, they are treated and re-injected to recharge the contaminated zone. Site management of oxygen, nutrients and the water regime serves to contain hydraulically the contaminated zone. In this manner, off-site migration of mobile contaminants or potentially harmful metabolites is prevented.

For most circumstances, the principal factor limiting the rate of *in situ* bioremediation is the supply of amendments to the subsurface microbial population (Lee *et al.* 1988). Sites exhibiting subsurface saturated horizontal conductivities of less than 10^{-6} m s^{-1} (Thomas *et al.* 1987) are not considered amenable to this technology because of the retardation of mass transport mechanisms that are necessary for effective delivery of the amendments. Successful treatment relies on the degree of hydraulic control afforded by the delivery-recovery system. Without continual delivery of amendments and removal of metabolites, the system may become biologically inactive at one extreme or clogged with biomass because of excessive microbial activity at the other extreme. Only soluble transformation products will be recovered from the contaminated zone and poorly soluble metabolites, some of which may be toxic, may readsorb to the soil matrix. Soil washing with surfactant is therefore being used increasingly for the mobilization of trapped or adsorbed contaminants (Mahaffey *et al.* 1991).

2.2 Enhanced land treatment

Unfavourable environmental conditions that restrain *in situ* bioremediation, such as low operating temperatures, anoxic soil horizons and low or variable hydraulic conductivities, are often addressed in enhanced land treatment using an aerobic, on-site prepared-bed system. Enhanced land treatment methods have been used to successfully treat a wide variety of petroleum- and creosote-contaminated soils (Bartha & Bossert 1984, Bartha 1986, Visscher *et al.* 1990, Ellis *et al.* 1991).

Contaminated soil is excavated and amended with water, nutrients, electron acceptor, lime for pH adjustment and primary substrate and then returned to a lined land treatment unit fitted with a leachate collection and recirculation system (Sims 1990). Seed organisms may be used to enhance initial transformation rates. However, the ability of bacterial inocula to advance PAH degradation requires the imported organisms to compete and survive alongside the autochthonous population (Atlas 1977, Leahy & Colwell 1990). Covered treatment facilities allow the control of volatiles, temperature and the water regime within the unit. Tilling, together with the addition of straw, wood chips or similar organic matter controls soil tilth and enhances the aeration status of the soil/waste mixture. Performance monitoring should be conducted using a mass balance approach. This requires careful accounting for contaminant disappearance. Bioassay response data are necessary to demonstrate an overall change in toxicity of soil contaminants (Aprill *et al.* 1990).

2.3 Slurry bioreactors

Bioreactors for the controlled biotransformation of refractory pollutants are a recent development although the underlying biotechnology and process control technology is well understood (Visscher *et al.* 1990). Soil is treated as an aqueous slurry in a closed reactor using a well characterized and seeded microbial population. Process control allows reduced treatment times relative to *in situ* or enhanced land treatment methods. Consequently, slurry bioreactors are being considered for the treatment of clayey soils and for situations in which field temperatures adversely affect biotransformation rates. Reactors may be operated in the aerobic or anaerobic mode although the anaerobic microbial population is generally less flexible in adapting to changes in substrate availability and is less tolerant of inhibitory toxic metals (Kirk & Lester 1991).

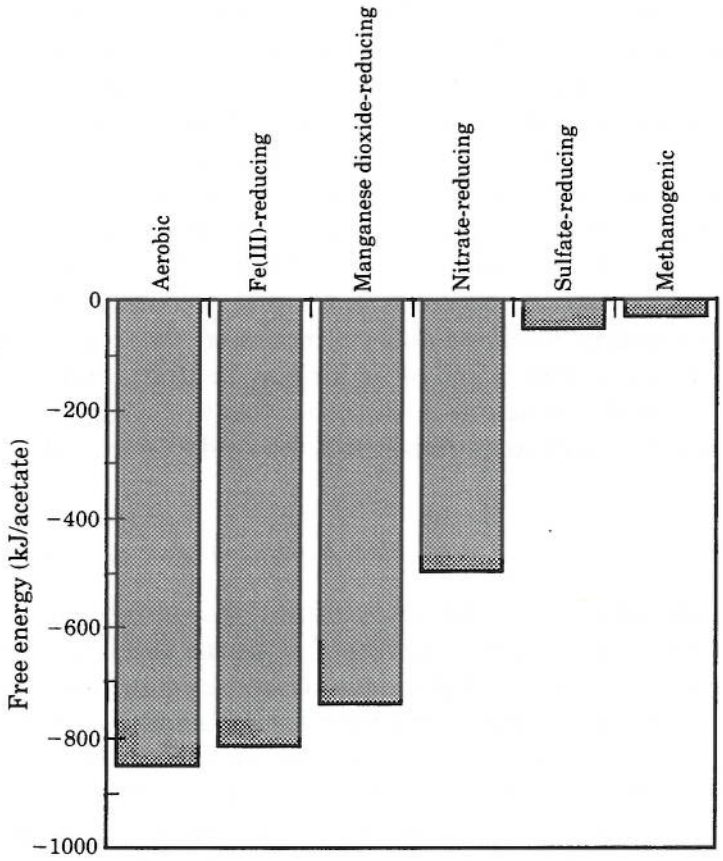


Fig. 1. The amounts of standard free energy available from the metabolism of one mole of acetate under various conditions. The free energy values ($\Delta G^{o'}$) from Lovley & Phillips (1988).

An integrated process train consisting of soil washing, biological water-phase treatment and slurry phase bioreactor unit processes has recently been reported by Stinson *et al.* (1992) for the treatment of sandy soils contaminated with mixed wood-preserving wastes at the MacGillis and Gibbs Superfund site near Minniapolis. Pentachlorophenol (PCP) and PAH removal efficiencies of 87% $^{w}/_{w}$ or higher were achieved by soil washing. Furthermore, 94% $^{w}/_{w}$ PCP in the process water was removed using the biological water treatment process. The fines from soil washing were treated as a 7% aqueous slurry in the bioreactor unit over a 14-day period achieving 70–90% $^{w}/_{w}$ reductions in identified PAHs.

2.4 Anaerobic/anoxic treatability studies

Under aerobic conditions, O_2 serves as the terminal electron acceptor for the oxidation of organic compounds by heterotrophic organisms. When the rate of O_2 consumption by a microbial population exceeds the rate of O_2 diffusion into an environment, anaerobic conditions prevail. However, biodegradation of organic matter still occurs under anaerobic conditions with some ion or compound, other than O_2, serving as the terminal electron acceptor.

The rate of microbial growth and activity is related to the amount of free energy that is liberated through the oxidation of an organic substrate. Figure 1 compares the amounts of free energy available from the oxidation of acetate, under different growth conditions.

Acetate was chosen for this example because it is a common intermediate in the metabolism of many organic compounds under aerobic or anaerobic conditions. Clearly, the maximum free energy yield occurs under aerobic conditions. Therefore, to date, most biotreatability studies, pilot-scale and full-scale applications of bioremediation have centred on aerobic treatment. However, significant anaerobic activity occurs in the subsurface and soils high in clay content containing soil aggregates $> \sim 3$ mm may have anaerobic centres because of their water-adsorbant properties and fine mesoporous structure. Anaerobic treatment offers substantial advantages for chlorinated compounds that readily undergo reductive dechlorination (Suflita *et al.* 1982, Hrudey *et al.* 1987, Vogel *et al.* 1987, Brown *et al.* 1987, Quensen *et al.* 1990). Until quite recently, however, aromatic hydrocarbons were thought to be entirely resistant to microbial attack in the absence of molecular oxygen. However, independent observations on the biotic removal of toluene and xylene isomers from landfill leachate led to the confirmation of a methanogenic route for the biotransformation of these substrates (Grbić-Galić 1991). Similarly, Edwards *et al.* (1992) have shown that these monoaromatic hydrocarbons can be mineralized under sulfate-reducing conditions.

When soils and freshwater sediments become anaerobic, ferric iron is often the most abundant potential electron acceptor for microbial metabolism (Lovley & Lonergan 1990). As shown in Fig. 1, the amount of free energy available under Fe(III)-reducing conditions is nearly equal to that under aerobic conditions, and is much greater than that available under sulfate-reducing or methanogenic conditions. Thus, ferric iron may be the most important electron acceptor in anaerobic, subsurface environments. Recently, Lovley & Lonergan (1990) demonstrated the biodegradation of toluene, phenol and *p*-cresol under ferric iron-reducing conditions. However, the potential of FE(III)-reducing microbial populations to degrade other aromatic compounds associated with petroleum- or creosote-contaminations is still largely unexplored.

Anoxic PAH degradation studies on low molecular weight analogues have been reported by Al-Bashir *et al.* (1990) and Mihelcic & Luthy (1988, 1991). Using ^{14}C-labelled naphthalene in pristine and weathered oil-contaminated soils, Al-Bashir *et al.* (1990) demonstrated reversible naphthalene desorption from the soil matrix and 90% mineralization over a period of 50 days at a rate of ~ 1.8 ppm d^{-1} for the first 50 ppm of substrate. Recently, Mihelcic & Luthy (1988, 1991) successfully demonstrated the mineralization of PAH under denitrification conditions in acclimated soil-water suspensions. While effectively demonstrating naphthalene mineralization efficiencies of 55–100%, these observations confirmed that the bioavailability of substrate remains a dominant factor constraining effective substrate utilization. These preliminary investigations may, in time, serve as a basis for full-scale pre-treatment of soils contaminated with low molecular weight PAH providing the mass transfer limitations can be effectively managed.

3. Constraints on the bioremediation of heavy hydrocarbon wastes

Petroleum- and coal tar creosote-contaminated sites pose a number of problems for effective remediation because of:

(a) the occurrence of contamination in more than one medium (soil, soil vapour, groundwater, distinct hydrocarbon phase);
(b) the existence of a complex and problematic matrix of organic and inorganic contaminants with a diverse range of environmental and toxicological properties;

(c) the presence of heterogeneous subsurface conditions, which are difficult to characterize; and
(d) sub-optimal environmental conditions for on-site and *in situ* treatment.

In addition, expensive analytical procedures are required for the reliable performance monitoring of treatment processes. Typically, hydrocarbon contamination has to be quantified by oil and grease (solvent-extractable material) or total petroleum hydrocarbon measures. The presence of solvent-extractable organic material at hydrocarbon-contaminated sites provides insufficient evidence, by itself, to justify proposing bioremediation technologies. Remedial technology selection requires a rational review of the process capabilities, limitations and site-specific constraints to insure cost-effective use of clean-up funds.

3.1 Waste composition

3.1.1 Hydrocarbon wastes

The chemical composition of hydrocarbon wastes can vary substantially depending on the nature (natural or synthetic crude, coal-tar creosote, carrier oil), composition (e.g. paraffinic, naphthenic, aromatic or intermediate crude oil), degree of processing of the source material (light naphtha, kerosene, residual fuel oil) and the extent of weathering experienced by the exposed waste product (Nyer & Skladany 1989). Petroleum hydrocarbons have historically been classified according to four generic classes; the saturates (*n*-alkanes, branched alkanes, cycloparaffins), the aromatics (mono, di and polynuclear), the resins (pyridines, quinolines, carbazoles, sulphoxides and amides) and the asphaltenes (polyhydric phenols, fatty acids, ketones, esters, metalloporphyrins, polymeric naphthenic ring compounds) (Speight 1984, Leahy & Colwell 1990). Petroleum composed of significant proportions of the latter two classes are generally characteristic of "heavy" oils (Tissot & Welte 1984).

Coal-tar creosote represents a secondary distillation product of gasified coal, in which the main chemical classes are the homocyclic polynuclear aromatics ($\sim 85\%^{w}/_{w}$), the heterocyclic polyaromatics ($\sim 3\%^{w}/_{w}$) and the phenols ($\sim 12\%^{w}/_{w}$) of various degrees of substitution (Mueller *et al.* 1989*a*). The chemical complexity of all fossil fuels, including refined products, is extreme. Process residues such as coal tar, pitch and still bottoms may typically contain several thousand individual components (Drake & Jones 1983, Enzminger & Ahlert 1987). The waste streams from auxiliary unit operations, the residues of secondary process chemicals, carrier oils associated with wood treating solutions, biotransformation products from the decomposition of hydrocarbons and wood fragments and alternative wood preservatives and process chemicals used on site will all contribute additional complexity to the residual contamination encountered in the soil.

3.1.2 Weathered wastes and recalcitrance

Hydrocarbon wastes that have been chronically exposed to soil over decades present additional difficulties for biological treatment. Weathering processes such as evaporation, photolytic loss, hydrolysis and biotransformation, selectively reduce the concentration of easily degradable substrates leaving behind refractory residues that resist further microbial attack (Bossert & Bartha 1984). Many residual compounds possess low Henry's Law constants (K_H), high octanol-water (K_{ow}) and high soil organic carbon-water (K_{oc}) partition coefficients. Such residues are usually non-volatile or semi-volatile

and they partition preferentially to the residual oil phase, to soil organic matter (SOM) and to solid surfaces. For growth on hydrocarbons, microorganisms require an aqueous phase, at least at the microscopic level, in which these substrates are dissolved. Thus, because of the unfavourable partition coefficients for many common contaminants, the bioavailability of these constituents is severely restricted (Smith *et al.* 1989, Mihelcic & Luthy 1991).

The microbial transformations of hydrocarbons in the soil environment have been thoroughly and regularly reviewed (Atlas 1981, Cerniglia 1984*a,b*, Bartha 1986, Leahy & Colwell 1990, Cerniglia 1993). Soil microorganisms display an impressive diversity in their metabolic capabilities and microbiologists continue to isolate and characterize soil microorganisms capable of utilizing petroleum and creosote waste components as carbon and/or energy sources (Mueller *et al.* 1989*b*, 1990a,b, Kelly & Cerniglia 1991). Susceptibility to biotransformation is a function of chemical structure, the degree and nature of substitution of the parent compound and, more generally, molecular weight. The following generalized sequence of decreasing susceptibility to biotransformation among chemical classes has been reported (Atlas & Bartha 1987, Leahy & Colwell 1990): *n*-alkanes > branched chain alkanes > branched alkenes > low molecular weight *n*-alkyl aromatics > monoaromatics > cyclic alkanes, polynuclear aromatics > > > asphaltenes. Compounds in petroleum or coal-tar creosote are intimately mixed and co-dissolved, a circumstance that may influence the rates of biotransformation of individual components in a positive or negative sense (Bartha 1986).

While the biotransformation of *n*-alkanes (Watkinson & Morgan 1990), aromatic hydrocarbons (Arvin *et al.* 1989, Heitkamp *et al.* 1988) and certain heterocyclic components of hydrocarbon wastes (Fedorak & Westlake 1984*a,b*) has been demonstrated, many authors have noted the refractory nature of the asphaltenes (Westlake *et al.* 1974, Bossert & Bartha 1984, Semple *et al.* 1990). Westlake *et al.* (1974) observed changes in the chemical composition of four crude oils towards the asphaltene and heterocyclic component classes following microbial utilization by a mixed culture over a 10-day period. Increases in the asphaltene content of weathered oils suggest that during biotransformation, other petroleum fractions are transformed into asphaltenes. Such changes apparently occur via free-radical initiated polymerizations to yield cross-linked, high molecular weight residues (Bossert & Bartha 1984). Huddleston & Cresswell (1977) noted for an oil initially containing 22% $^{w}/_{w}$ paraffins, 28% $^{w}/_{w}$ aromatics and 50% $^{w}/_{w}$ resin-asphaltenes, that 82% $^{w}/_{w}$ of the paraffins, 60% $^{w}/_{w}$ of aromatics but only 1% $^{w}/_{w}$ of the resin-asphaltenes fraction of the oil were lost over a 22-month period during land treatment. These observations suggest that only a small fraction of heavy asphaltic-naphthenic oils are biotreatable within a realistic time frame (Bartha 1986). These are prominent constituents of residuum pits and flash pits at many petroleum-contaminated sites and are key components in Bunker C residual fuel oil, widely used for the delivery of coal-tar creosote to untreated timber at wood-treatment facilities (Pollard & Hrudey 1992).

Investigations into the persistence of heavy oil constituents in soil microcosms including N-, S- and methyl-substituted PAH indicated that certain components (acridine, carbazole and dibenzothiophene) and their immediate biotransformation products are also among persistent components of heavy oil wastes and they could serve as indicators of residual soil contamination (Bulman *et al.* 1990, Hosler *et al.* 1991). This research has underscored the need in treatability studies to distinguish biotransformation (conversion of parent compound to another organic compound) from mineralization (conversion of the substrate to CO_2, H_2O and inorganic ions).

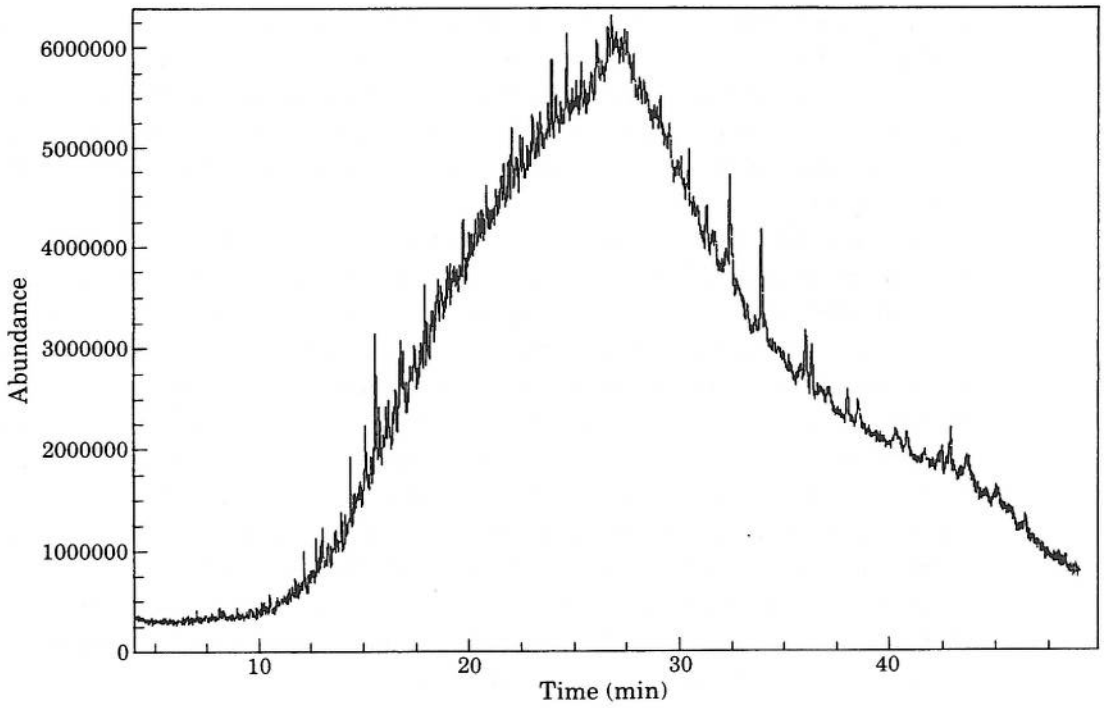


Fig. 2. Gas chromatogram of a solvent extract of weathered oil-contaminated soil.

The broad unresolved hump, characteristic to the gas chromatograms of many weathered oils (Fig. 2) has been attributed to the presence of a complex of linear long-chain alkanes (Gough & Rowland 1990) and the alicyclic alkanes including the hopanes, steranes and diasteranes. These are also proposed as indicators of residual petroleum contamination (Atlas 1981, Volkman *et al.* 1992).

Co-oxidation is frequently cited as an important mechanism for the degradation of recalcitrant substrates in the soil environment (Sims & Overcash 1983, Keck *et al.* 1989). For the high molecular weight PAH (>4 rings), co-oxidation may be a major degradation mechanism. Co-oxidation occurs when an organism growing on a particular substrate gratuitously oxidizes another substrate from which it is unable to obtain either carbon or energy (Atlas & Bartha 1987). Relationships of this kind have been used to explain discrepancies between recorded half-lives in single compound and mixed waste studies (Sims *et al.* 1987) and this phenomenon may contribute to the observed differences in apparent degradation rates between fresh and weathered wastes in soils (Gauger *et al.* 1990).

Biotransformation has been demonstrated for soil-bound components within the phenolic, heteroaromatic and polynuclear aromatic fractions of coal-tar creosote (Arvin *et al.* 1989, Mueller *et al.* 1989*a*, 1991*a,b*). A significant portion of the water-soluble fraction (BTEX, 2-3 ring PAH, phenols and low molecular weight heterocyclic compounds) is potentially degradable in contrast to the ⩾4 ring PAH, dibenzothiophenes, trimethylphenols, pyrrole and the tetra- and pentamethylcarbazoles that resist microbial attack. (Mueller *et al.* 1991*b*) have stressed that substantial biodegradation of high molecular weight PAH and other carcinogenic components in creosote-contaminated soils and sediments is integral to effective site remediations. Soil used in a solid-phase bioremediation (enhanced land treatment) study by these workers was

contaminated with a mixture of creosote/PCP to 1% by weight. Treatment was stimulated by nutrient supplementation, tilling and incubation at 23°C over a 12-week period. The differing PAH profiles of contaminated surficial soils (weathered) and contaminated (unaged) sediments were illustrative of potential biodegradation behaviour. Generalized patterns of biodegradation were consistent with the existing literature; phenols > low molecular weight heterocyclics > low molecular weight PAH > high molecular weight PAH > PCP. Microbial activity toward PAH components in the unamended unaged sediment-bound wastes began only after extensive degradation of the creosote phenols was observed. Mueller *et al.* (1991*b*) expressed doubt over the utility of land treatment for the effective remediation of weathered creosote contaminated soils at the Pensacola, Florida site.

3.2 Temperature-climatic considerations

Each microorganism possesses a growth temperature range over which it can remain active. Cessation of activity occurs at a minimum temperature because membrane gelling stops transport of nutrients and waste products across the cell membrane. At a maximum temperature, protein denaturation results in enzyme dysfunction, deterioration of the cell membrane, and ultimate thermal death (Brock & Madigan 1988). Furthermore, widely fluctuating seasonal and diurnal temperatures are generally unfavourable to the maintenance of a stable, active hydrocarbon-degrading microbial population.

Temperature has a marked influence on equilibrium (partition) and kinetic (rate) constants as described by van't Hoff isochore and Arrhenius equations respectively. Temperature also affects the viscosity and aqueous solubility of hydrocarbons. The reported optimum temperature range for the biodegradation of petroleum is 30–40°C (Bossert & Bartha 1984, Leahy & Colwell 1990) although site specific conditions may play a role in selecting a soil population with a lower optimal temperature (Morgan & Watkinson 1989*b*). Atlas (1981) reports petroleum degradation rates an order of magnitude slower at 5°C. Furthermore, at low temperatures, the volatilization of low molecular-weight hydrocarbons is significantly reduced. These solvent compounds (C_5–C_{10}) are widely held to be inhibitors of hydrocarbon degradation, at high concentration, because of their capacity to disrupt the phospholipid membrane (Atlas 1981, Pfaender & Buckley 1984, Leahy & Colwell 1990, Watkinson & Morgan 1990).

Climatic considerations are important in the design and operation of enhanced land treatment systems in that they indicate management requirements for temperature and water regimes within the treatment bed. Modifications and control of soil temperature can be achieved by irrigation to increase the soil heat capacity or the addition of mulches to reduce diurnal and seasonal temperature fluctuations (Dupont *et al.* 1988). Decreasing temperature also increases oily waste viscosity. Under low temperature conditions, wastes become increasingly viscous and extremely difficult to mix. If year-round treatment is to be provided, heating and temperature control costs could substantially increase land treatment costs.

The effect of temperature (10–30°C) on PAH persistence was studied by Coover & Sims (1987*a*) in unacclimated agricultural sandy loam soil. They found temperature was not the primary constraint for the biotransformation of high molecular weight PAHs. In their study, 50–89% by weight of these compounds remained following a 240-day study at 30°C. At 10°C, 73–93% by weight of these PAHs remained. In contrast, the lower molecular weight (<4 ring) analogues showed appreciable increases in apparent

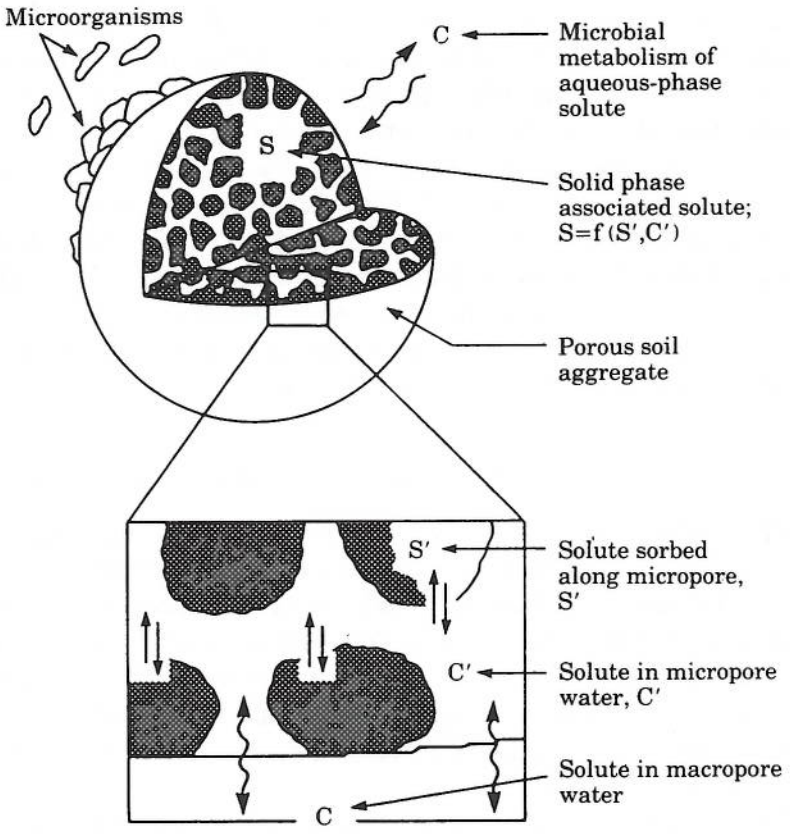


Fig. 3. Conceptual drawing of the processes occurring during the microbial degradation of a hydrophobic organic compound in a soil-water suspension. Microorganisms are size excluded from the micropores, and local equilibrium exists between solute in micropore water and on micropore surfaces. (Reprinted, with permission, from Milhelcic & Luthy, 1991, copyright 1991 American Chemical Society).

degradation with increasing temperature. These workers also observed that the Arrhenius relationship may occasionally be inappropriate for describing the effect of temperature on PAH degradation rates in soil and they advised caution in applying microcosm derived values to field situations (Dibble & Bartha 1979, Coover & Sims 1987*a*).

3.3 Bioavailability and multiphase partitioning

In the context of biological soil treatment, bioavailability refers to the fraction of substrate available for microbial attack. Transformation occurs most readily in the aqueous phase, and this process is severely restricted by oil-phase partitioning, adsorption and rate-limiting diffusion processes that limit the aqueous phase concentration of substrate (Dzombak & Luthy 1984, Smith *et al.* 1989). The conceptual distribution of hydrophobic organic compounds within soil aggregates and the dependence of aqueous phase partitioning to provide substrate accessibility for degrading microorganisms is depicted in Fig. 3 (Milhelcic & Luthy 1991).

In acknowledgement of this key limitation, work at the Gas Research Institute, Chicago on the management of former manufactured gas plant sites, has focused specifically on developing strategies to overcome mass transfer limitations using slurry bioreactors and bioemulsifiers. For soils that have been exposed to PAH contaminants over extended times, deep penetration of the clay particles is likely to have occurred. Without specific action, these substrates will not rapidly desorb to become bioavailable

(Smith *et al.* 1990). Agglomeration of individual contaminated soil particles, because of the viscous, hydrophobic nature of bulk creosote and refinery wastes, can also physically separate residual PAH contamination from soil water where biological activity resides (Smith *et al.* 1990). These restraints are now widely recognized and a major focus of bioremediation research now centres on process engineering solutions to these mass transport limitations (McCarty 1991).

3.3.1 Oil phase equilibrium partitioning

The environmental fate of bulk hydrocarbon fluids as non-aqueous phase liquids (NAPLs) is determined by the volume released, the area of infiltration, the duration of release, the bulk properties of the NAPL and soil media, and the subsurface flow conditions (Dracos 1987, Mercer & Cohen 1990). Partitioning of hydrophobic organic contaminants and their primary, abiotic reaction products in the environment is dominated by their distribution in the oil phase (Smith *et al.* 1989), which exists either as free oil (NAPL) or as residual saturation on soil resulting from the gravitational movement of NAPLs through the soil column. Most partitioning studies have been limited to two-phase systems rather than an evaluation of the multiphase partitioning of waste mixtures, in which co-solvent, competitive and inhibitory effects contribute to overall behaviour (Gan & Dupont 1989).

Isotherm studies of the three-phase (oil, soil, water) partitioning of semi-volatile hydrophobic organics, PCP and 2-chlorobiphenyl, suggest that the oil phase could be as much as 10-fold more effective than SOM as a host environment (Boyd & Sun 1990). Similar results were observed by Jackson & Bisson (1990) for the three-phase partitioning of polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF) and PCP in wood-preserving oil, with K_{os} values (oil-soil partition coefficients) of between 47–100 and 10–57 for aged and fresh wood-preserving oils respectively. These findings have important implications for the biotransformation of compounds in weathered matrices because retention of degradable substrates within the aged hydrocarbon matrix will further reduce their bioavailability to the active microbial populations.

3.3.2 Equilibrium partitioning between the aqueous phase and soil organic matter

Uptake of organophilic contaminants to SOM has been largely envisaged as an equilibrium distribution process involving permeation of the three-dimensional SOM network, which conceptually behaves as a solvent (Rao 1990). Supporting evidence comes from the observed linearity of sorption isotherms over a range of concentrations (Karickhoff *et al.* 1979, Means *et al.* 1980), from the inverse relationship between aqueous solubility and the soil adsorption coefficient (Bossert & Bartha 1986) and from the apparent absence of competitive effects when co-solutes are present (Rao 1990). This approach has served as a basis for estimating the normalized K_{oc} values of hydrophobic contaminants, across a range of soil types, based on the fraction of organic carbon, f_{oc}, in the soil (Karickhoff *et al.* 1979). Means *et al.* (1980) demonstrated that K_{oc} was independent of clay mineralogy for pyrene, 7,12-dimethylbenz[*a*]anthracene, 3-methylcholanthrene and dibenz[*a*]anthracene sorbed onto a series of 14 soils and sediments.

3.3.3 Adsorption at mineral surfaces

The thermodynamic forces controlling the relative stability or exclusion of hydrophobic compounds in the aqueous phase have been detailed by Voice & Weber (1983). Solute

molecules can be driven out of solution if the system (adsorbant and solute) can achieve a thermodynamically favourable state. Such a situation must also consider the energetic hydrophobic bonding characteristics of the sorbent. The equilibrium partitioning model may be less appropriate for polar organic compounds or contaminants possessing polarizable heteroatoms where active site processes may dominate. Means *et al.* (1982), for example, have suggested that montmorillonite clay-organic interactions may be responsible for the adsorption of 2-aminoanthracene particularly where the organic carbon/montmorillonite ratio is low.

Mineral surfaces also harbour hydrophobic regions capable of the Van der Waals attraction of non-polar organic compounds (Dragun 1988), though these interactions are often considered negligible in contrast to the solvent properties of residual oil and SOM in contaminated soil environments. However, Smith *et al.* (1990) introduce the term "biostabilization" referring to tight and irreversible bonding of hydrophobic contaminants to the soil matrix. They hold this phenomenon partially responsible for the extreme variability in reported PAH biotransformation half-lives (Sims & Overcash 1983, Bulman *et al.* 1987). Tightly bound substrates, present in the soil system for many decades, may require equally long times to desorb or diffuse before becoming bioavailable. Smith *et al.* (1990) have associated fine-grained soils (clays and silts) with a specific affinity for PAH compounds. Treatment strategies for mobilizing contaminants are currently focusing on the use and efficacy of synthetic or naturally-secreted surfactants (Aronstein *et al.* 1991, Laha & Luthy 1991).

3.3.4 Non-equilibrium mechanisms

The chemical basis for the kinetic control of adsorption processes rests on the existence of site specific adsorbant-adsorbate interactions at colloid surfaces. Johnson *et al.* (1989) have also suggested that simple diffusion can play a role in carrying organic contaminants across low permability clay strata. The binding and solute diffusion of non-polar high molecular-weight compounds within the polymeric matrix of SOM may be active-site dependent and rate-limited (McCarthy & Jimenez 1985, Rao 1990, Lyon & Rhodes 1991). The magnitude of the association for pyrene on 14 different humic and fulvic acids, for example, was found to be modified by their relative aromaticity as determined by infrared, ultraviolet and ^{13}C NMR spectroscopy (Gauthier *et al.* 1987).

The physical basis of sorption kinetics requires consideration of accessibility to sorbent surfaces. Penetration of soil aggregates is explained in terms of the radial diffusion of contaminants into naturally porous particles (Hendricks & Kuratti 1982, Wu & Gschwend 1986). Chemical species diffuse through pore fluids and are retarded by microscale partitioning between mobile and immobile (intra-aggregate) particle solids. Similar diffusion models have been used to describe the kinetics of activated carbon adsorption (Bansal *et al.* 1988). Use of the diffusion model for hydrophobic organic contaminants in soil indicated that large particles were slower to adsorb solutes than similar small aggregates. Adsorption/desorption can theoretically be controlled by decreasing the tortuosity (diffusive path length) within the aggregate or exposing a greater surface area. Wu & Gschwend (1986) modelled the diffusive exchange mechanism and found it to be a function of chemical (molar volume, hydrophobicity) and particle (shape, tortuosity, porosity) properties and consistent with Fickian diffusion. These model predictions have been experimentally verified by Carberry & Lee (1990) who observed differential biotransformation rates for the degradation of No. 2 and No. 6 fuel oil in fine clay and coarse soil under simulated spill conditions. Contaminants

exhibiting a greater hydrophobicity exhibited slower soil uptake rates (lower molecular diffusivity). This finding is important for chronically-exposed sites. Although reversibly adsorbed, extremely hydrophobic contaminants such as the high molecular weight PAHs may be extremely slow to desorb from their isolated intraparticulate positions.

3.4 Waste toxicity

3.4.1 Toxicity of creosote and refinery wastes and transformation products

The general response of a microbial population to hydrocarbon exposure is a rapid increase in the hydrocarbon-utilizing component of the community (Pfaender & Buckley 1984). For example, the addition of Swan Hills and Norman Wells crude oil to soil plots in north-central Alberta resulted in significant increases in the size of the culturable microbial population after 12 and 22 days respectively (Jobson *et al.* 1974, Cook & Westlake 1976). These responses may be severely attenuated by excessive hydrocarbon loads and interfering waste components (short-chain *n*-alkanes; BTEX, high molecular weight PAH). A treatability concentration range may therefore exist, above which the contact toxicity of waste compounds inhibits metabolic activity and below which microbiota may switch to alternative substrates. In the latter case, a reduction in contaminant concentration may be achieved only through exploitation of co-oxidation (Keck *et al.* 1989). Attention must be paid to the contribution to toxicity from transformation products. From their investigations into the potential biotreatability of a heavy oil waste from a bitumen upgrading plant, Hosler *et al.* (1991) indicated that the toxicity of biotransformation products may be an important limitation for land treatment of these process residues.

In an assessment of the treatability of four complex hazardous wastes, API separator sludge, slop oil solids, PCP wood-preserving waste and coal-tar creosote waste, treatment was evaluated as a function of waste loading rate, soil moisture and time (Sims *et al.* 1987). Treatment potential of the four wastes was evaluated in sandy loam and clay loam soils. All wastes demonstrated a high degree of aqueous toxicity as measured by the Microtox™ acute toxicity bioassay. Wood-preserving wastes exhibited greater toxicity than the petroleum sludges, and contained appreciably higher levels of priority PAH and PCP. Waste-soil loadings were selected on the basis of the bioassay response, which, for the creosote waste were set at 0.4, 0.7 and 1.0% $^{w}/_{w}$ for sandy loam and 0.7, 1.0 and 1.3% $^{w}/_{w}$ for the clay loam soil. Results confirmed increasing biotransformation half-lives with increasing molecular weight. For each waste-soil matrix, toxicity of the water-soluble fraction increased initially, reflecting initial intoxication by metabolic products, and then decreased. Mutagenicity evaluations using the Ames *Salmonella typhimurium* bioassay demonstrated the persistence of mutagenic activity for both wood-preserving wastes in the clay loam over the 400-day treatment period.

3.4.2 Salinity

High salinity levels can disrupt the tertiary protein structure, denature enzymes and dehydrate cells (Atlas & Bartha 1987). Many refinery wastes contain salts (KCl, NaCl) resulting from desalting operations during the preliminary processing of crude oil (Vernick *et al.* 1984, Environment Canada, 1990). At salt-damaged sites, remediation is often restricted by structural deterioration of the soil which, if it has progressed beyond the immediate soil horizon, is particularly difficult to address and may require flushing and calcium treatment (Dupont *et al.* 1988). Few studies have dealt explicitly with the

effect of salinity on microbial activity although the destructive effect of salt on soil productivity is well recognized (Miller & Donahue 1990). Ward & Brock (1978) found that the rates of hydrocarbon metabolism decreased with increasing levels of salinity (3.3–28.4% salinity) for a series of hypersaline evaporation ponds of the Great Salt Lake, Utah. Atlas (1981) interpreted this study as a basis for questioning the feasibility of biodegradation in hypersaline environments.

Highly sodic soils exhibit reduced oxygen and water permeability. Sodium exchange at the interlamellar clay surface results in progressive dispersion of clay domains from surficial soils and reaggregation in the lower soil horizon. The resultant effect is a reduction in soil permeability and a subsequent restriction in water availability. Soils containing a high proportion of layer silicates are particularly susceptible to sodium imbalances with critical sodium adsorption ratios (SAR) of 8–10, above which soil swelling precludes successful operation of land treatment units (Overcash & Pal 1979).

3.4.3 Metals

Refinery and wood-preserving wastes often contain appreciable quantities of metals (commonly Pb, Cd, Hg, Zn, Cu, As, Cr, Ni, V). For petroleum wastes, these are either derived from metalloporphyrins (generally $< 100\ \mu g\ g^{-1}$) or associated with unit operations that employ metal catalysts or additives for enhancing product quality. For example, prior to the development of alkanolamine sweetening, lead (II) oxide was used in substantial proportions for the removal of sulphur from crude oils.

The metal content of wood-preserving wastes is usually associated with the use of alternative treatment chemicals (chromated copper arsenate, CCA; ammoniacal copper arsenate, ACA). Unlike organic contaminants, metals cannot be degraded although in some instances (As, Se, Cr, Hg) their chemical state may be altered (McLean 1991). Metals associated with these wastes exist in the soil environment in a variety of soluble or solid-bound forms. In solution, they may be present as free ions or more likely as anionic, cationic or neutral complexes. In their bound state, metals exist adsorbed to colloidal or suspended particles, as SOM chelates, as individual or co-precipitates and as exchanged ions at the surface of clay minerals (Evans 1989). In the case of the latter, there is limited evidence that ion exchange acts to protect the soil microbiota from direct metal toxicity (Babich & Stotzky 1977).

Inhibition of microbial activity is generally associated with the more toxic metals that have demonstrated adverse effects at concentrations below $1\ mg\ l^{-1}$ in solution (Bowen 1966); Ag(I), Be(II), Hg(II), Sn(II), Co(II), Ni(II), Pb(II) and Cr(VI). It is now widely accepted that the free metal concentration in solution is responsible for toxic effects experienced by soil microorganisms (Gadd 1991). Toxicity can occur via a number of mechanisms:

(a) enzyme inhibition;
(b) co-precipitation or chelation with essential metals limiting their bioavailability;
(c) catalysis of essential metabolites; or
(d) through direct competition and substitution with essential metals impairing cell function or acting as antimetabolites (Overcash & Pal 1979, Gadd 1991).

The non-essential metals (e.g. Pb, Sn, Al, Be, Tl, Sb, Cd) are generally believed to exert toxic effects at much lower concentrations than observed for metals that are required for biological activity (e.g. Fe, Cu, Co, Cr, Ni). Recent evidence from a quantitative assessment of the effects of metals on the microbial degradation of 2,4-dichlorophenoxyacetic acid suggests that metallic pollutants may be inhibitory at levels lower than

previously expected (Said & Lewis 1991). Aqueous concentrations of metals that caused a doubling of the half-life for 2,4-dichlorophenoxyacetic acid in lake sediment were $10\,mg\,l^{-1}$, $27\,mg\,l^{-1}$ and $52\,mg\,l^{-1}$ for Cu(II), Cd(II) and Zn(II), respectively. In contrast, Wood & Wang (1983) have provided a review of selected microbial species that have developed intra- and extracellular mechanisms for eliminating elevated concentrations of toxic metals.

3.5 Soil texture and structure

The significance of soil texture to bioremediation lies in its overriding control of the water regime (infiltration, retention, yield) aeration status, soil temperature, and tilth (workability). Evidence from a systematic examination of the effect of grain size on aerobic *n*-hexadecane degradation indicates that soils higher in surface area facilitate utilization up to a point where decreasing grain size may introduce other constraints. Würdermann *et al.* (1990) recorded decreases in the time taken to mineralize one third of the *n*-hexadecane substrate with increasing soil surface area up to a value of $20\,m^2\,g^{-1}$. Further increases in surface area ($60\,m^2\,g^{-1}$ to $750\,m^2\,g^{-1}$) were not matched by enhanced mineralization rates. Any discussion of the merits of fine-grained soils in the field, therefore, must show an appreciation of their moisture, nutrient and oxygen-limiting capabilities.

In soils with a clay content of $\gtrsim 12\%\,^{w}/_{w}$, aggregation can result in the entrapment of microorganisms and substrate within a pore space thus providing microsites at which localized enzymatic activity may be observed (Nedwell & Gray 1987). However, soils containing high clay content and soil aggregates $\gtrsim 3$ mm may have anaerobic centres because of their water-adsorbent properties and fine mesoporous structure. Mott *et al.*(1990) examined the biodegradation of a heavy gas oil ($61.9\%\,^{w}/_{w}$ saturates, $38.1\%\,^{w}/_{w}$ combined aromatics) in soil microcosms applied to uncontaminated silty-clay loam aggregates of 19–25 mm (coarse), 5–10 mm (medium) and 1–2 mm (fine) in diameter. Results from this 14-day incubation study demonstrated that aggregate size prior to oily-waste application greatly affects biotransformation; as aggregate size decreases, transformation rates increase. Grinding of waste-soil matrices, once mixed had little overall effect, possibly because oil does not disperse well once applied. Modelling of this effect led to the proposition that the effect of aggregate size is actually one of available surface area before application. For chronically exposed hydrocarbon-contaminated soils, the implications are that extensive tilling for the sole purposes of exposing non-degraded oil may be unprofitable.

Few studies have dealt specifically with the biotreatability of contaminated fine-grained soils and most enhanced land treatment operations have been performed using sandy soils. Limited data exist for a number of clay loams (Kincannon & Lin 1985, Coover & Sims 1987*b*) which are among soils considered potentially suitable for land treatment (Dupont *et al.* 1988, Sims 1991). Song *et al.* (1990) discuss the bioremediation potential of sand, loam and clay loam soils contaminated with $5–13.5\%\,^{w}/_{w}$ of various petroleum oils. Fuels were characterized by their chemical class compositions and loaded onto fertilized and lime-amended, clean soil columns. Aeration was performed weekly by inserting a steel wire into the soil columns approximately 15 times. The environmental persistence of the mid-distillate fuels increased in the series jet fuel $<$ heating oil $\approx$ diesel oil $<$ bunker C, reflecting the increasing proportion of high molecular weight refractory components. These oils demonstrated significant reductions in concentration over a single growing season and were earmarked for field scale

evaluation. Bunker C was shown to be structurally recalcitrant in this 48-week study and gasoline removal occurred by evaporation in preference to biotransformation. Half-lives of degradable fuels in this study were shown to be longest in sand, which has poor water retention and low microbial diversity, but only slightly shorter in clay loam and loamy soil.

4. Conclusions

Assessing the potential biotreatability of hydrocarbon-contaminated soils requires careful consideration of a wide range of related constraining factors, for which information must be gathered during initial site characterization. Identification and quantitative measurement of solvent-extractable organic material at contaminated sites is a clearly inadequate basis for judging the potential of bioremediation technologies. The low bioavailability of hydrophobic compounds within the waste-soil matrix has become recognized as a major constraint to achieving specified soil remediation criteria for these compounds. Furthermore, any discussion of biological soil treatment potential requires that a distinction be made between biotransformation and mineralization (complete biodegradation). Some transformation products may be toxic and may resist further biotransformation and many hydrocarbon wastes contain refractory components that resist microbial attack. Finally, adequate attention must be paid to the toxicity of corresponding biotransformation by-products.

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FEASIBILITY OF BIOLOGICAL AERATED FILTERS (BAFs) FOR TREATING LANDFILL LEACHATE

T. STEPHENSON[1]*, S. J. T. POLLARD[2] AND E. CARTMELL[1]

[1]School of Water Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK
[2]Integrated Waste Management Centre, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

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ABSTRACT

Ammonia can be removed from landfill leachate using aerobic biological treatment processes. The biological aerated filter (BAF) combines biological treatment and subsequent biomass separation in one reactor providing a small footprint alternative to conventional systems. Leachate from an operational landfill was found to be aerobically treatable using the OECD recommended Modified Zahn-Wellens test. This leachate was used as feed to a pilot-scale BAF at influent chemical oxygen demand (COD) and ammoniacal-nitrogen concentrations of 765 mg l^{-1} and 568 mg l^{-1} respectively. During an initial period of stable operation without pH control, 33 %w/w of influent ammonia was removed. The reactor pH was 9.2 with little conversion to total oxidized nitrogen (<45 mg l^{-1}), this removal was accounted for primarily by air stripping. In a second period of stable operation, the reactor pH was reduced to pH 7.2 and ammonia removal increased to 97 %w/w with a concomitant increase in effluent nitrite concentration to an average of 524 mg l^{-1}. Biological aerated filters (BAFs) can be used to nitrify landfill leachates though onward denitrification of nitrite-nitrogen and COD polishing is required to reach typical discharge consent standards.

Keywords: Landfill leachate, biological aerated filters, ammoniacal-nitrogen, nitrification

INTRODUCTION

Landfill leachates are conventionally treated using aerobic biological processes (aerated lagoons [1] and sequencing batch reactors [2]). Anaerobic processes are also capable of removing biochemical oxygen demand (BOD) and chemical oxygen demand (COD) from leachates [3] but aerobic treatment is usually required for ammonia removal through two step nitrification - the conversion of ammonia to first nitrite, then nitrate, with the supply of oxygen [4]. Other aerobic processes proposed for leachate treatment include rotating biological contactors (RBCs) [5], suspended carrier reactors [6] and biological aerated filters (BAFs).

BAFs are submerged media wastewater treatment reactors combining aerobic biological treatment and biomass separation by depth filtration [7]. They adopt a granular media as the support for biofilms that also provides depth filtration (Figure 1). BAFs offer a small footprint alternative to conventional aerobic processes and operate at BOD loadings much higher than trickling filters and activated sludge plants. They have potential application especially where space is constrained and where BOD loadings are high. Carbonaceous BOD removal, solids filtration and nitrification are achieved in a single unit operation and process modifications allow for denitrification and phosphate removal [8]. BAFs are commonly used in municipal wastewater treatment for tertiary nitrification alone, especially for upgrading existing works, as they can operate at higher space loadings than trickling filters (Table 1); hence their attraction for leachate treatment. Given these advantages, the aim of this study was to assess the feasibility of applying BAFs to the treatment of methanogenic landfill leachates through treatment of an authentic leachate in a pilot-scale BAF.

Table 1. Typical ammoniacal-nitrogen loadings for trickling filters and BAFs to achieve >90 % removal when operating in tertiary treatment mode.

Unit process	Ammonia loading (kg NH_4-N m^{-3} d^{-1})
Tertiary filters	0.1 – 0.6
BAFs	0.6 - 1.0

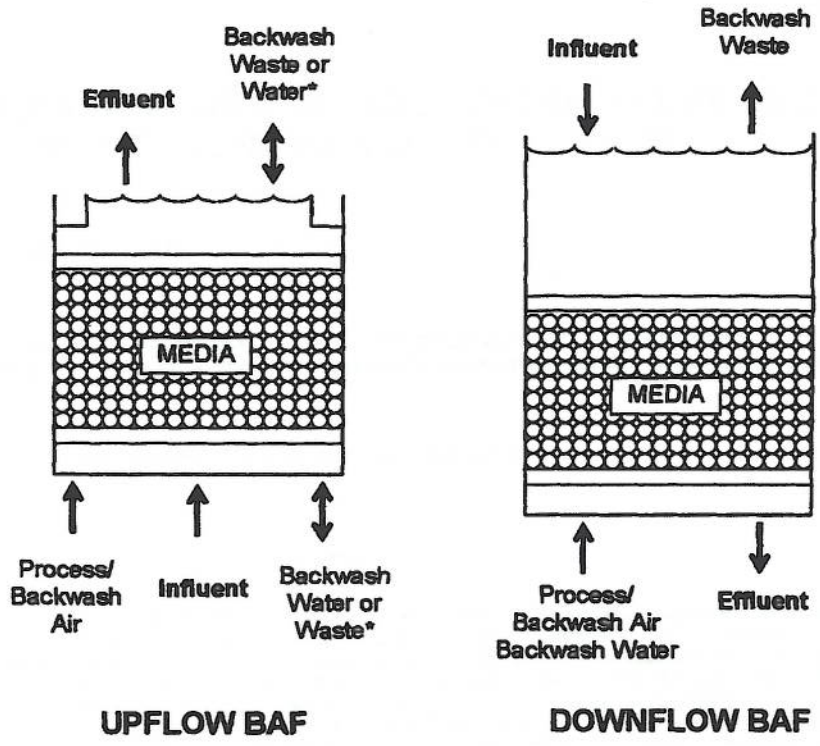


Figure 1. Schematics of upflow and downflow BAFs showing key features.

MATERIALS AND METHODS

Pilot-Scale Biological Aerated Filter Plant

The pilot-scale BAF plant was an upflow 5.3 m high column, 0.43 m diameter, based on the proprietary Capital Controls ColOX design. The granular media (height 2.1 m) was supported by 0.90 m of underdrain, giving a media volume of 0.31 m^3. The skid-mounted column was fitted with controls, pumps, blowers, a clearwell and mudwell (Figure 2), each approximately 0.5 m^3 in volume. The media was crystal quartz sand with a diameter of *ca.* 1.5 to 2.2 mm and an

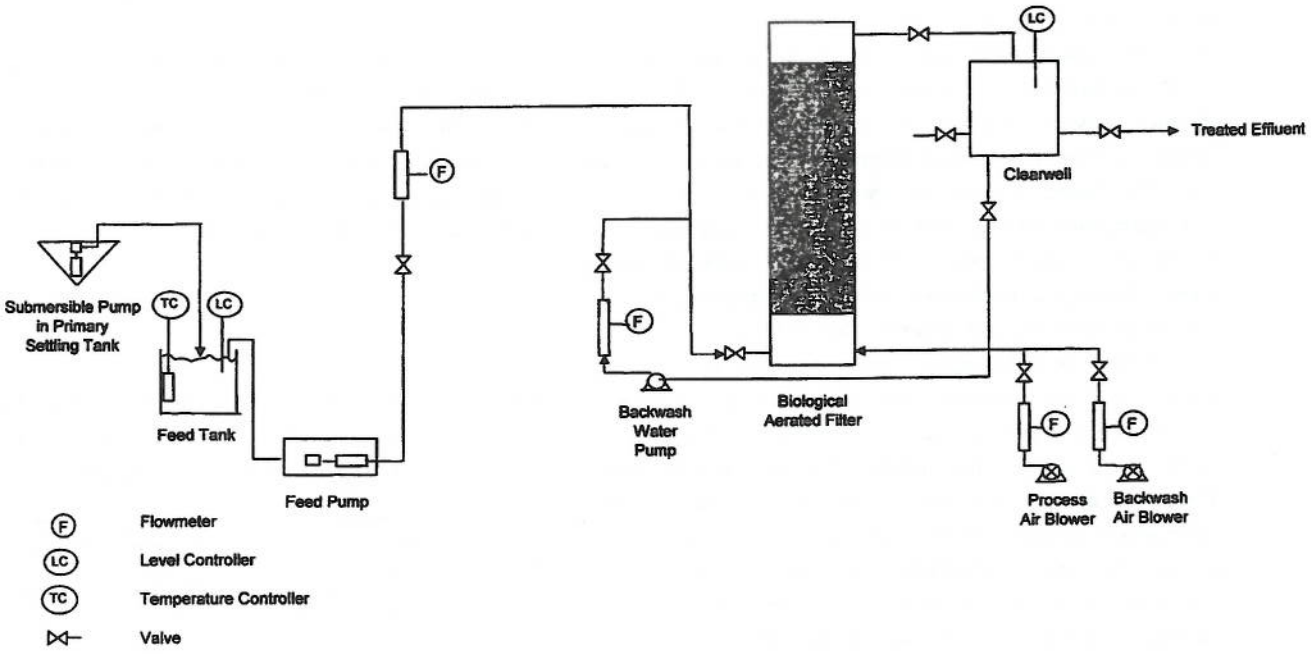


Figure 2. Schematic of pilot-scale BAF and ancillary equipment.

effective porosity of 40 %v/v. The media was supported by a layered underdrain of equal heights (0.30 m) of 40 mm, 14 mm and 10 mm gravel. To ensure sufficient wetting of the column, a flow of at least 151 l h^{-1} was maintained through a recycle. Leachate was fed to the pilot-scale BAF using a peristaltic pump with a capacity of 0-100 l min^{-1} (700 series, Watson-Marlow Ltd, Cornwall, UK). Backwash was supplied by means of a peristaltic pump of 60 m^3 h^{-1} capacity (model A006422, Grundfos Pumps Ltd, Leighton Buzzard, UK). Air and liquid flow were monitored by means of a Platon plastic tube VA flowmeter with a 40-440 l min^{-1} range and a plastic tube flowmeter with a 300-3000 l h^{-1} range, respectively (VA, CT Platon Ltd, Basingstoke, UK). Bulb vales (Durapipe S&LP, Staffordshire, UK) were used to control both hydraulic and gas flowrates. An automatic motorised valve (Ultravalve Ltd, Halsowen, UK) was used to prevent backwash water from siphoning back through the effluent pipe.

Operational Parameters

For start-up, the BAF was seeded with nitrifying activated sludge from a municipal sewage treatment works. The pilot-plant was run in batch mode for 3 d until ammonia removal was established. Then, influent leachate was diluted to approximately 50 mg l^{-1} NH_4^+-N, corresponding to one tenth of the maximum expected load, i.e. 0.01 kg NH_4^+-N $m^{-3}d^{-1}$, with the loading increasing to a maximum of 0.07 kg NH_4^+-N m^{-3} d^{-1}, representing a COD loading rate of 0.10 kg COD $m^{-3}d^{-1}$. The BAF was operated for two stable operating periods, one without pH control and one with the addition of hydrochloric acid to reduce pH. Leachate is usually deficient in alkalinity and phosphate for biological treatment to be successful. To provide 7.14 mg of alkalinity (as $CaCO_3$) per mg of NH_4^+-N, 4686 mg l^{-1} (as $CaCO_3$) was added to the feed as sodium biocarbonate (GPR Merck, Dorset, UK). To provide a nutrient balance sufficient for biological nitrification, i.e. a COD:P ratio of 100:1 [9], stored leachate was dosed with trisodium orthophosphate (Merck, Dorset, UK). However, after problems were experienced with precipitate formation, a 1:1 mix of sodium dihydrogen orthophosphate and dipotassium hydrogen orthophosphate (Merck, Dorset, UK) was used. The pH of the leachate remained unaltered at pH 7.8 both before and after nutrient dosing.

Treatability, Optimisation and Monitoring

A methanogenic leachate with a measured COD concentration of 786 mg l^{-1}, chloride *ca.* 10,000 mg l^{-1} and ammoniacal nitrogen of 652 mg l^{-1} was sourced from two locations at a landfill site in the UK and its treatability prior to BAF treatment examined in batch tests. Stored leachate characteristics monitored over a 6-week period were found to be stable. Bench scale treatability studies, adopting the OECD Zahn-Wellens test, were used to investigate COD removal over 28 d [10]. Standard methods were used for surrogate parameter analysis including suspended solids (SS) [11], BOD_5 [12], total (TCOD) and soluble COD (SCOD) [13] and ammoniacal-nitrogen (NH_4-N) [14]. Samples were filtered through GF/C grade filter paper (Whatman Ltd, UK) prior to analysis of soluble COD (SCOD) and other soluble species. Total oxidised nitrogen (TON) and nitrite-nitrogen (NO_2^--N) were determined by standard methods [15] and nitrate-nitrogen (NO_3^--N) determined by difference. Phosphate, alkalinity and chloride were monitored in the leachate influent using recommended techniques [16, 17, 18]. Dissolved oxygen and pH in the BAF study were measured by probes (Jenway Models 9070 and 3070 respectively).

RESULTS

Bench Scale Treatability Studies

Leachate samples sourced from two locations had COD concentrations of 1406 mg l^{-1} and 1662 mg l^{-1}; and were diluted to initial concentrations of 253 mg l^{-1} and 396 mg l^{-1} respectively in the Zahn-Wellens tests. Both samples were found to be biodegradable with >80 %w/w COD removal. A mixture of the two samples was then tested at three initial COD concentrations of 287, 396 and 479 mg l^{-1}. After 28 d, the lowest concentration was found to be most degradable at 97 %w/w COD removal; the highest concentration least easily degraded at 49 %w/w COD removal (Figure 3).

Pilot-Plant Trials

Influent leachate characteristics were monitored throughout the pilot-plant trial (Table 2). Total and soluble COD, and ammonia concentrations were relatively stable, whereas suspended solids concentrations decreased during operation from approximately 191 mg l^{-1} to <100 mg l^{-1}. This decrease coincided with delivery of a second batch of leachate and a switch in dosing trisodium orthophosphate to the potassium/sodium hydrogen orthophosphate mixture. A corresponding increase in soluble phosphate from <2 mg l^{-1} to >10 mg l^{-1} was noted. The pH of the leachate remained constant at pH 7.8; chloride was also constant at 1000 mg l^{-1}.

The temperature of the pilot-plant varied from 15 °C to 19 °C during the study. Dissolved oxygen concentrations in the effluent averaged 6.0 mg l^{-1}, indicating that oxygen was not limiting. Effluent alkalinities and phosphate concentrations were well above the detection limits throughout the trial, again indicating that neither were limiting nitrification. At no point was the BAF backwashed to remove excess solids as there was no significant buildup of headloss, as indicated by the depth of liquid on the top of the column.

Eight days after start-up, the pilot-plant was observed for a further 17 d stable operating period without pH control. Performance in terms of total BOD removed was excellent, as anticipated from the treatability tests, with >90 %w/w removal (Table 3). Suspended solids removal was

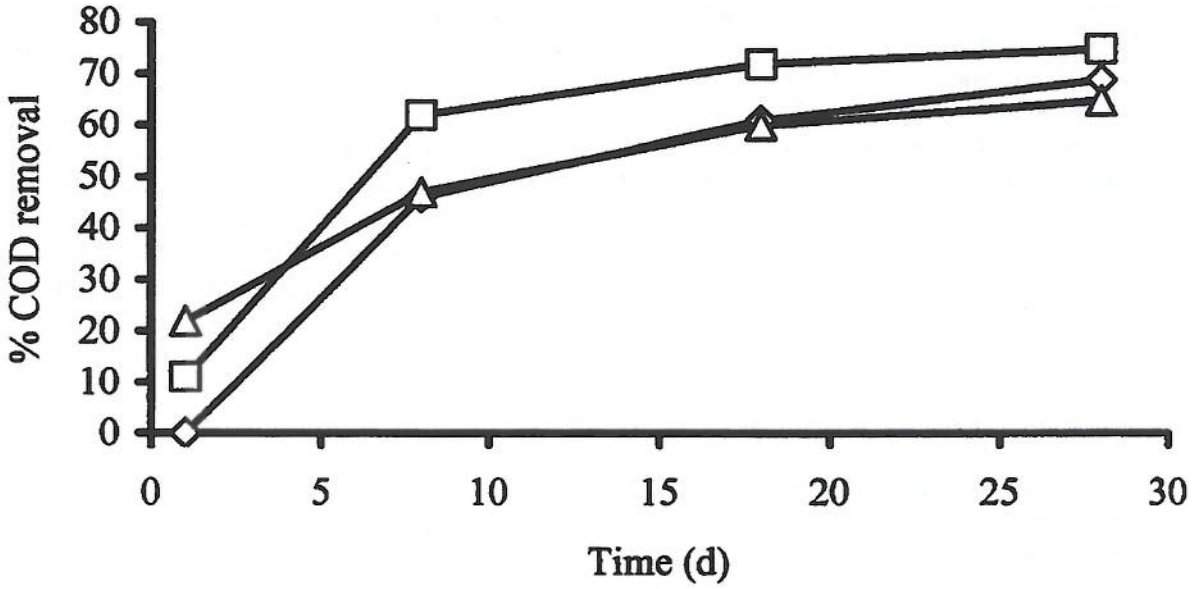


Figure 3. Percentage biodegradation of leachates at starting COD concentrations of 287 mg l^{-1} (□), 396 mg l^{-1} (△) and 479 mg l^{-1} (◇).

Table 2. Influent leachate characteristics throughout pilot-plant trial.

Determinand	Average	Maximum	Minimum	No. of tests
Temperature (°C)	17	19	15	39
pH-value	7.8	7.8	7.8	33
Total alkalinity (mg l^{-1} as $CaCO_3$)	4520	4619	4338	12
Soluble orthophosphate (mg l^{-1} as P)	1.7[a]	1.2[a]	1.2[a]	4[a]
	10.4[b]	10.5[b]	10.2[b]	3[b]
Chloride (mg l^{-1} as Cl)	1,000	1,000	1,000	4
SS (mg l^{-1})	119	191	66	22
TCOD (mg l^{-1})	765	905	625	18
SCOD (mg l^{-1})	722	859	616	10
BOD_5 (mg l^{-1})	76	144	45	4
NH_4-N (mg l^{-1})	568	652	533	19
TON (mg l^{-1})	4	10	0.5	13
NO_2-N (mg l^{-1})	0.3	0.9	0.01	13
NO_3-N (mg l^{-1})	4.1	10	0.3	8

[a]trisodium orthophosphate dosing
[b]sodium/potassium hydrogen phosphate mix

Table 3. Average suspended solids, BOD and COD performance for the BAF pilot-plant.

Parameter	Influent (mg l^{-1})	Effluent (mg l^{-1})	Removal (%)
Suspended solids	132	35	73
Total COD	787	506	36
Soluble COD	719	588	18
Total BOD	86	6	93

>70 %w/w. However, COD removal was poor, indicating a high proportion of recalcitrant (hard) COD was present. During this period, effluent pH rose to an average of pH 9.2 with only 33 %w/w of influent ammonia removed (Table 4). Of this removed ammonia, < 8 %w/w was accounted for by the average effluent TON.

After the first stable operating period, pH control was initiated. The reactor pH was lowered to pH 7.1 – 7.8 by dosing hydrochloric acid. Over an 8 d period, nitrification

Table 4. Average ammonia removal and oxidised nitrogen production during 17 d stable operation without pH control.

Parameter	Influent ($mg\ l^{-1}$)	Effluent ($mg\ l^{-1}$)	Removal (%)
Ammonia -N	581	392	33
Total Oxidised N	4.1	45	-
Nitrite -N	0.1	35	-
Nitrate -N	4.3	8.8	-

improved until steady-state ammonia removal of 99 %w/w was achieved. The BAF was then monitored during stable operation for a further 8 d, during which period ammonia removal remained at 99 %w/w (Table 5). A mass balance indicated that 95 %w/w of the influent ammonia could be accounted for in the effluent, with the majority present as nitrite. High effluent concentrations of nitrite confirmed that the first stage of nitrification was functioning but that the second stage was not (Table 5).

Table 5. Average ammonia removal and oxidised nitrogen production during 8 days stable operation with pH controlled at pH 7.2.

Parameter	Influent ($mg\ l^{-1}$)	Effluent ($mg\ l^{-1}$)	Removal (%)
Ammonia -N	578	6.2	99
Total Oxidised N	0.6	543	-
Nitrite -N	0.3	524	-
Nitrate -N	0.3	4.7	-

DISCUSSION

It is well established that ammonia can be removed by stripping from aqueous effluents. Ammoniacal nitrogen is removed by volatilisation of dissolved ammonia; the rate of ammonia transfer is enhanced by increasing the pH thereby converting a greater proportion of the ammonium ion to free ammonia [19]. The optimum pH was found to be in the range pH 10.5 to 11.5 and that air requirements increase with decreasing pH for a given ammonia removal [20]. The free ammonia (FA) concentration is a function of the total ammonia concentration, pH and temperature of a solution [21]:

$$FA\ as\ NH_3\left(mg\,l^{-1}\right) = \frac{17}{14} * \frac{total\ ammonia\ as\ N\left(mg\,l^{-1}\right) * 10^{pH}}{\left(\frac{K_b}{K_w}\right) + 10^{pH}} \qquad (i)$$

where K_b and K_w are the ionisation constants for ammonia and water respectively. Using this equation, during the first stable operating period, the ammoniacal-nitrogen concentration was 581 $mg\ l^{-1}$; therefore 192 $mg\ l^{-1}$ was present as free ammonia. This was 33 %w/w of the total ammonia concentration – corresponding to the percentage removal of ammonia. However, as there was some conversion of ammonia to nitrite and nitrate accounting for 8 % of the removal, 25 % could be accounted for due to ammonia stripping.

During the second stable operating period, pH adjustment stimulated nitrification, but only to nitrite as opposed to nitrate. Lowering the pH decreases the proportion of ammonia present as dissolved gas compared to the ammonium ion. The former is the substrate for the first stage of nitrification, therefore the conversion to nitrite is stimulated [4]. However, as has been noted [21] and summarised [22], high concentrations of nitrite at the operating pH used in this study inhibit the conversion to nitrate by *Nitrobacter*.

Discharge of effluent to the environment with high nitrite concentrations would be unacceptable. However, the ability of processes to denitrify nitrite has been demonstrated previously [23]. Therefore nitrification-denitrification can be achieved without the need to supply the additional energy for nitrate production. While it is likely that BAF systems similar to the one assessed here can be applied to leachates, optimisation will need to be undertaken in terms of aeration [24], flow direction [25], media type [26] and size [27].

CONCLUSIONS

The study confirms the potential feasibility of the small footprint BAF process for the treatment of domestic landfill leachate, with ammonia-N concentrations reduced to below 10 $mg\ l^{-1}$ and BOD to below 20 $mg\ l^{-1}$. Onward anoxic denitrification of nitrite-nitrogen and COD polishing is required to reach typical discharge consent standards.

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Assessment of municipal waste compost as a daily cover material for odour control at landfill sites

Claire Hurst[a], Philip Longhurst[a,*], Simon Pollard[a], Richard Smith[a], Bruce Jefferson[b], Jan Gronow[c]

[a]*Integrated Waste Management Centre, Cranfield University, Bedfordshire, MK43 0AL, UK*
[b]*School of Water Sciences, Cranfield University, MK43 0AL, UK*
[c]*Environment Agency, Science Group – Waste and Remediation, Olton Court, 10 Warwick Road, Olton, Solihull, West Midlands, B92 7HX, UK*

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Practical measures to improve landfill odour control are investigated.

Abstract

The ability of municipal waste compost as a daily cover material to reduce the odorous emissions associated with landfill surfaces was investigated. Trials were carried out using landfill gas, a certified sulphurous gas mix and ambient air as a control. Odorous gas was passed through portable test column filled with compost at different densities (590 kg/m^3 and 740 kg/m^3). Gas samples were taken from the inlet, outlet and at varying column depths and examined using a combination of sensory analysis (olfactometry) and a novel analytical method (Transportable Selected Ion Flow Tube – TSIFT). Results for the trials using landfill gas showed a 69% odour reduction (OU/m^3) through the column for compost with a bulk density of 590 kg/m^3, and a reduction of 97% using compost with a bulk density of 740 kg/m^3. TSIFT analysis showed an overall decrease in the concentration of terpenes, and sulphurous compounds in the outlet gas from the column for both bulk densities. No significant trend could be identified for the concentrations at different depths within the column. Results show the ability of compost to reduce landfill odours under differing conditions. The inconclusive data provided by TSIFT analysis may be due to the analysis of compounds that are not contributing to odour, and thus highlights the potential for synergetic effects and the importance of sensory measurement when examining odorous emissions.
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Keywords: Landfill; Daily cover material; Odour; Municipal waste compost

1. Introduction

Municipal waste landfills are large heterogeneous areas in which organic wastes undergo degradation in anaerobic, acidic environments resulting in a high generation rate of landfill gas (Davoli et al., 2003; Schmidt et al., 1998). Emissions from municipal landfill sites can potentially be detrimental to both local and global air quality (Allen et al., 1997). Landfill gas consists of up to 65% v/v methane and 35% v/v carbon dioxide, both of which are considered to be greenhouse gases contributing to global climate change (Allen et al., 1997). Trace volatile organic compounds represent less than 1% v/v of landfill gas. However, these compounds are often odorous (Bradley et al., 2001). With increased levels of urbanisation and consequent location of landfills in close proximity to highly populated areas, there has been an increasing level of intolerance to odour, which is now arguably the greatest nuisance associated with landfill sites (Bradley et al., 2001). Consequently, odour control

* Corresponding author. Fax: +44 1234 751671.
E-mail address: p.j.longhurst@cranfield.ac.uk (P. Longhurst).

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has become an increasingly important aspect of regulation of landfills. A reduction in odorous emissions is one of several objectives associated with the use of daily cover material at landfill sites (Environment Agency, 2000). Conventionally, material suitable for use as daily cover has been sourced from waste generated by the construction and demolition industry, however, with a global decline of the industry, coupled with the introduction of landfill tax, and increasing pressure to recycle and reuse resources, the amount of suitable material for daily cover being sent to landfill is declining (Greedy, 1995). There is a need to identify suitable alternatives to traditional daily cover materials. Materials investigated to date include paper mill sludge, fly ash, mulched wood material and foams (Bracci et al., 1995; Bradley et al., 2001; Carson, 1992; Hancock et al., 1999; Shimaoka et al., 1997). With the increasing drive towards sustainable waste management, use of a waste derived product such as compost, widely used in bio filters, appears favourable. The ability of compost to remove chlorinated hydrocarbons and sulphur compounds has been reported by Muntoni and Cossu (1997).

Investigating the capacity of alternative daily cover (ADC) materials to attenuate odorous emissions can be undertaken using olfactometry, or via the quantification of potentially odorous compounds using chemical analysis. The latter provides quantitative on the presence of potentially odorous emissions. In contrast, olfactometry provides information on the odour threshold and thus potential sensory impact from the perception of the individual. Therefore, ideally a combination of the two techniques would be required to assess the efficiency of a material to reduce the release of odorous compounds into the atmosphere.

This study investigated the ability of compost to reduce both the sensory impact of the odour concentration from the landfill gas and an understanding of the chemical compounds and their reduction that can potentially contribute to that odour.

2. Materials and methods

2.1. Test apparatus

The test apparatus comprised of an 800 mm long, 120 mm diameter, gas proof, acrylic cylinder, sealed at each end with acrylic plates and rubber seals (Fig. 1). The effective packing height was 600 mm, allowing entry and exit spaces of 100 mm. Six gas sampling ports, with air tight valves, were located at 100 mm intervals throughout the packing height, allowing gas samples to be taken at different compost depths. Air tight valves were also located at the gas inlet and outlet points. The test material was supported on a perforated plastic plate.

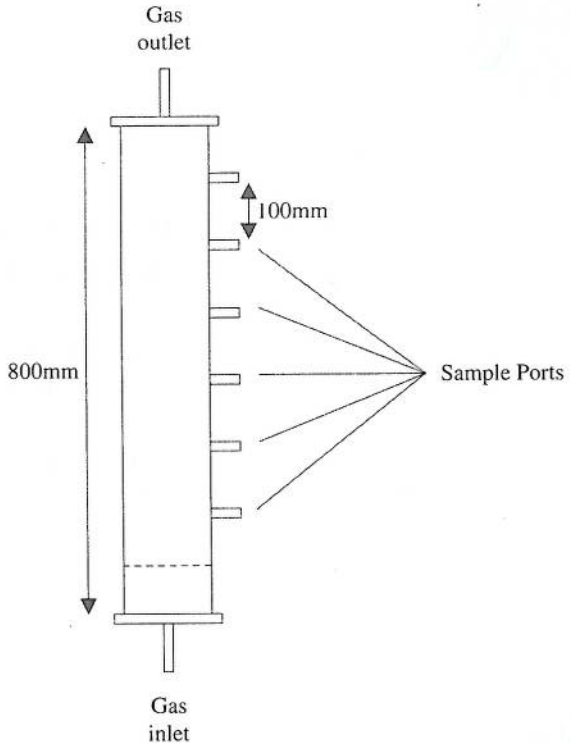


Fig. 1. Test rig used to assess effectiveness of compost as a daily cover material for odour reduction.

2.2. Daily cover material

Municipal solid waste compost was used to represent daily cover material, however, the experimental methodology may be applied to other materials. Three compost treatments were investigated as shown in Table 1. The moisture content of the compost as supplied was 35% w/w. To achieve a moisture content of 50% w/w the appropriate volume was added. Two compost densities were investigated to represent the compaction likely to occur on site during the application process. Compost was placed in the column and compacted either by gently shaking to achieve a bulk density of 590 kg/m^3, or rammed in four layers by dropping a 3 kg weight 50 cm onto the compost surface to achieve a bulk density of 740 kg/m^3.

Table 1
Compost and gas treatments

Treatment number A	Compost treatment		Gas treatment		
	Density (kg/m^3)	Moisture content (%)	Landfill gas	Standard gas	Ambient air
a	590	35	√	√	√
2	740	35	√	√	√
3	740	50		√	√

Table 2
Certified standard gas supplied by BOC Gases, Manchester

Component	Concentration
Dimethyl disulphide	0.25 ppm
Methyl mercaptan	2.5 ppm
Hydrogen sulphide	70 ppm
Carbon dioxide	35% v/v
Methane	Balance

2.3. Sample gases

Three sample gases were passed through the column in a series of experiments (Table 1). To test the robustness of the test column and sampling regime a certified standard gas (BOC Gases, Manchester, UK) containing sulphurous compounds was used (Table 2).

Experiments using landfill gas were undertaken at a landfill site in Eastern England. A single gas well, located in Stage 2 of the site was isolated from the main gas collection system.

To establish the background generated by the compost alone, ambient air was passed through the column. The emissions generated from the compost are shown in Table 3. The heterogeneity of the compost material is indicated by the large standard deviations.

2.4. Operating conditions

Once the column had been filled with appropriate compost treatment, all sampling ports, except the inlet and outlet, were closed. The column was operated in up-flow mode to simulate the landfill surface emissions. Gas flow rate through the column was measured and maintained at 250 ml/min using a gas flow meter, providing an empty bed retention time (EBRT) of 36 min. Time restrictions dictated a gas flow rate greater than surface emission rates likely at landfill sites, and it was recognised that similar, previous studies had used a considerably lower flow rate of 10 ml/min (Humer and Lechner, 1999; Muntoni and Cossu, 1997).

The column was allowed to equilibrate and vent to the atmosphere for an hour. Gas samples were taken from the inlet and outlet points of the column for olfactometry and Transportable Selective Ion Flow Tube (TSIFT) analysis (Section 2.5.2 below). Samples were also taken at different compost depths (10, 30 and 50 cm) for TSIFT analysis.

Table 3
Emissions from compost when passing ambient air through a compost depth of 60 cm at 250 ml/min for 96 min (Mean ± standard deviation)

Parameter	Value
Odour concentration (OU/m^3)	709 (±463)
Terpenes (ppb)	120 (±58)
Dimethyl sulphide + ethanethiol (ppb)	123 (±53)
Dimethyl disulphide (ppb)	31 (±25)
Hydrogen sulphide (ppb)	2 (±7)
Ammonia (ppb)	31 (±42)

2.5. Sample analysis

2.5.1. Olfactometry

Odour concentration measurements were carried out in accordance with the CEN draft protocol 'Air quality – determination and odour concentration by dynamic dilution olfactometry' (CEN, 2001).

2.5.2. Transportable selective ion flow tube (TSIFT)

TSIFT combines gas kinetics, chemical ionisation, flow techniques and mass spectrometry to allow the detection and accurate quantification of trace gases without the need for pre concentration and water removal. Studies by Španěl and Smith (1998) have indicated the suitability of the TSIFT technique for the detection and measurement of dimethyl sulphide (DMS), dimethyl disulphide (DMDS) and ethanethiol, with concentrations provided in parts per billion (ppb).

2.5.3. Compost analysis

Moisture content and pH are important parameters in the operational efficiency of compost bio filters (McNevin and Barford, 2002). Prior to the start of each experiment a sub-sample of compost was taken and analysed for moisture content (BS 7755., 1994) and pH (BS 7755., 1995). At the end of each experiment compost samples were taken at 10 cm increments throughout the depth of the column, and analysed for moisture content and pH.

3. Results and discussion

3.1. Odour reduction

One of the objectives of daily cover material is to reduce odour emissions from the working surface (Environment Agency, 2000). It is debated whether it is the newly deposited waste or rogue emissions of landfill gas that cause the odours associated with landfill sites, though it is recognised that the use of daily cover would be of an advantage when dealing with deposition of malodorous wastes (Greedy, 1995).

Trials using landfill gas indicated a 69% reduction in the outlet odour concentration (OU/m^3) when compared with the inlet odour concentration 69% having passed through the column of compost with a bulk density of 590 kg/m^3, and a reduction of 97% when the bulk density of the compost increased to 740 kg/m^3, representing a significant ($p \leq 0.05$) improvement in odour reduction with increased bulk density.

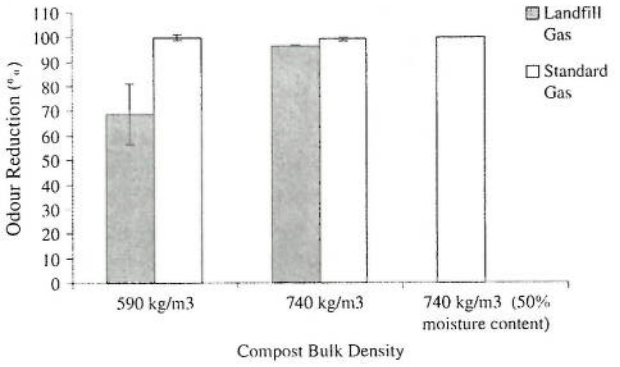


Fig. 2. Mean reduction in odour concentration achieved by passing landfill gas and standard gas through a 60 cm column of MSW compost, at 250 ml/min for 96 min ($n = 3$, means ± SD).

Trials using the standard gas yielded a reduction in odour concentration ranging between 97% and 99%, with no significant difference between treatments (Fig. 2). Mean odour emission from the compost alone ranged between 78 and 1510 OU/m^3, with an average value of 709 OU/m^3. No significant difference was found in the emissions from the different treatments. The large range of values may be a reflection of the heterogeneity of the compost, with the additional error associated with olfactometry analysis of up to ±40% (IPPC Guidance Note H4 – Part 2, 2002).

3.2. Removal of individual compounds

Odours are often associated with sulphur compounds including hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide (e.g. Bradley et al., 2001). A review of potentially odorous compounds present in landfill gas and a list of the most significant compounds compiled (Table 4) has highlighted the importance of sulphurous compounds and formed the basis for the choice of chemical compounds investigated, allowing comparison with previous studies (Parker et al., 2002).

3.2.1. Removal of individual compounds from standard gas

Compost with a bulk density of 590 kg/m^3 and 35% w/w moisture content showed the ability to significantly ($p \leq 0.05$) reduce the concentration of all the compounds investigated within the first 10 cm of the column. Concentrations of DMS and ethanethiol were reduced by 38% v/v, while concentrations of the DMDS, hydrogen sulphide and methanethiol were all reduced by more than 90% v/v. Increasing compost depth did not result in further significant reduction in compound concentration, with the exception of DMS and ethanethiol where concentrations were reduced by a further 7% v/v in the subsequent 20 cm of compost (Fig. 3).

Table 4
Summary of the most odorous compounds present in landfill gas identified in the present study and an independent review

Rank odour importance	Findings of current study	Findings of independent review (Parker et al., 2002)
1	Methanethiol	Hydrogen sulphide
2	Ethyl butanoate	Methanethiol
3	Ethanethiol	Butanoic acid
4	Dimethyl sulphide	Ethanal
5	Dimethyl disulphide	Carbon disulphide
6	Diethyl sulphide	Ethyl butanoate
7	Butanoic acid	1-propanethiol
8	Hydrogen sulphide	Dimethyl disulphide
9	1,1-dichloroethane	Ethanethiol
10	Diethyl ether	1-pentene
11	Propan-1-ol	Dimethyl sulphide
12	Methyl butanoate	1-butanethiol
13	Pentanethiols	Propanoic acid
14	Propyl propanoate	Butyl ethanoate
15	Propyl benzenes	Butanal

No significant reduction in the concentration of any of the standard gas constituents was observed when the compost bulk density was increased to 740 kg/m^3.

However, when the bulk density was maintained at 740 kg/m^3, and the moisture content increased to 50% significant reductions ($p \leq 0.05$) in concentration were observed when comparing inlet and outlet results. Concentration reductions ranged from 28% for DMS and ethanethiol to 100% for hydrogen sulphide. When examining the depth profile for compound reduction, all gases showed a significant reduction in concentration after the first 10 cm of compost. Reductions of 67% were observed for DMS and ethanethiol, 82% for DMDS and more than 95% for hydrogen sulphide and methanethiol. DMS and ethanethiol were the only compounds to show a significant reduction in concentration at each sampling depth, but still only achieved an overall removal of 28% through the entire column depth (Fig. 4).

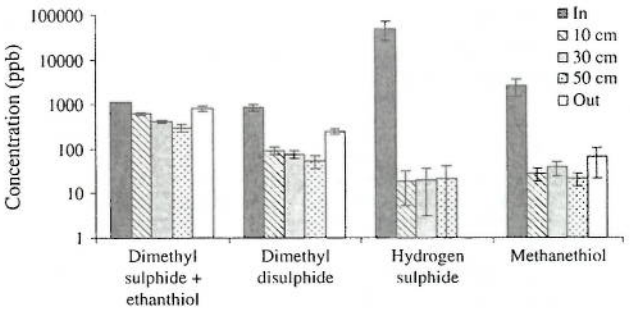


Fig. 3. Concentrations of selected compounds present in standard gas at increasing compost depth when passed through a column of MSW compost, with a bulk density of 590 kg/m^3, 35% moisture content, at 250 ml/min for 96 min ($n = 3$, means ± SD).

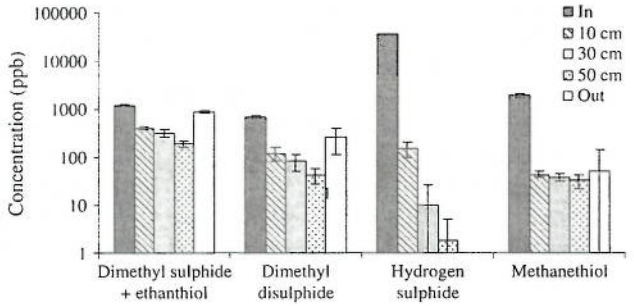


Fig. 4. Concentrations of selected compounds present in standard gas at increasing compost depth when passed through a column of MSW compost, with a bulk density of 740 kg/m^3, 50% moisture content, at 250 ml/min for 96 min ($n = 3$, means ± SD).

3.2.2. Removal of individual compounds from landfill gas

Results (Fig. 5) indicated that whilst compost with a bulk density of 590 kg/m^3 exhibited a capacity to remove small amounts of terpenes, DMS, ethanethiol, DMDS and hydrogen sulphide, there were no significant reductions.

However, when compost with a bulk density of 740 kg/m^3 was used, there was a significant reduction ($p \leq 0.05$) in overall concentrations of terpenes, DMDS and hydrogen sulphide from the inlet to the outlet, representing a compost depth of 50 cm. The first 10 cm of compost was responsible for the most significant reduction in compound concentrations, removing between 63 and 100% v/v of the original concentrations, with subsequent depth increments of 10 cm having no significant effect on the removal of the compounds. Interestingly, significant increases ($p \leq 0.05$) in the levels of terpenes, DMS and ethanethiol and DMDS were found when comparing concentrations in compost at a depth of 50 cm and the outlet samples. Concentrations of ammonia did not differ significantly through the depth of the column.

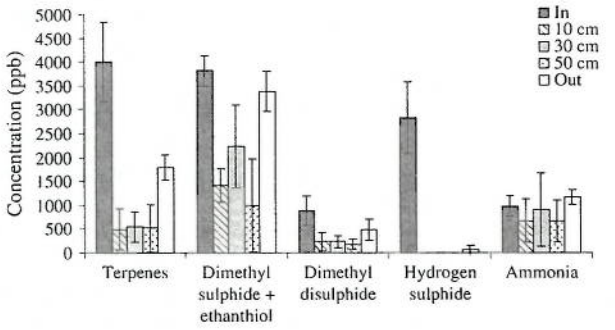


Fig. 5. Concentrations of selected compounds present in landfill gas at increasing compost depth when passed through a column of MSW compost, with a bulk density of 740 kg/m^3, at 250 ml/min for 96 min ($n = 3$, means ± SD).

The inconsistency of the results in the present study may be due to a synergetic effect between additional compounds present in landfill gas, as discussed in Section 3.1.

Odour and individual compound removal were both accompanied by insignificant changes in moisture content and pH within the column for all gas and compost treatments suggesting minimal biological activity within the column.

3.3. Correlation between reduction of odour and individual compound concentrations

The quantification of odour is complex and not easily definable, with personal influences, cultural influences, education and expectation all having an influence. The analysis of odour can be carried out either by olfactometry or chemical analysis. In the present study the concentrations of all the individual compounds analysed using the TSIFT, with the exception of ammonia, consistently exceeded the odour threshold values shown in Table 5. An attempt was made to identify any correlations between odour measurements and individual chemical compound concentrations.

No significant correlation could be found between the concentration of individual compounds in the landfill gas and olfactometry results. Previous studies by Bradley et al. (2001) noted that there appeared to be a pronounced synergetic effect between compounds, as when considered individually, few compounds produced a noticeably unpleasant odour. This highlights the difficulty in predicting emissions when several odours are combined (Bradley et al., 2001).

There were significant correlations ($p \leq 0.05$) between the compound concentrations present in the standard gas with the exception of DMS.

In considering results from the ambient air samples, the inconsistent presence and low concentration of low level of hydrogen sulphide may account for the insignificant correlation between analytical and sensory measurement. The high odour threshold of ammonia and measured concentrations not exceeding that threshold explains the absence of any correlation between

Table 5
Reported odour threshold ranges for the compounds analysed using TSIFT (Woodfield and Hall, 1994)

Compound	Reported odour threshold ranges	
	(mg/m^3)	(ppb)
Terpenes	0.0000018–0.0001	0.0003–0.0177
Methanethiol	0.000003–0.038	0.0015–19.0
Ethanethiol	0.000043	0.0166
Dimethyl sulphide	0.00034–0.0011	0.1316–0.4259
Hydrogen sulphide	0.00076	0.536
Dimethyl disulphide	0.0011–0.046	0.2809–11.75
Ammonia	0.1–11.6	140.67–1631

TSIFT and olfactometry data in both the ambient air and landfill gas samples.

Several attempts have been made to relate odour concentrations with the concentrations of individual odorants. Hobbs et al. (1999) were unable to find any correlation between olfactometry response and measurements of hydrogen sulphide when examining emissions from pig slurry. In contrast, Noble et al. (2001) found a close correlation between the combined concentration of hydrogen sulphide and DMS and odour concentration for on-site emissions from mushroom compost, with the relationship unaffected by compost conditions, i.e. whether it was aerated or unaerated, pre- or post-wetting. The relationship was not as good when comparing hydrogen sulphide and DMS separately with odour measurements. No correlation was found between ammonia and odour concentrations even though ammonia levels exceeded odour threshold levels in 95% of the samples taken.

Thus, the results from this and previous studies (e.g. Bradley et al., 2001; Hobbs et al. 1999, Davoli et al., 2003) appear to confirm that a definitive assessment of the sensory impact of odour can only truly be measured via olfactometry.

3.4. Operational implications

3.4.1. Storage of compost stockpiles

The use of compost at landfill sites would require the establishment of stockpiles on site and could have implications with regard to odour, chemical emissions and leachate formation. As an organic material, a priority is to minimise the handling time to reduce potential hazards and nuisance, and these are likely to be more critical in warmer weather and increasing proximity to the general public (Walker, 1997). Investigations by Hancock et al. (1999) concluded that stockpiles of mulched woody material (MWM) and mixtures of MWM with clayey soils did not represent a source odour and that in a managed landfill environment the generation of leachate should not pose a problem. It was found that after 16 days of exposure to a total of 18 mm of rainfall, the stockpiles remained oxygenated, with only minor oxygen depletion and carbon dioxide production. Odour flux measurements indicated that increased odour was detected from stockpiles containing up to 50% soil and was described as 'mildly unpleasant/neutral earthy/grass/compost' by the odour panel. In general, storage times are site specific and will vary with site characteristics, and seasonal, storage and processing conditions (Walker, 1997).

3.4.2. Depth of application

Currently the minimum depth of daily cover material required is 150 mm. The results from the present study indicate that there would be no benefit in increasing this depth requirement as the majority of the removal of potentially odorous chemical compounds occurred in the first 100 mm depth of cover. While the long term consequences of using a greater amount of daily cover material are discussed in Section 3.4.3., caution should be applied to the possibility of reducing the minimum cover requirements, and should be addressed on a site by site basis, considering the type of waste being received, proximity to the local community and meteorological conditions.

3.4.3. Preservation of void space and increased landfill life

One of the most significant disadvantages associated with the use of daily cover material is the void space it occupies that would be available for primary waste. This represents both a commercial disadvantage for the operator by filling a valuable space resource with a low value waste, but also a disadvantage to the community as a whole as the landfill space will fill at a faster rate (Greedy, 1995). If the minimum licensing requirement of 150 mm of cover material is applied to every 2 m of waste a 7.5% reduction in void space can occur, and this may increase to 25% when the covering of the landfill flanks is included (Greedy, 1995). By using an alternative daily cover material the volume occupied by cover soil in a site could be reduced from 25% to 13% of the fill capacity, representing a significant extension of the operating life of the landfill and potentially a substantial increase in operating revenue (Haughey, 2001).

4. Conclusions

The suitability of the developed sampling technique for the testing of compost material was shown by good repeatability of results obtained by passing a standard gas through the test column. This sampling technique could therefore be applied to other cover materials, under varying operating parameters to simulate different climatic conditions.

Results obtained by TSIFT analysis indicated the potential role of the technique in the study of landfill gas composition, while highlighting the need for a more comprehensive analysis suite.

Field trials have shown that MSW compost has the ability to reduce odorous emissions from landfill sites by up to 97%, with removal efficiency increasing with compost bulk density. Frechen (1995) estimated that the specific emission rates from an active depositing area ranged between 4000 and 30 000 $OU/m^2/h^{-1}$ and therefore based on the findings of this trial, emissions could be potentially reduced to 120–900 $OU/m^2/h^{-1}$ by the use of compost as a daily cover material.

Field trials have also indicated the ability of MSW compost to reduce emissions of selected sulphurous

compounds, with between 63 and 100% of the inlet concentration removed in the initial 10 cm of compost depth. Other studies support its ability to remove sulphur compounds and chlorinated hydrocarbons from landfill surface emissions (Muntoni and Cossu, 1997). Therefore, the use of a compost daily cover could potentially reduce the impact of emissions on the health of the surrounding community, by reducing the release of individual compounds and by also reducing odour complaints, and thus facilitating better relations between the general public, operators and regulators.

Poor correlation between individual compound and odour concentrations obtained from trials using landfill gas, in comparison to those using standard gas, indicate the possibility of other compounds present in landfill gas contributing to a synergetic effect to produce odorous emissions. The potential synergy between compounds highlights the need for sensory measurement in the assessment of odorous emissions from landfill sites.

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Producer responsibility, waste minimisation and the WEEE Directive: Case studies in eco-design from the European lighting sector

Annika Gottberg [a,c], Joe Morris [a,*], Simon Pollard [b], Cecilia Mark-Herbert [c], Matthew Cook [a]

[a] *Institute of Water and Environment, Cranfield University, Bedfordshire, UK*
[b] *Integrated Waste Management Centre, Cranfield University, Bedfordshire, UK*
[c] *Department of Economics, Swedish University of Agricultural Sciences, Box 7013, 750 07 Uppsala, Sweden*

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Abstract

The EU Directive on Waste Electrical and Electrical Equipment (WEEE) (2002/96/EC), to be implemented in stages from August 2004, attempts to tackle the growing quantity WEEE by making producers responsible for the costs of the collection and recycling of their products at the end of usable life. This is considered to give producers a financial incentive to reduce waste at source through eco-design. This link is, however, under-researched and little is known generally about the effectiveness of extended producer responsibility (EPR) and policies to promote it.

This paper presents the findings of an exploratory study to address these important gaps in knowledge. Literature review was used to develop an analytical framework to explain the relationships between the drivers for eco-design and the role of policies to promote EPR. This was applied to eight case studies of firms from the European lighting sector. While quantitative data to confirm the link between EPR and eco-design were difficult to obtain, the case studies showed that EPR has had little effect on product development so far. Within the sector studied, most producers have been able to pass on incremental costs associated with EPR to customers with negligible effects on sales. This reflects perceptions in the lighting sector that, because demand for products is relatively price inelastic and the regulation affects all producers equally, EPR is unlikely to drive eco-design at least in the short run. The cases also showed that choice between individual and centrally provided waste recovery schemes rested on perceptions of relative costs and practicability. It was evident that other drivers, such as bans on hazardous substances, product declarations and supply chain pressures, were often more effective promoters of eco-design. Thus it seems a mix of policy measures is required rather than reliance on economic instruments alone.
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Keywords: Extended producer responsibility; Eco-design; Environmental policy; WEEE

* Corresponding author. Tel.: +44 1525 863306; fax: +44 1525 863344.
E-mail address: j.morris@cranfield.ac.uk (J. Morris).

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1. Introduction for revision

Policy discourse concerned with sustainable development has called the environmental efficiency of modern production and consumption practices into question (Meadows et al., 1972; Weizacker et al., 1998; Perman et al., 1999; Hawken et al., 2000). Two aspects have been of particular concern, namely: excessive and inefficient use of natural resources and the generation of large quantities of emissions and noxious residuals, including solid waste, that have a deleterious effect on the earth's ecological systems. Actions to de-carbonise economies, improve the efficiency of resource use and minimise potential pollutants have become key elements of policy and law to promote sustainable development (Berkout, 2002; Tietenberg, 2003; Dti, 2003; Segger and Khalfan, 2004; Hawkins and Shaw, 2004). In this context, this paper considers actions to address the growing quantities of waste electronic and electrical equipment (WEEE) generated within the European Union by promoting extended producer responsibility (EPR).

Following an overview of policies to promote EPR in the electric and electronic goods sector, evidence is presented from literature of the links between eco-design and EPR and of factors which influence business decisions to undertake eco-design. The research methodology is then set out, describing an analytical framework developed from literature and used to analyse eight exploratory case studies in the European lighting sector. The paper ends with conclusions which point to the need for an improved understanding of company responses to drivers of eco-design, including those associated with environmental policies.

2. Policy context

2.1. Waste minimisation and extended producer responsibility

Within the European Union, policies to address waste issues are increasingly formulated by the European Commission and subsequently enacted by Member States. While traditionally these have sought to remediate the environmental impacts of landfill and incineration, preventative policy measures are now receiving greater attention (OECD, 2002; Connelly and Smith, 2003). Such policies have focused on achieving waste minimisation and generally prefer waste reduction, followed by product reuse and materials recovery in order to avoid disposal to landfill (Davoudi, 2000; McDougall et al., 2001; Wilson et al., 2001; Commission of the European Communities, 2003; Jönsson et al., 2003).

Recent policies to achieve waste minimisation have sought to attain this through extended producer responsibility (EPR). As the term implies, this makes producers responsible for managing the potential environmental effects of their products from the point of sale throughout a product's entire life cycle (OECD, 2001). Crucially, such legislation extends producer responsibility into the post-consumer stage and transfers responsibility for dealing with products at the end of their usable life from local authorities, taxpayers and consumers to the producer.

EPR may be implemented through a mixture of regulatory, economic and voluntary policy instruments (Lindhqvist, 2000). While economic instruments are receiving increasing interest in government policy-making circles (Dryzek, 1997; Tews et al., 2003), regulation remains the predominant environmental policy instrument (Gouldson and Murphy, 1998) and has been used at both national and supra-national levels within the EU to implement EPR.

2.2. EPR and waste electrical and electronic equipment

The quantity of waste electrical and electronic equipment (WEEE) disposed of within the European Union has been of particular concern, especially given the predicted increase in WEEE of 3% to 5% per year (Cooper, 2000; Dti, 2002a; Mayers and France, 1999). Such waste presents particular environmental challenges given the complexity of electrical and electronic components and their potentially hazardous nature.

Discussions in the EU about how generation of WEEE might be curbed by EPR began in the early 1990s (Mayers and France, 1999). These resulted in the EU Directive on Waste Electrical and Electrical Equipment (2002/96/EC), which was adopted in Jan-

uary 2003 and is to be implemented in stages from August 2004. It seeks to address WEEE arising from households and businesses and specifies quantitative targets for separation, collection and recycling of WEEE, which is free of charge to the households. The Directive assigns financial responsibility for such activities to producers (Official Journal of the European Union, 2003). It comprises some 18 articles, including Article 4 that requires a commitment to adopt product designs that facilitate waste minimisation. However, at the time of the study upon which this paper reports, the European Commission had not yet conveyed the measures deemed adequate for compliance with Article 4.

While the UK Government was required to transpose the WEEE Directive into national law by 13 August 2004, it will now undertake this during summer 2005 and implement the Directive's producer responsibility obligations for household and non-household WEEE along with associated take-back obligations on retailers/distributors from January 2006 (Dti, 2005). The UK government consulted on article 4 in 2004 and hoped to achieve compliance through voluntary agreements and new product standards. There appear to be no plans for quantitative targets.

The approach to compliance with the WEEE Directive varies amongst Member States of the European Union (Cooper, 2000). For example, Netherlands and Sweden have already legislated on EPR for WEEE. In the Netherlands all categories of WEEE except information and communications technology (ICT) are subject to a compulsory scheme managed by a producer responsibility organisation (PRO). Here, fees set to recover the annual costs of the scheme are added to the price of new products (Ministry of Housing, Spatial Planning and the Environment, the Netherlands, 1998, 2001). In Sweden, a not-for-profit organisation collects and recycles WEEE, with fees set to cover the costs of the operations. However, producers of electrical and electronic equipment (EEE) can choose to fulfil their obligations individually by undertaking the necessary activities themselves or by individually contracting them out (Naturvardsverket, 2002). For joint, collective schemes, fees are based on the sale value of new products, whereas the charges for individual solutions are set when products become waste.

3. Eco-design and EPR

Innovatory activities undertaken by firms to develop cleaner products may be conceptualised as eco-design. Eco-design is concerned with the development of products which are more durable, energy efficient, avoid the use of toxic materials and which can be easily disassembled for recycling (Roy, 2000; Sherwin, 2000; Lewis and Gertsakis, 2001; Bhamra, 2004). It emerged in the 1990s with the realisation that by changing product concepts and thus associated inputs and production processes it is possible, at least in principle, to avoid the generation of wastes and the costs of abatement.

Table 1 summarises how eco-design provides opportunities to minimise waste and improve the efficiency of resource use through modifications to product size, serviceable life, recyclability and in use characteristics. It is clear that eco-design must take a whole life perspective in that measures taken in one stage can lead to trade-offs in another. The take up of eco-design will reflect the extent to which firms think they will be better off as a result. Table 1 also shows some of the perceived potential disadvantages to firms of eco-designs which may act as barriers to adoption. From a policy perspective, it is important to understand why firms adopt eco-design, and the extent to which take up might be influenced by EPR.

Studies show that factors which influence a firm's decision to undertake eco-design are various and may be divided into drivers that are external and internal to the organisation. Legislation and customer demand have been cited as the most important external drivers of eco-design (Argument et al., 1998; McAloone, 1998; van Hemel, 1998). The importance of legislation as a stimulus for eco-design is supported by evidence that changes in product design have been induced by producer responsibility in the packaging, automobile and electrical and electronic equipments (EEE) sectors (Davies, 1996; Lindhqvist, 2000; Tojo, 2001; Zoboli, 2000). However, other studies show that many companies in the EEE sector are not aware of, and fail to anticipate, producer responsibility (Naturvardsverket, 2002; Trenchard and Gowland, 2003). With respect to customer demands, Dalhammar (2002) notes the increasing importance of market drivers, although this may not be entirely independent

Table 1
Eco design and waste minimisation: opportunities and limitations

Opportunity	Achieved by	Potential disadvantage/limitations
Reduced product size/mass	Using less bulky, less heavy materials	Less bulky materials may be more complex and thus unfavourable for recycling
	Reduced product dimensions	
	Making products foldable for storage and transport	Increased efficiency in material use may result in cost and price cuts that encourage increased production and consumption, with limited net gain
Extended product life	Using durable materials	Products become outdated in design and performance
	Facilitating repair through easy dismantling and replacement of components	New shorter life products may have lower environmental impacts in the use phase that off-set the environmental gains of a long life
	Avoiding highly fashion-sensitive styles	Obsolete products in fashion driven markets
Improved recycling potential	Facilitating disassembly	Some complex materials have less mass, saving energy during the use phase, or are more durable than easy-to-recover materials
	Reducing number of components	
	Reducing complexity of materials	
		Easily recyclable materials may have substantial environmental impacts during other life cycle stages, e.g., virgin aluminium
Improved performance in use	Reduced mass	Increased complexity
	Use of energy saving devices	Increased risk of failure
	Incorporating automatic controls	Compatibility with existing infrastructure and systems
	Extended maintenance intervals	

Adapted from Lewis and Gertsakis (2001), van Hemel (1998) and Persson (2001).

of environmental legislation which places controls on the use of particular substances or components.

Internal stimuli may be more important than external drivers (van Hemel and Cramer, 2002) or may exceed external drivers after the initial triggering effect of the latter (McAloone, 1998). Research has identified a range of internal drivers, but the findings vary among different studies. Examples are opportunities to innovate (Sherwin, 2000; van Hemel and Cramer, 2002), potentials for cost savings and commercial advantages, and staff and management commitment (McAloone, 1998; van Hemel and Cramer, 2002).

In addition to external and internal drivers, characteristics such as company size may influence product development (Brown and Eisenhardt, 1995) and eco-design in particular (Argument et al., 1998; van Hemel and Cramer, 2002). Supply chain pressure appears to have been a greater motivating factor for eco-design in smaller companies than in larger ones (van Hemel and Cramer, 2002; McAloone, 1998). Furthermore, the degree to which a given manufacturer adopts the principles of eco-design may reflect its country of origin and prevailing environmental standards and expectations. For this reason, national origin is seen to affect corporate environmental engagement (Kolk et al., 2001). Germany, the Netherlands, the Nordic countries and Japan have been ranked among the most advanced nations in terms of environmental policy and achievements in, for instance, emission reduction and waste minimisation. Britain, on the other hand, has been viewed as an environmental laggard in recent years (Connelly and Smith, 2003; Drake et al., 2003; Dryzek, 1997). Companies that operate in different countries are of course subject to different national environmental laws such that the impact of the home country origin on exporting companies may be limited as Kolk et al. (2001) found when they observed national differences in environmental reporting behaviour among large multinational companies.

Research indicates that little is known about the link between EPR and eco-design to develop cleaner products. Two studies (Argument et al., 1998; Tojo, 2001) looked at producer responsibility in large companies exclusively but did not specifically examine the economic mechanisms of the policy. Both were conducted before producer responsibility for WEEE was in force, and only one of them explored electrical waste. However, while there are few specific insights from eco-design literature, economic principles may offer useful insights here. These suggest that the incentive to avoid costs associated with EPR is

thought to give firms an economic inducement to undertake innovatory activities which may be conceptualised as eco-design. However, this depends on whether the marginal costs associated with EPR are sufficiently large to have a negative impact on the financial performance of the firm, and linked to this, what proportion of costs (see Table 2) are likely to be borne by producers and customers respectively (Turner et al., 1994; Tietenberg, 2003). This in turn depends on the price elasticity of the demand for goods. If producers can transfer costs to customers via product price without affecting demand substantially, there is little incentive to innovate in order to reduce costs. This is the case where, perhaps through market dominance, branding and product differentiation, there are perceived to be few close substitutes for particular products, or where expenditure on the products is a very small proportion of total spending. In the longer term, however, substitutes are likely to emerge, such that there will be a tendency towards more elastic, price sensitive demands for particular products (Lipsey and Chrystal, 1995). In practice, it is difficult to calculate price elasticities for individual, differentiated products which often target particular segmented markets. Furthermore, price elasticity of individual products is often greater than for product groups as whole, in spite of attempts by producers to achieve the converse. Of course large scale, monopolistic producers may be able to exploit potential price inelasticity to their advantage, passing on additional costs almost entirely to their customers.

The response of producers to environmental charges also depends on whether they can avoid them (Drury, 2001). The charges paid to joint schemes are usually fixed per unit of product according to product types regardless of brand and detailed product specification. They vary in total according to sales volume. The charges may also vary over time depending on the administrative efficiency of the collection organisation and the development of collection and recycling facilities. However, a company cannot influence these charges in the short term by conducting eco-design since the charges rarely distinguish between brands and specification. Reductions in recycling costs that may arise over time by improved recycling techniques or by changes in product design by one or a few large producers are likely to benefit all producers of the product category that are members of the joint scheme. This could encourage a 'free rider' attitude amongst some manufacturers, diluting the effect of a joint scheme. For some producers, the only way to avoid charges may be to reduce production and sales. Where unit charges are high, the result could be convergence of product design and concentration of production into fewer hands.

Conversely, with individual contracts between producers and waste management companies, it may be possible to negotiate unit charges that vary with the end-of-life properties of the particular products (Dti, 2002b; Spicer and Johnson, 2004). Therefore, the potential to achieve short term cost savings through product development may be greater with individual solutions than joint schemes.

Thus, although the link between EPR and eco-design is relatively unexplored in the eco-design literature, economic principles provide useful insights. These accord a key role to the costs of EPR borne by the producer, especially how ability to transfer these to consumers influences a firm's responses to EPR. The limited findings from the eco-design literature were combined with these insights to form an analytical framework, which is presented in the subsequent section.

Table 2
Business costs of Extended Producer Responsibility (EPR)

Cost categories	Key cost components
Transaction costs	Identifying appropriate solutions and contractual partners; negotiating and managing contracts, reporting (Lipsey and Chrystal, 1995)
Collection	Containers at collection points, other equipment, maintenance, labour, transport, depending on waste volumes and distances between collection points (Theisen, 2002). Storage in the case of retailer take-back; staff time for planning and administration of operations
Recycling	Labour, equipment and space for (manual or automated) sorting, disassembly and processing; depending on waste properties and volumes (Leverenz et al., 2002). Staff time for planning and administration of operations
Miscellaneous	Provisions for environmental, health and safety protection (Leverenz et al., 2002). Waste management licences; auditing, information between different stakeholders

4. Research method

Given limited evidence of the link between EPR and eco-design, the research conducted here was classified as exploratory. Findings from literature were used to construct an analytical framework. This does not offer comprehensive ontological equivalence but rather was used as a heuristic device for exploring and conceptualising the link between EPR and eco-design. A balance between parsimony and explanatory completeness was struck and resultant conceptual insights used to guide investigation and facilitate analysis.

Consistent with the requirements of exploratory research (Robson, 2002), the conceptual framework identifies the input/drivers, process/responses and output/impacts of eco-design in the context of waste minimisation from the producer's perspective and provides a general outline of the relationships between these (Fig. 1). Limitations should be noted here as although the framework suggests a linear progression, there are many feedback loops and potential links with other factors which were not explored in this enquiry.

A multiple-case study approach was deployed and deemed appropriate to provide a broad understanding of eco-design and the likely response to the WEEE directive across a range of organisations (Robson, 2002; Miles and Huberman, 1994). Individual firms from the European lighting sector formed the unit of analysis and were selected to cover the following features perceived to influence the response to the WEEE Directive:

- companies that develop and market products;
- companies both with and without a reputation in eco-design;
- both relatively large and small companies (the latter classed as SMEs);
- companies with joint and individual WEEE solutions, respectively;
- from both environmentally leading and lagging countries;
- from countries with and without national producer responsibility for WEEE.

4.1. Case study design

For the purpose of this exploratory study and to reduce the degree of variation amongst case studies, it was decided to focus on and draw detailed insights from one product category. Preliminary enquiry showed that a number, albeit small, of companies had adopted individual and others had adopted joint

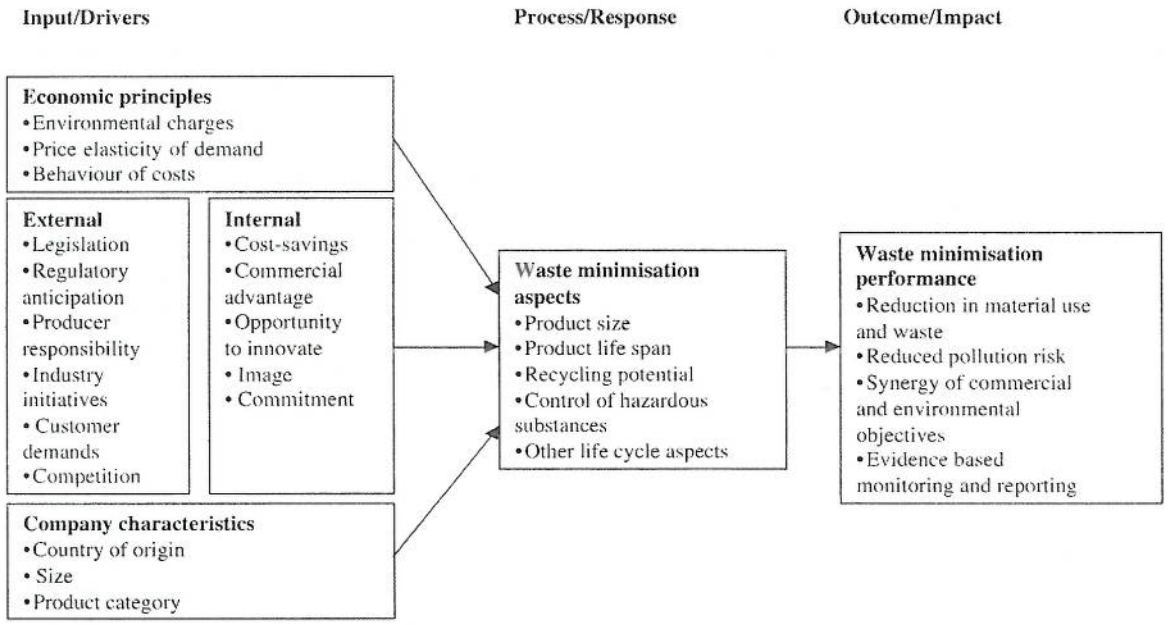


Fig. 1. Framework for the analysis of waste minimising aspects of eco-design.

WEEE solutions for lighting products. Furthermore, the environmental impacts of lighting products have recently received attention by UK organisations such as the Waste and Resources Action Programme (WRAP) and the Environment Agency of England and Wales (EA). In an attempt to promote eco-design, WRAP identified that the quality of recycled glass limits the potential market for recyclates as input material in lamp production and has attempted to overcome this barrier by providing technical and practical guidance to glass reprocessors (Hartley, 2003). As participants in a project to facilitate compliance with policies on product specification and producer obligations, the EA identified the lighting industry as one of seven prioritised sectors (Coleman and White, 2003). In particular, the EA is attempting to help small and medium size enterprises (SMEs) to interpret and meet new legislation on producer responsibility. Table 3 summarises the case companies with further details given in Appendix A.

Data from different sources such as company documents and semi-structured interviews were collected to enhance the richness of the data and reveal views of and performance in environmental management, eco-design and producer responsibility for WEEE (Yin, 1993). Quantitative data on performance was sought, but was found lacking because the case companies either did not undertake measurements, make data available, or the data did not exist in suitable form. Nevertheless, qualitative information derived from key informants on the above issues provided a picture of the influence of producer responsibility on eco-design.

Using the analytical framework detailed above, a semi-structured questionnaire was prepared to ensure that themes relevant to the aim of the study were explored in a consistent way (Appendix B). Two or more informants were interviewed in each case study organisation to reduce the possible bias of reliance on single informants. Most of the interviews were carried out by means of pre-arranged telephone conversations because this increased the accessibility of informants and provided a cost-effective medium compared to face-to-face interviews (Neumann, 2003). At one company, both face-to-face and telephone interviews were conducted and this confirmed that lack of visual information available in the latter did not appear to affect the quality of communication and outcomes. Notes were taken during interview, summarised and sent to the informants to allow for comments or clarification. Not all informants provided feedback on the summary. Of those that did, some informants made some amendments, whereas others agreed with the original text.

Previously, similar qualitative methods have proved useful for understanding how industry responds to waste policy instruments (Kautto and Melanen, 2004). With more time and resources, a systems approach would allow further analysis of the interaction of the various factors influencing eco-design (Hemmelskamp et al., 2000), enabling elaboration of the framework contained in Fig. 1.

Table 3
Summary of case studies in lighting sector

Case	Nationality	Size	Products
A	Dutch	Large	Lamps and lighting products
B	German	Large	Lamps and lighting products
C	Swedish	Large	Luminaires
D	Swedish	Large	Luminaires
E	British	SME	Luminaires
F	German	SME	Luminaires
G	British	SME	Luminaires
H	Swedish	SME	Luminaires

5. Results and discussion

The analysis of eight case study organisations in the lighting sector showed the extent to which waste minimisation was linked to product development, the role of economic mechanisms in the promotion of producer responsibility and major motives for eco-design at company level. These are discussed in turn, drawing on results from the cases summarised in the supporting appendices. With respect to product types, distinction is made between lamps (the component that generates light) and luminaires (combined lamps, fittings and controls).

5.1. Waste minimisation and product design

It proved difficult to derive objectively verifiable evidence in the case study organisations of the relationship between product development and waste minimisation and therefore of the possible influence of EPR on eco-design. Available information was largely anecdotal or confined to highly aggregated

data published by the larger companies, with achievements commonly presented as examples of single products (Appendix C). Furthermore, in some cases, reported reductions in waste appeared to be independent of eco-design, being mainly due to improvements in recycling technologies and new uses for recyclates. There is a clear need to monitor, evaluate and report the achievements of interventions such as EPR in order to inform policy. This is a sensitive topic, however, given the need to respect commercial confidentiality.

5.2. Economic mechanisms of producer responsibility as a driver of eco-design

It is often argued that environmental regulation impacts negatively on the competitiveness of business. Few concerns, however, were expressed by respondents regarding the effects on competitiveness of producer responsibility for WEEE. Furthermore, all cases viewed their competitors as equally affected by the policy. Three of the cases in this study were subject to producer responsibility for WEEE in their home countries. All other cases generated some of their revenue from exports, some to countries with, and some to countries without national WEEE policies. Generally, products were not modified for different markets, except for country specific fire regulations and voltage.

How have companies responded to the economic mechanisms of WEEE? Two of the large Swedish companies (cases C and D) that are subject to a national WEEE policy earn at least 50% of their turnover in Sweden. Both companies joined the dominant collective scheme and paid a fixed entry fee, a fixed annual membership fee and a fee per product sold charged at two rates depending on the weight of the products (Appendix D). Both companies added these costs to the prices of the products. Neither perceived any negative impacts on sales and competitiveness. Consequently, customers carried the larger part, if not all, of the cost burden and there was little incentive for the companies to adopt eco-design to avoid the costs of producer responsibility the costs. Willingness for customers to absorb the additional costs, an indication of price inelasticity of demand, may be explained by the fact that additional costs only amount to one or two percent of the total product price. In such circumstances market mechanisms may not encourage companies to adopt eco-design as a means of reducing waste at source and whole life costs.

The limited incentive for eco-design was reinforced by the fact that fees are fixed for a particular type of product rather than varying with the end-of-life properties of a particular brand or detailed design. For this reason, companies could not avoid the costs in the short term through product development. In the longer term, a company joining a producer responsibility scheme may be able to reduce the costs for end-of-life management through eco-design if it has a large market share such that a large proportion of the total waste of a particular waste category derives from that company. Relatively large volumes of waste with consistent properties suited for recycling can reduce average costs. An informant in case D mentioned this possibility but remarked that this was not currently a consideration.

Neither case D nor H (a Swedish SME) had considered an individual solution to their producer responsibility due to the perceived high transaction and resource costs involved. They had, however, not attempted to calculate the potential costs and benefits of this option, nor of an eco-design option. In case D, a contributing factor may be that the decision about producer responsibility for WEEE was taken independently by the environmental manager and only later presented to the financial and accounting functions (Appendix D). The latter appeared to look at it as an environmental issue unrelated to product development and production with limited cost implications beyond the management of environmental effects. In the Swedish SME, however, the decision was made by the managing and marketing director who can be expected to have an integrated view of the cost implications of the decision. The choice in favour of the joint scheme relative to that for an individual solution appeared to be based on a broad assessment of the relative costs of options. This is an important point: unless environmental and financial decision making are integrated within businesses, the extent to which economic instruments can make a difference to business behaviour may be limited (Bennett and James, 1999). The cases show that this is particularly relevant for product development.

The other Swedish company (C) had chosen an individual solution (Appendix D). As with case D,

the decision was taken by those responsible for environmental functions within the company. The main reason given by the informants was the existing collection and recycling infrastructure in the form of a network of retail outlets with bring-back schemes and contracts with a waste management company for recycling of waste from all business processes. This infrastructure reduced the transaction costs of the individual solution. Although the company claimed to engage in eco-design, the recycling charges did not vary with the end-of-life properties of the products. The company did not monitor the amount of returned WEEE relative the total waste and recycling, but the proportion was believed to be small and the waste contract had not been renegotiated after the implementation of the national WEEE policy. Other reasons for this may be that the company accepted WEEE from brands belonging to other organisations in their bring-back schemes and that EEE was only a small part of the total product range. Hence, the scope to avoid the costs of WEEE in the short term through eco-design was limited.

The increase in total product costs due to producer responsibility for WEEE was relatively small for most cases: between 0.5% and 3%. Furthermore, that part of the costs derived from other brands returned by customers or electrical and electronic waste arising from business processes rather than end-of-life products was not calculated (Appendix D). This may also explain why company C, allegedly, had not increased product prices following the implementation of the Swedish WEEE legislation. Consequently, the company rather than its customers carries the additional costs. It was reported that there had been little influence on product development due to the relatively low costs incurred hitherto. The situation may be different for companies marketing predominantly EEE and receiving large volumes of WEEE.

Are higher charges likely to provide an incentive for eco-design? Case A and B were not yet subject to producer responsibility for WEEE for lighting equipment but had assigned corporate task forces to deal with the forthcoming EU Directive. Their trade association reportedly had estimated the recycling costs at some 60% of the product price (Appendix D), but this seems high and probably reflects a strategic bias. However, the informants in the cases suggested that the effect on eco-design would be limited due to product characteristics of lamps, varying recycling techniques among recyclers and the fact that competitors were seen as equally affected by producer responsibility legislation. Due to the high level of standardisation, the ease with which products could be copied, the small unit size of each product and the difficulties of sorting large number of end-of-life lamps according to brand, companies advocated a joint responsibility. This reduces the extent to which costs could be avoided in the short term through eco-design. The informant in case A, which was the most advanced in eco-design of all cases, said that it was difficult to calculate the cost and benefits of eco-design. The company undertook eco-design of its different product categories because it believed it offered commercial advantage. However, in the case of lamps and producer responsibility for WEEE, case A and B's cost-reducing strategies focused more on influencing legislation and developing recycling techniques than on eco-design.

5.3. Motivations for eco-design

Are there conflicting or complementary drivers behind efforts in waste minimisation and eco-design? There were no indications that reduction in the unit size of products was motivated by producer responsibility (Appendix E). All cases except the Swedish SME claimed that they sought reduction in product size in dimension and/or mass in order to achieve potential cost savings in input materials, packaging and transport. In reality, however, technical and fashion requirements were perceived to overshadow such potential cost savings. Handling small components was also associated with relatively high average costs, outweighing the savings in input material. Policy interventions which influence the cost of materials could change this balance, however.

With regard to product life span, attitudes varied according to type of product involved. Longevity was a selling point for lamps, whereas luminaires were believed to be replaced before the end of their usable life because of changing fashions (Appendix E). Thus, there was a limited interest in extending product life span, although an informant in one case perceived that susceptibility to fashion trends varied amongst different types of customers. Thus, policy measures to encourage increased product life span are likely to

be more effective if they address demand as well supply side issues.

Luminaires were usually designed to allow dismantling for the replacement of lamps and control and switch mechanisms. In effect, this practice leads to longer product service lives. British and German SMEs built in these replacement/servicing characteristics with little awareness of environmental issues and producer responsibility for WEEE. Article 4 in the WEEE Directive does not prescribe product longevity. Instead it states that product reuse should be encouraged. Neither lamp nor luminaire producers showed any interest in design for reuse. This seems to be because the promotion of second-hand product use has traditionally been outside the producer's remit. Furthermore, a combination of the fashion obsolescence of household luminaries and the longevity of industrial luminaires has reduced the importance of their reuse as an environmental or indeed financial target.

Awareness and concern about product recycling appeared to be related to general environmental awareness, which was greater in the large companies than in the SMEs. In environmentally active companies, recycling seemed to be a part of 'life cycle thinking' (Appendices 3 and 5). Policy debates about recycling and producer responsibility may have contributed to this. Cases A and B, Dutch and German respectively, monitored the recycling potentials of some of their products. The latter reported that improved recyclability occurred as early as the early 1980s, well before the discussions about producer responsibility for WEEE. The main reason was to save costs by reusing glass as a production input. The large Swedish companies reported an interest in the recyclability of their products, which could be a result of a relatively strong societal commitment to recycling and participation in segregating waste at source (Naturvårdsverket, 2002). However, recyclability was currently not prominent in product development. The eco-design guidelines in case C included end-of-life aspects which applied to all product categories and not only electrical and electronic equipment, confirming the limited effect of producer responsibility for WEEE on eco-design.

Public debates and government bans or restrictions of certain dangerous substances were strong incentives for eco-design in the four large companies and the Swedish SME (Appendix C). The Swedish lighting industry, through its trade association, has an environmental product declaration (EPD) of materials and substances used in its products and communicated by means of an eco-label. This EPD was referred to by all Swedish cases. It helped to promote environmental issues in case H, the only environmentally active SME in the study. Of course, the presence of dangerous substances affects the recyclability of products. It is not regulated in the WEEE Directive, but in a separate Regulation of Hazardous Substances (ROHS) Directive (2002/95/EC). Two cases specifically mentioned this as more important for eco-design than the WEEE Directive. Thus, regulation seems to have a greater and more immediate effect on eco-design than the type of economic policy incentive currently associated with WEEE.

Energy consumption during the use phase is a potentially significant environmental impact of lighting equipment. It is not included in the producer responsibility for WEEE but was frequently mentioned as an eco-design aspect (Appendix E). In particular the SMEs with no manifest environmental commitment were keen to emphasise the environmental friendliness of their efforts in this aspect. The fact that energy efficiency was an important sales argument appeared to be the main reason for making improvement. It should be noted that for other categories of EEE, such as vacuum cleaners, high energy consumption associated with a larger electric motor may be viewed as a sign of quality by customers. In the case of lighting products, product labelling can help overcome this by communicating light output rather than energy consumption. The way that product performance in use is communicated is a particularly important component of eco-design.

Evidence of environmental criteria in customer purchasing behaviour was reportedly relatively rare, but mainly experienced by the large companies and the Swedish SME. Some informants felt that much depended on the type of clients. Differences could also be noted within given customer categories between countries. A British SME perceived architects to be interested mainly in quality and style and not in environmental performance. The Swedish SME, however, found architects to be environmentally aware. Case D and H, both Swedish, had also experienced environmental demands from public procurers, albeit in terms of general evidence for envir-

onmental commitment rather than actual product contents and performance.

The three largest companies claimed to make environmental demands on their component suppliers. These demands were mostly generic, for instance, requiring compliance with legislation, restrictions of certain substances and some degree of environmental management. In case A and C, purchasing codes were applied to all product categories regardless of whether they were subject to producer responsibility for WEEE or not. There was no evidence that supply chain pressure was directly influenced by or furthering the objectives of producer responsibility for WEEE.

6. Conclusions and recommendations

This paper has explored evidence from literature and selected case companies of the link between EPR and eco-design in the context of WEEE and policy interventions to reduce it. Although the limitations of such exploratory research are widely accepted and understood (Robson, 2002), the results are considered to provide an indicative platform of knowledge to inform empirical testing of the relationships referred to above, allowing for variations in industrial and national circumstances and practices. The conclusions and recommendations here are made with these limitations and cautions in mind.

The research showed that placing financial responsibility on producers for collecting and recycling WEEE did not appear to have perceived negative effects on business sales and competitiveness. The latter suggests that demand for lighting products is price inelastic in the short term and/or that the charges were too small to have a significant negative impact on participating firm's customers. Consequently, charges for producer responsibility do not appear to be sufficient in themselves to stimulate eco-design. These findings appear to challenge the claims in the literature that internalising the costs of waste management necessarily leads to changes in product design (Cooper, 2000; OECD, 2001), especially when these can be passed on to users. In the longer term, however, there may be inducements towards eco-design in pursuit of cost minimisation and competitive advantage, but again this depends on industry and market circumstances.

With respect to the choice of collection scheme, whether individual or joint, much appears to rest on perceptions of relative costs of schemes, with limited consideration of the opportunity for eco-design under each solution. A tentative conclusion drawn here is that companies may prefer to adopt an individual solution for product responsibility if transaction costs are relatively low compared to joint schemes, each product unit has a high value, products are highly differentiated, can be sorted according to brand at a relatively low cost, and the number of returned products is relatively high. It was not evident, however, as suggested by some researchers, that individual solutions to WEEE designed to cater for the particular products of a company are likely to be more effective than joint schemes in stimulating eco-design.

Perceptions of relatively low costs for joint schemes have encouraged their choice, although there was a remarkable lack of calculations of actual costs and benefits. This partly reflected the fact that in some companies the choice was an environmental rather than a financial management decision, made difficult by the challenge of estimating the market costs and benefits of eco-design. The cost increase imposed by producer responsibility was often too small to outweigh other product requirements such as fashion trends. However, higher charges may not necessarily have a stronger effect on eco-design since competitors are felt to be equally affected and demand in this sector is believed to be relatively price inelastic. Rather than promoting eco-design per se, companies appear to seek cost reductions across all business activities, influence legislation and develop recycling techniques as the most effective cost-reducing strategies. Consequently, rather than rely on producer responsibility alone, complementary incentives are likely to be needed to progress eco-design. Although, some evidence was found of achievements in waste minimisation through product development, it was difficult to corroborate due to lack of objectively verifiable environmental monitoring and reporting, especially amongst SMEs.

Command and control in the form of substance bans were observed to be effective external drivers of eco-design. Substance bans will take effect through the ROHS Directive. Similarly, it is possible to pre-

scribe product design standards that will facilitate recycling, although these would require updating as recycling technologies develop. Furthermore, there may be trade-offs amongst environmental properties whereby for example longevity requires the use of more complex materials.

Improved environmental performance during the use rather than end-of-life stage may be a stronger driver of eco-design than producer responsibility policies, with producers seeking to capture enhanced perceived user value as a source of competitive advantage. For example, energy efficiency of lighting products was particularly noticeable in SMEs who otherwise exhibited low environmental awareness. The only SME in the study undertaking environmentally conscious product development was encouraged by a combination of environmental demands from public sector procurers and an environmental product declaration. The fact that the product declaration was also the basis for an ecolabel strengthened the stimulus. This shows the benefit of a diverse, fit for purpose approach to promoting producer responsibility. In future, product declarations will include compatibility with the WEEE directive. It is important that the standards included in the latter reflect changing technology and are updated to encourage continuous improvement.

The limitations of this study provide opportunities for further research. The findings here reflect business responses to the WEEE legislation during the early stages of implementation. There should be continued monitoring to determine the achievements of the Directive against its stated aims and whether the responses by businesses are consistent with the principles of sustainable development. In this latter context, it is important to view the WEEE Regulations in a strategic context as they affect the design and development of products and processes, business competitiveness and over-all resource use efficiency. Indeed, there is a requirement on the environmental regulator to consider the impacts of its interventions on the viability of businesses. Policy makers need to know that the WEEE does more than provide another hurdle for business to jump over, that it will make a difference, and that the responses that emerge are fundamental to product and process design rather than short term coping strategies. In this respect continuous long term monitoring and evaluation of the policy is required to determine actual business achievements in waste minimisation through product development. This might be achieved by working closely with trade associations and business networks.

WEEE combines regulation with some limited use of economic instruments although these are mainly set at recovering the costs of the scheme rather than providing economic incentives as such. There is scope for the latter but this requires a better understanding of the underlying costs and benefits of alternative strategies for waste management in the EEE sector so that incentive charging scheme can be set accordingly. Indeed, the industry itself is best placed to determine appropriate charging regimes that will deliver policy targets in the most economically efficient way whilst retaining flexibility to accommodate different business circumstances at any point in time. As in other sectors, it should also be possible to design charging or permitting schemes in accordance with the degree of environmental risk.

In a wider sense these findings suggest that it is often difficult to determine the influence of any one policy instrument, in this case charges for WEEE recovery, on stimulating innovatory approaches in companies to improve resource use, waste management and sustainability. From this perspective, a better understanding of how environmental management decisions are made within organisations is essential, using the components and linkages presented in Fig. 1 as a starting point. It is apparent that responses to environmental policy are strongly influenced by many factors external and internal to the firm, including markets, competition, technology and institutions. This exploratory review of the WEEE Directive in the lighting sector confirms that understanding these wider factors is an essential prerequisite for effective policy-making and that in most cases a mix of policy interventions is likely to be appropriate.

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Appendix A. Case characteristics

Case	Main product type[a]	Household/business markets	Home country	Export	Employees	Trade assoc. member	Informants
A	Lamps	Both households and businesses	The Netherlands	Global	47000 (lighting division)	Yes	Eco-design manager
B	Lamps	Both households and businesses	Germany	Global, Europe 35%, Americas 50%, Asia Pacific 12%	35000	Yes	Head of environmental affairs/technical director
C	Luminaires	Mostly households; special B2B department in the retail outlets	Sweden	Subsidiaries in 31 countries, in Europe 80%, North America 17%, Asia 3%	70000 (entire company)	No	International environmental manager Environmental manager Sweden, retail outlets Environmental manager, product development Product engineer, lighting division
D	Luminaires	Mainly business; unusual that households are end-users	Sweden	Subsidiaries in north-western Europe; sales to Middle East and Australia, outside Sweden: ≈50%	1200	Yes	Environmental manager Development manager Accounting manager
E	Luminaires	Mainly business; households may be end-users of a small portion of sales	UK	Sales offices in the Netherlands, France and the Middle East	90	No	R and D/marketing manager Engineering manager (products)
F	Luminaires	Both households and businesses	Germany	Sales offices in 30 countries, global sales	150	Yes	Design engineer (Financial director)
G	Luminaires	Mainly business; household purchase through webpage	UK	Mostly domestic sales; some export to Russia	15	No	Product engineer Project engineer
H	Luminaires	Mainly business; households are end-users of a small portion of the sales	Sweden	Mostly domestic sales; some export to the Nordic countries and Germany	20	Yes	Managing/marketing director Product development and production manager

[a] Lamp: bulbs, tubes and similar. Luminaire: light fitting.

Appendix B. Survey questions

Informant
Role in the company; years in this position; background

Environmental criteria in product development and driving forces
Who determines product criteria?
Are there any environmental criteria in the product development process?
When and why were they introduced?
What environmental/waste minimisation aspects are emphasised? (particularly product size, product life span, reuse, repair, disassembly, recyclability)
Are the criteria binding or voluntary?
Are the achievements monitored; how?

Producer responsibility
Are you familiar with the term producer responsibility?
What actions did the company's awareness of producer responsibility for WEEE lead to, if any?
What options were considered for the responsibility and why?
What kind of solution did the company choose for fulfilling its producer responsibility for WEEE?
What were the reasons for the choice?
Who was involved in the decision?
What is the basis for the charges for producer responsibility? (fixed or variable)

Costs, prices, competitiveness
What costs are monitored and controlled in the product development process?
Does/will the costs of producer responsibility affect product prices?
How has/will this affect(ed) sales and competitiveness?
How has/will the company tried/try to influence its costs for producer responsibility?

Appendix C. Case study evidence of eco-design and waste minimisation-general; indicators and achievements

Case	General eco-design drivers and practices, including supply chain pressure	Waste minimisation indicators	Achievements
A, Neth lamps	Early 1990s management envisaged the business importance of eco-design; co-operation with academics. Computer-based tool to measure environmental impacts of products; Increasing customer demands from customers for environmental management and green products; environmental demands on suppliers through a staged model: from substances via environmental management to environmental best practice	% or times improvement; baseline: previous product % recyclability; total use hours (sample products)	25–60% weight reductions. 6 times longer life (individual products), near 100% recyclability (no baseline)
B, Ger lamps	Examples of material reuse, product size reduction and improved recyclability in the 1960s, 1970s and 1980s driven by cost saving potentials; now environmental considerations from product planning stage. ROHS Directive more important for eco-design than WEEE Directive. Environmental demands from European business customers; demands on suppliers re substances and environmental programmes	% or times improvement; baseline: previous product % recyclability; total use hours (sample products)	Example of reduced size, but no indicator or over-all figures; examples of increased product life but not no over-all figures; 100% recyclability (no baseline)
C, Swe lum	Product size reduction since the start due to cost saving potentials; eco-design tool/guidelines developed from experiments with LCA in mid-1990 — applied to all product categories where relevant; voluntary except for certain binding rules; few direct environmental demands from customers; Work with suppliers through staged model for action plans and EMSs	Sample products (of which one lighting) times or % improvement	Little on lighting products; claimed: energy consumption of lamp, size reduction, extended life
D, Swe lum	Late 1990s: eco-design opportunity to ensure continuous improvements required by EMS, although requirement not directed at products; environmental checklist applied in product development; Some environmental demands from public procurers	No	N/A (claimed: changes in substance contents, data not made available)
E UK, F Ger, G UK SME, lum	Product specs based on customer requests—no direct environmental customer demands. Waste minimisation and environmentally friendly aspects where they are driven by commercial advantages	No	N/A
H, Swe SME lum	Environmental aspects of products discussed in the company's product committee; except EPD, no formal environmental guidelines, recyclability said to be considered. Some environmental demands from architects and public procurers	No	Claimed: changes in substance contents; no absolute over-all achievements reported

Appendix D. Case study results on costs of producer responsibility

Case	Producer responsibility solution	Cost % product price	Costs transferred to product price (elasticity)	Cost avoidability, short term (ST), long term (LT)	Cost-reducing strategies	Solution decided by
A, Neth lamps	Advocate visible fees; (joint)	≈60%[a]	Yes; no anticipated effect on competitiveness	ST: No, LT: Co-operation producers–recyclers to develop recycling techniques and product properties	Influence legislation; develop recycling technology; Different techniques by recyclers prevent cost savings by product design	Corporate task force
B, Ger lamps		≈60%[b]	Yes; no anticipated effect on competitiveness	ST: No, LT: Co-operation producers–recyclers to develop recycling techniques and product properties	Influence legislation; develop recycling technology; Highly standardised products prevent competitive advantage through eco-design	Corporate task force
C, Swe lum	Individual: contractors	Costs not calculated nor added to product prices	No. Low WEEE volumes → low costs incurred	ST: (Reduced take-back; not actively applied method), LT: Contract renegotiation: costs variable with eol properties. Not considered currently	Cost-reductions in all business activities, not end-of-life specifically	Env managers
D, Swe lum	Joint (PRO)	≈0.5–3%[c]	Yes; no perceived effect on sales/competitiveness. (Yes; no anticipated effect on competitiveness)	ST: No, LT: Yes, due to large market share	None related to cost transferred to customers (cost savings in material input)	Env manager.
E UK SME lum	Not considered*	Not estimated	(Yes; no anticipated effect on competitiveness)	Not considered	Not considered	not considered
F, Ger SME lum	Low faith in joint schemes	Not estimated	(Yes; no anticipated effect on competitiveness)	Not considered	Not considered	Jointly by various functions
G UK, SME lum	Not considered	Not estimated		ST: No, LT: Not considered	None. Costs would be transferred to customers	Not considered
H, Swe SME lum	Joint (PRO)	≈0.5–3%[d]	Yes; no perceived effect on sales/competitiveness	ST: No, LT: Not considered	None related to producer responsibility; costs transferred to customers	Managing Director

Producer responsibility for WEEE only applied to cases C, D and E. Responses from the other cases were based on anticipatory action or assumptions.

[a] Estimates by trade association.

[b] Estimates by trade association.

[c] Estimation based on unit prices published by PRO applied to sample product prices. No weighting has been carried out for the relative sales volumes of different product; Not estimated or not considered by companies.

[d] Estimation based on unit prices published by PRO applied to sample product prices. No weighting has been carried out for the relative sales volumes of different product; Not estimated or not considered by companies.

Appendix E. Waste minimisation and eco-design drivers and constraints by case companies

	Product size reduction		Product longevity		Disassembly		Recycling potential		Substance restrictions		Energy savings	
Drivers	Cost savings in material input (packaging and transport)	B*, C, D, E, G	Customer demand	A, B (F)	Replacement of lamps and control gear	E, G, H	Material reuse (=cost saving)	A, B	Public debates and regulations	A, B C, D	Sales argument (win–win economic-env)	A, B, C, D, E, G
	Customer preference for unobtrusive fittings	F			Easy assembly → easy disassembly	F	Environmental life cycle considerations	A, (B) C, D, (H)	Specific mention of the ROHS Directive	B, C		
	Ease of installation	D					(Products already easily recyclable)	(B),E, F, G				
Constraints	Large rooms requiring large individual product	D, H	Replaced before end of service life due to fashion changes	D, E, F, G, H					No current substitute	A, C	Trade-off with restriction on heavy metals	B
	Small components = difficult/expensive to produce	A, F	Need for more durable expensive materials and investment in tooling	E								
	Compromised safety and quality (smaller surface to dissipate heat)	G										

*Letters indicate case identity. Dr: Driver. Con: Constraint.

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ESTIMATING POLLUTANT REMOVAL REQUIREMENTS FOR LANDFILLS IN THE UK: I. BENCHMARK STUDY AND CHARACTERISTICS OF WASTE TREATMENT TECHNOLOGIES

D. H. HALL[1], D. DRURY[1], J. R. GRONOW[2], A. ROSEVEAR[3], S. J. T. POLLARD[2] AND R. SMITH[2*]

[1] Golder Associates (UK) Ltd., Attenborough House, Browns Lane Business Park, Stanton-on-the-Wolds, Nottingham, NG12 5BL, UK
[2] Integrated Waste Management Centre, Sustainable Systems Department, School of Applied Sciences, Cranfield University, MK43 0AL, UK
[3] Environment Agency, Kings Meadow House, Kings Meadow Road, Reading, RG1 8DQ, UK.

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ABSTRACT

Introduction of the EU Landfill Directive is having a significant impact on waste management in the UK and in other member states that have relied on landfilling. This paper considers the length of the aftercare period required by the municipal solid waste streams that the UK will most probably generate following implementation of the Landfill Directive. Data were derived from literature to identify properties of residues from the most likely treatment processes and the probable management times these residues will require within the landfill environment were then modelled. Results suggest that for chloride the relevant water quality standard (250 mg l^{-1}) will be achieved with a management period of 40 years and for lead (0.1 mg l^{-1}), 240 years. This has considerable implications for the sustainability of landfill and suggests that current timescales for aftercare of landfills may be inadequate.

Keywords: Equilibrium, completion, emissions, municipal solid waste (MSW)

INTRODUCTION

In this work, presented here as the first of a series of three companion papers, we consider that landfill pollutant removal requirements are intrinsically linked to the concept of environmental equilibrium. Equilibrium is defined here as that state when emissions from a landfill site occur at a rate that allows sufficient natural attenuation in the surrounding environment to prevent environmental harm, so management is no longer required. To embody the principles of sustainability, equilibrium can only be achieved when the management period (post-closure when the site has ceased accepting waste for disposal, alternatively known as the aftercare period) is measured in decades rather than centuries. Throughout aftercare, the landfill licence or permit holder is required to take active measures to control pollution from the site. This involves monitoring, ensuring integrity of management and engineering systems such as leachate, landfill gas and restoration, and if necessary, taking corrective action until such time as licence or permit surrender is accepted by the regulator. In the UK, the Pollution Prevention Control (PPC) regime [1] requires an estimate of the time taken for a landfill to achieve completion, but guidance is lacking.

When assessing equilibrium there are a number of issues that must be considered. Firstly, it is expected that landfill liner performance will diminish with time and therefore the rate of leachate or gas leakage may increase. Secondly long-term hydraulic performance of a landfill is dependent on the management and control of leachate levels. If a landfill operator ceases to manage their liabilities, financial provisions allow the regulatory authorities to take over management of the site. Financial provision is usually restricted to a 30-60 year period.

The setting of biodegradable municipal waste (BMW) diversion targets in the EU Landfill Directive [2] and the need to pre-treat waste prior to landfilling is bringing about considerable changes to the composition of wastes going to landfill. There are concerns relating to the sustainability of landfill in general and there is a growing recognition of the long timescales required to achieve equilibrium status; there is a possibility that the change in the nature of waste going to

landfill may exacerbate this problem.

In the current study, treated wastes going to landfill were assessed using the number of years to achieve equilibrium status. A current-day landfill, designed and operated largely in compliance with today's UK guidelines was used as the benchmark. We have reviewed residue flows that can be anticipated from various waste pre-treatment and treatment processes with the aim of determining the revised properties of the waste residues that are destined for landfill. Factors that affect the biodegradable content, particle size or density of the material, or lead to the removal of metals etc. could influence the behaviour, both biological and chemical, of waste residues to an extent that landfill management options might not be the same (or even appropriate) for all waste streams. Ultimately, the success or otherwise of the options studied depend on both time and cost to achieve equilibrium status. Those techniques or combinations of technology and landfill management that can approach the definition of equilibrium were identified, and the ability to operate the scheme within the current legislative constraints considered. The waste processes investigated are shown in Table 1 as variants of mechanical biological treatment (MBT), refuse derived fuel (RDF) and energy from waste (EfW).

This study has, as a consequence of data shortages, concentrated primarily on the inorganic components of leachate. Beyond understanding the origins of these compounds, little is known of their mass balance through various waste treatment processes. Data relating to the elemental composition of municipal solid waste (MSW) is available for the primary fractions (*i.e.* paper, plastic, textiles, etc.) but we found few data indicating the elemental analyses of the various residues of treatment processes. Leachate data provide a means of integrating over a large mass of waste, but provide little insight into the total contaminant mass present where solubility limitations restrict the concentrations of some metals.

BENCHMARK STUDY: LEACHATE MODELLING

To provide a benchmark for the comparison of results from this study, leachate modelling was undertaken to determine the equilibrium status of a typical UK landfill designed and operated on a pre-Landfill Directive basis. The basic scenario was similar to that used for the modelling undertaken to support the definition of European Waste Acceptance Criteria [3] and for this we utilised a published source term model [3, 4]. Figure 1 shows the basic hydrogeological scenario that forms the basis of the calculations.

The software used for this work was GoldSim [5], which has a probabilistic visual spreadsheet platform capable of transient modelling. Modifications were made to the basic scenarios in the GoldSim model used for the UK contributions to the setting of the leaching limit values given in the EU Decision [6] establishing criteria and procedures for the acceptance of waste at landfills. These modifications were carried out to reflect the work contained in the latest release of LandSim 2.5 [7]. They included the gradual unavoidable degradation of the liner and cap (assuming HDPE construction) and the option to simulate the end of managed control (*e.g.* removing all management controls of leachate levels, recirculation and removal).

In order to provide a framework for the assessment, values were calculated for each species for which a leaching limit value was given in the EU Decision [8] and additionally for ammonium. The point of compliance for the species was the base of the unsaturated zone for List I substances [9], the edge of the landfill for List II substances and a point 200 m from the site boundary for highly mobile List II and non-listed substances. For each, a water quality standard or guideline was applied. These were either the relevant EU

Table 1. Overview of waste processes investigated.

Waste treatment process	Description
MBT product	Where mechanical biological treatment results in a product that should have been useable but is unable to be sold or used and must be disposed of to landfill.
MBT/C	MBT incorporating composting.
MBT/AD	MBT incorporating anaerobic digestion.
RDF co-incineration	Refuse derived fuel produced by mechanical sorting only.
RDF dedicated incineration	Refuse derived fuel produced by mechanical sorting only.
RDF – flock only	Where flock cannot be sold for incineration and is destined to landfill.
RDF/MBT	Where RDF results from a more sophisticated MBT process.
EfWMB	Energy from waste (mass burn).
EfWFB	Energy from waste (fluidised bed).
ATT	Advanced thermal treatment – pyrolysis/gasification.

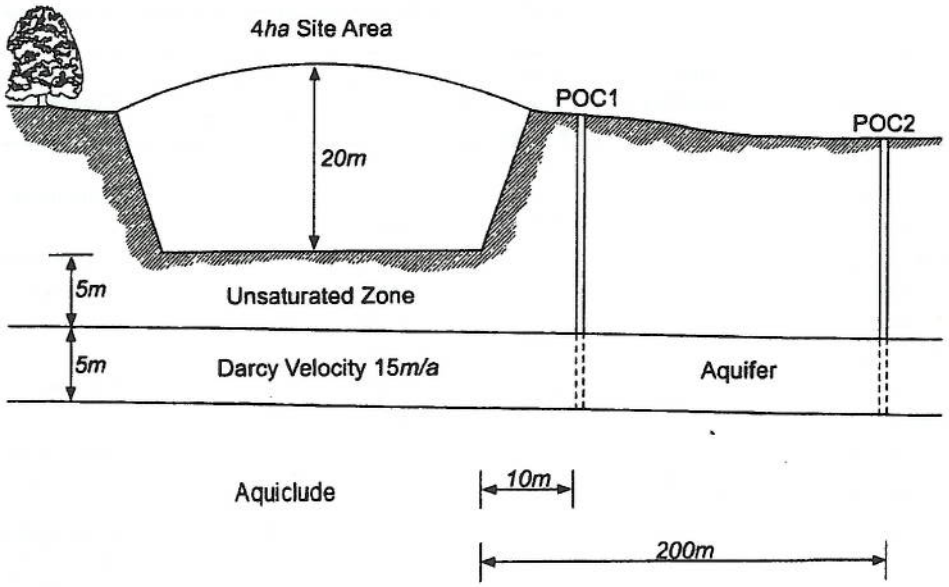


Figure 1. The basic hydrogeological scenario for the basis of calculations.

drinking water standard [10] or, where not available, the World Health Organisation drinking water guideline [11]. Also used was a kappa value for each species that served to describe the rate of concentration decline, and an appropriate individual contaminant/subsoil interaction (K_d) value for the liner and geosphere. Information about kappa and K_d values was taken from [3].

The model was run to determine the end of the aftercare period, *i.e.* when groundwater quality at the relevant point of compliance remained below the relevant water quality standard or guideline. This is a challenging modelling exercise, as emissions from the landfill are dynamic and need to be below certain emission criteria prior to the management system being switched off. The result of removal of management control will be an increase in leachate levels and a comparable increase in leakage rate. Hence, shortly after the removal of management control, there will be a period when the flux of contaminants from the site increases as a result of increased leakage. By treating the period of management control as a variable and running the model with this input represented as a logarithmic uniform probability distribution function varying between 3 and 2000 years, the appropriate time scale was determined for each contaminant.

RESULTS - BENCHMARK STUDY

The results are shown in Tables 2 and 3, which, with Figures 2 and 3, give an insight into the methodology. Achievement of equilibrium status for conventional landfills is likely to be controlled by a number of key species; chloride, lead, zinc and other metals. That is not to say that these controlling species will remain the same for other landfill types containing residues different from those in a typical current landfill used as the benchmark.

The benchmarking of a standard landfill showed that many of the contaminants achieve equilibrium status, with respect to leakage to groundwater, in a surprisingly short period. In this example, even ammoniacal nitrogen met the criterion within a relatively short period. However, other contaminants, notably lead, took a considerable amount of time to reach stabilisation. The leachate concentrations used as a starting point in this exercise are taken from the geometric mean values within LandSim, which in turn are based on published research [12].

A second scenario was run with the leachate concentrations set to the C_0 values prescribed for stable, non reactive hazardous waste going to a non-hazardous landfill. C_0 is the initial peak concentration of the contaminant in the leachate (mg l^{-1}) when subject to the standard upflow percolation test [13]. Results were significantly different with most species requiring an aftercare period in excess of 1000 years and 50% requiring a management period of greater than 2000 years (Table 3).

Figure 2 shows the relationship between receptor concentration and management time for chloride for a non-flushing landfill that has accepted predominantly raw MSW. It is clear that the relationship between the length of management time and the reduction of receptor concentrations is not linear.

Each point on the graph is the result of modelling a different management period using a logarithmic sampling

Table 2. Results of a preliminary benchmarking exercise for a current modern landfill.

Contaminant	Point of compliance See note 2	Initial concentration (see note 3)	WQS	Years to achieve equilibrium	Comments
		mg l^{-1}	mg l^{-1}		
Antimony (Sb)	1				Not routinely measured
Arsenic (As)	1	0.013	0.01	<3	
Barium (Ba)	1				Not routinely measured
Cadmium (Cd)	US	0.01	0.005	<3	See note 1
Chromium (Cr)	1	0.18	0.050	<3	
Copper (Cu)	1	0.1	0.05	<3	
Mercury (Hg)	US	0.00009	0.001	<3	See note 1
Lead (Pb)	1	0.17	0.01	400	
Molybdenum (Mo)	1				Not routinely measured
Nickel (Ni)	1	0.24	0.02	<3	
Zinc (Zn)	1	5.09	0.1	1100-1300	Only applicable to the acetogenic phase of the landfill, therefore this is not a real issue.
Selenium (Se)	1				Not routinely measured
Fluoride (F)	2				Not routinely measured
Sulphate (SO_4)	2	263	250	<3	
Chloride (Cl)	2	1466	250	40-60	
Ammoniacal Nitrogen (NH_4)	1	495	0.5	<3	Assumed to biodegrade with a half life of 6 yrs

Note 1 – The water quality standard for List I substances has been used in the modelling. If the minimum reporting values [38], are used for these two species then the time period runs to in excess of 2000 years).
Note 2 – The point of compliance (POC) – US is the base of the unsaturated zone, point 1 is groundwater at the boundary of the site, and point 2 is groundwater at a distance of 200 m downstream.
Note 3 – Based on the mean values from the LandSim 2 defaults for non-List 1 substances.

scale. The relevant water quality standard (WQS) for chloride is 250 mg l^{-1} and this was achieved with a management period of 40 years (Table 2). It must be stressed that the leachate chloride concentration at this time (*i.e.* 1275 mg l^{-1} at 40 years) would not meet the WQS. However, the processes of natural attenuation and dilution result in compliance if the management of leachate ceases at this time. It must also be stressed that on the cessation of leachate management there is an expectation that leachate treatment (or removal) ceases, leachate levels will rise, and leakage will increase in line with the increased leachate head. Furthermore, it should be noted that the concentration at the receptor did not reach 250 mg l^{-1} at 40 years. This maximum concentration occurred at 156 years, some 116 years after the management of the site ceased.

Figure 3 shows a similar relationship for lead. In this case, the aftercare period required to reach equilibrium status was approximately 400 years (Table 2). The leachate concentration at this time was 0.12 mg l^{-1} (twelve times the WQS). The actual time taken for the maximum groundwater concentration to be realised was 4000 years. There is therefore a large disjoint between the time when management of leachate could cease and the time when the maximum concentrations in groundwater will be realised.

NATURE AND CHARACTERISTICS OF TREATMENT TECHNOLOGY RESIDUES

Almost all municipal waste authorities in the UK are involved with a certain amount of pre-treatment of MSW in the form of separate collection of some recyclables direct from households or from collection points. Some have increased this basic minimum diversion from landfill with the addition of materials recycling facilities (MRF) for more efficient removal of recyclables, or the provision of thermal and biological treatment facilities intended to be significant alternatives to landfill such as incineration or composting. For this study a number of representative treatment options were selected and the effect of these on the timescale for management of the landfilled residues was assessed.

Table 3. Results of benchmarking exercise for a current modern landfill using WAC leachate concentrations for hazardous waste going to a non-hazardous landfill.

Contaminant	Point of compliance See note 1	Initial concentration mg l^{-1}	WQS mg l^{-1}	Years to achieve equilibrium	Comments
Antimony (Sb)	1	0.15	0.005	>2000	Not routinely measured
Arsenic (As)	1	0.3	0.01	>2000	
Barium (Ba)	1	20	0.7	>2000	Not routinely measured
Cadmium (Cd)	US	0.3	0.005	>2000	
Chromium (Cr)	1	2.5	0.05	1100-1300	
Copper (Cu)	1	30	0.05	>2000	
Mercury (Hg)	US	0.03	0.001	>2000	
Lead (Pb)	1	3	0.01	>2000	
Molybdenum (Mo)	1	3.5	0.07	1300-1450	Not routinely measured
Nickel (Ni)	1	3	0.02	1500-2000	
Zinc (Zn)	1	15	0.1	>2000	
Selenium (Se)	1	0.2	0.01	930-1000	Not routinely measured
Fluoride (F)	2	40	1.5	1450-2000	Not routinely measured
Sulphate (SO_4)	2	7000	250	1300-1450	
Chloride (Cl)	2	8500	250	930-1000	
Ammoniacal Nitrogen (NH_4)	1	2000	0.39	1100	Assumed to biodegrade with a half life of 6 yrs

Note 1 - US is the base of the unsaturated zone, point 1 is groundwater at the boundary of the site, and point 2 is groundwater at a distance of 200 m downstream.

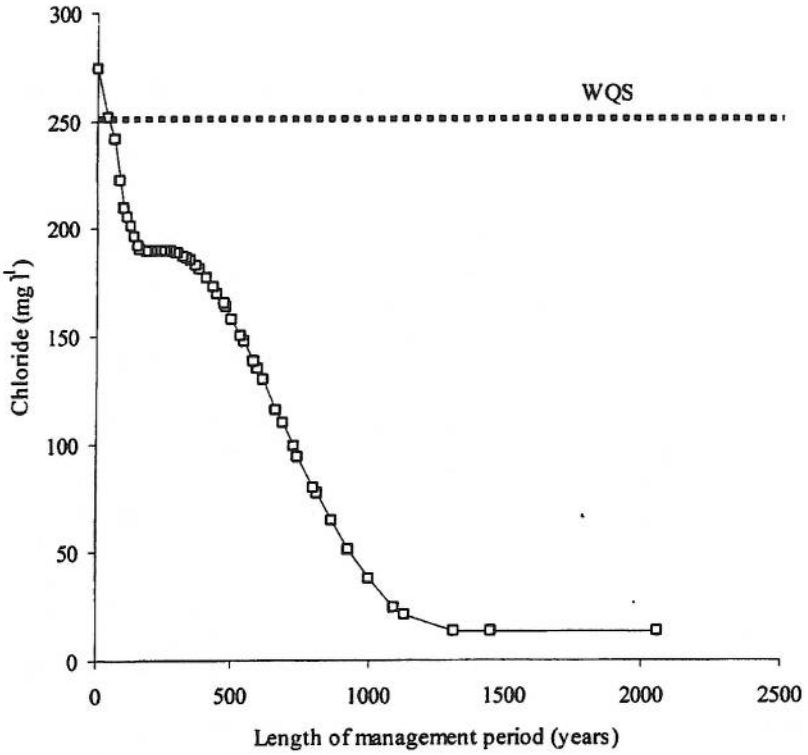


Figure 2. Maximum receptor concentration versus length of management time for chloride.

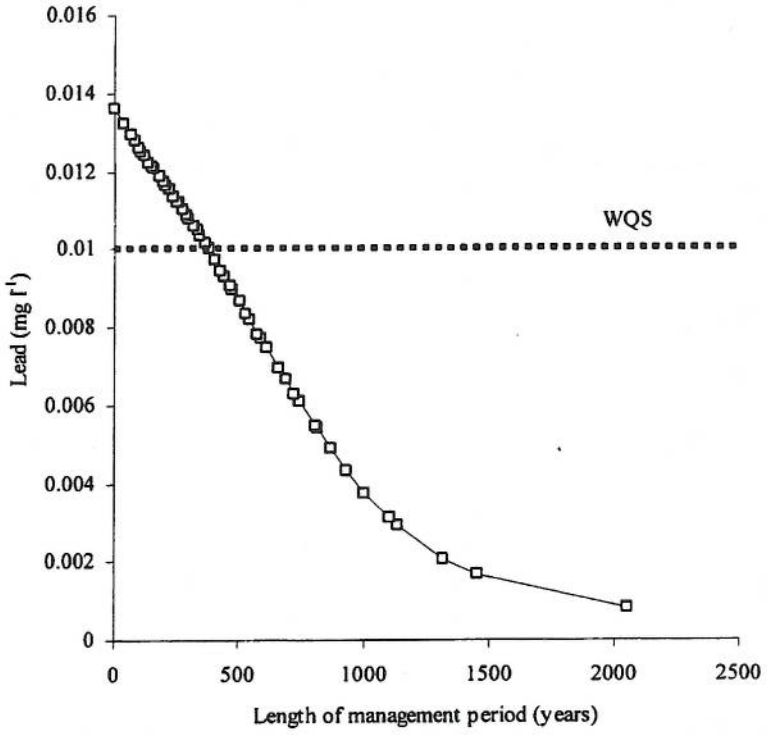


Figure 3. Maximum receptor concentration versus length of management time for lead.

Experience has shown that to achieve BMW reduction rates as high as those set by the Landfill Directive requires more than simply providing separate collection of recyclables [14]. Inevitably, therefore, the residues that will be landfilled in the future will be from a series of technologies and processes. In terms of process flows or combinations of the different technologies, a number of recent developments in the UK were reviewed and some UK disposal authorities' early waste strategies were studied to determine the most likely scenarios.

Waste sorting splits raw MSW into several waste streams; some of which are typically suitable for recycling. For the purposes of this study, waste sorting was reviewed as an integral part of the wider treatment process, rather than as a stand-alone technology. Consequently, little attempt was made to analyse the potential effects of residues obtained solely from waste sorting.

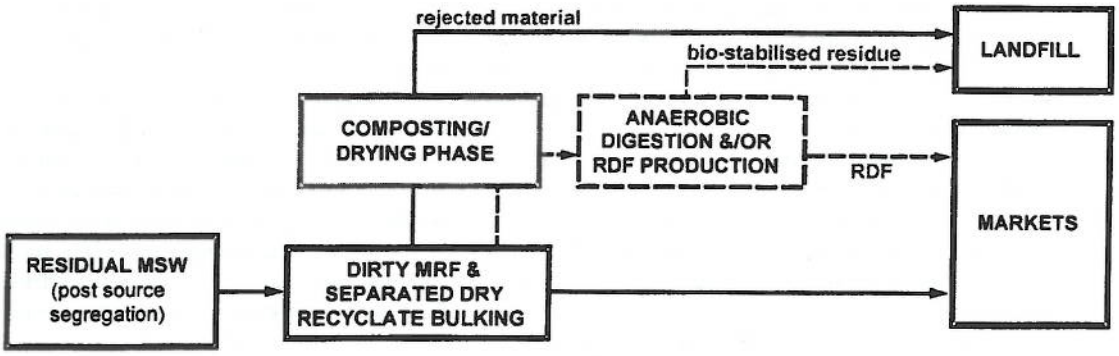
Materials Recovery Facilities

Materials Recovery Facilities (MRFs) are becoming more common throughout the UK and it is envisaged that they will remain an integral part of municipal waste recovery processes in the UK. Commonly paper, cardboard, plastics and metals suitable for recycling are derived as marketable bailed materials following sorting and separation during MRF operations. Unsorted residues may be disposed of to landfill. MRFs can be categorised into clean and dirty variants. Clean MRFs process source-segregated material for recovery. Dirty MRFs (Figure 4) are simpler forms of MRF, most of which have now been phased out. Dirty MRFs process the entire collected (unsorted) waste stream.

Mechanical Biological Treatment

MBT is a generic term for a range of processes used to treat MSW (normally post source segregation) by means of a combination of mechanical separation and biological treatment. Although different technologies may be used, they have similar characteristics. These commonly comprise three stages: mechanical size reduction, the driving off of moisture and, finally, material separation to segregate output streams for different purposes.

Figure 4 illustrates the fate of each material extracted from the process. In this study, all the systems involving the elementary steps are referred to as MBT. MBT outputs incorporate selected recyclable materials and a stabilised waste. Extraction of recyclables occurs both before and after biological processing of the residual waste.



DIRTY MRFs

All dirty MRFs operate on the residual waste streams tonnage levels for a given population will - at present - be higher than for dry co-mingled recyclates.
This will probably result in dirty MRFs scaled for rural communities.

Key

——— denotes existing practice
– – – denotes Landfill Directive compliant practice (which is illustrative of a form of Bio-Mechanical Treatment approach)

Figure 4. MBT system utilising a dirty MRF [39].

It is widely believed that MBT pre-treatment of waste prior to landfilling reduces landfill emissions compared to untreated MSW. It is, however, difficult to track an accurate mass balance of trace contaminants through the system.

During the process there is a reduction in mass which has been mainly attributed to the decrease in water content and the degradation of organic material. Weight reductions typically range between 20% and 40% [15-18]. Volume reductions are thought to be a result of the mechanical stage, *e.g.* shredding. They are reported to be between 35% and 79%, largely depending on the degree of landfill diversion during the MBT process. Virtually all plants have means of removing ferrous and non-ferrous metals, and many also attempt to remove a reasonable proportion of the plastics that enter the process.

MBT residues typically achieve a higher emplaced density within landfills than standard MSW. A value of 1.3 t m^{-3} was reported by Binner [19]. Scheelhaase and Bidlingmaier [20] found during lysimeter tests that storage densities of 1.6 t m^{-3} were achievable. They also reported a notable decrease in permeability between feedstocks and MBT residues as a result of the increased density, high homogeneity, smaller grain sizes and the high proportions of 'earthy' components of the material following MBT procedures. Some authors report hydraulic conductivity ranges from $<1 \times 10^{-10}$ m s^{-1} (<25 mm, 50 weeks treatment) to $<1 \times 10^{-11}$ m s^{-1} (<12 mm, 5 weeks treatment). However, a more recent report [21] shows the relationship between MBT residue permeability and applied load. Results range from 3×10^{-5} m s^{-1} for waste under a load of 50 kN m^2 to 6×10^{-9} m s^{-1} with an applied load of 550 kN m^2. These values are almost identical to those derived for raw MSW and as such indicate a comparable permeability. Care needs to be taken when comparing the results with raw MSW as the density of the two waste streams will be different.

Comparison of the organic matter content before and after the MBT process (using loss on ignition data) indicates degradation of between 50 and 70% by weight of organic dried solid matter. It should be noted that the composition of input material is a key-determining factor. Further intensive composting over a protracted period could reduce the weight of organic material (dried solid) to 12% of the original feedstock but this is unusual and would only result from highly selective waste streams. In most cases the loss on ignition value drops to 25 - 35 wt. % of organic dried solid matter after pre-treatment [20].

Through landfill simulation experiments, the influence of MBT pre-treatment has been compared to MSW in terms of leachate quality [15]. Available data demonstrate that for pre-treated waste the acidic phase (during which high strength leachate is produced from MSW) does not occur. Substantial reductions in long-term concentrations of Chemical Oxygen Demand (COD) and Total Nitrogen (as N) have been reported [22] compared to MSW, although the precise basis of these claims is uncertain. It is clear that leachate strengths are lower, but the composition of the non-degradable (hard) COD

is unknown. Data are also available from several small-scale outdoor lysimeters which contained MSW and MBT residual wastes, *e.g.* Kabbe, 2000, reported in Robinson *et al.* [18]. Results for heavy metals content from both of these example lysimeters were similar.

Leaching tests undertaken on samples of MSW and MBT residues, solely for ammonia and TOC have been reported [17]. Concentrations of ammoniacal-N were found to be similar for MSW and Mechanically Sorted Organic Residues (MSOR) of around 500 mg l^{-1}, but were notably lower for MBT waste, at about 150 mg l^{-1} [18].

The quality of MBT waste materials (and hence landfill leachate quality) will vary as a consequence of the extent of source-separation of the waste inputs (urban or rural source, seasonal collections), type of mechanical pre-treatment and type and duration of biological treatment [23].

Leachate quality data from full-scale landfill sites are also consistent with the loss of the acetogenic state in MBT waste landfills [19]. This is highlighted by comparatively high pH values during the first few years. Biochemical Oxygen Demand (BOD), COD and ammonium are all reported to be considerably lower in MBT pre-treated waste than in MSW landfills. The concentrations of some heavy metals are also reduced especially zinc, but it is recognised that the solubility of some metals (especially zinc) tend to reduce markedly at the onset of methanogenesis.

For organic compounds (*e.g.* mecoprop), evidence suggests that effective composting processes are able to reduce the subsequent concentration in the leachate to below those in sites accepting MSW and MSOR. In practice, the extent of removal of mecoprop from leachates may be a good surrogate measure of the efficiency of the composting process itself, to which waste fractions have been subjected. It is noted however that the degree of composting achieved and the efficiency of individual composting processes cannot be determined by the duration of composting. A further leachate quality summary for leachates from landfills/test cells containing untreated MSOR and MSOR subjected to various composting regimes was obtained from Bone *et al.* [23].

Robinson *et al.* report a suggested leachate source term for landfills accepting predominantly MBT residues [18]. This represented their best estimate based on an extensive desk study and independent sampling from a number of European landfill sites.

MBT/composting

Many MBT systems were originally developed as compost plants. The intention was to convert raw MSW into quality compost, but there are few examples where the product has achieved the necessary quality, and large quantities are landfilled. The quality of the compost derived from MBT systems varies considerably and is largely dependent upon the quality of input material and process retention period. While the residue has been "composted" in the process, it still contains some of the contaminants present in the feedstock. The suitability of the resultant material for beneficial application is generally limited to low grade uses such as landfill daily cover, 'brownfield' restoration or forestry.

In the context of MSW in the UK, the term composting has usually been taken to mean the green waste shredding and outdoor windrowing that is undertaken by many municipal authorities. This study assumed that no significant residue from this process would be sent to landfill.

Changes in the composition of the organic fraction of municipal solid waste during the biodegradation process and the final waste products are strictly dependent on the process conditions. The reduction of carbon content due to biodegradation increases with process temperature from 20% at 20° C to about 40% at 37° - 42° C [24]. The fate of heavy metals and non-degradable species is less certain and they are likely to be unaffected by the process. However, with the volume and mass reduction of the waste the concentration (but not the mass) of these contaminants is likely to increase.

Organic trace contaminants in conventional MSW include a number of species that are resistant to biodegradation in the anaerobic conditions that quickly become established in a modern MSW landfill. Species such as mecoprop, toluene and benzene do not undergo significant anaerobic degradation. While volatile species (such as the BTEX compounds) leave the landfill via landfill gas and may be destroyed within combustion plant, non-volatile species such as mecoprop will only be removed by leaching. The removal of these species via aerobic degradation within the composting process is beneficial, should the material be landfilled.

MBT/Anaerobic digestion

The digestion of MSW is not common in the UK. The success of anaerobic digestion (AD) of MSW depends upon a high degree of pre-sorting and mechanical separation. Anaerobic digestion reduces organic waste to a relatively stable solid residue similar to compost. The process can be completed in 2-3 weeks. There is the risk that the digestate will contain high proportions of heavy metals, particularly when treating unsorted waste as demonstrated in Table 4. Anticipating this, it is necessary to carefully oversee the feedstock going to the reactor. The main products from AD are biogas, a liquid fraction and a solid residue. No data could be obtained on the mass balance of contaminants.

Leachate quality data for landfills accepting AD residues are poorly documented. However, it is anticipated that leachates from those residues that have not been subjected to a post composting stage will be of a similar quality to a methanogenic leachate from a typical MSW site containing moderate levels of ammonia, residual hard COD, chloride concentrations comparable with MSW and the range of heavy metals typically found in MSW leachate.

For those sites that accept AD residues that have been composted following the AD stage, leachates are likely to be similar to leachates derived from MBT composted waste that is landfilled. Leachate concentrations from one site that had

Table 4. Typical anaerobic digestate heavy metal concentrations from MSW [40].

Parameter	Mixed collection Municipal solid waste mg kg^{-1} (dry basis)	Separated vegetable, fruit and garden waste mg kg^{-1} (dry basis)	Separated vegetable, fruit and garden waste and paper mg kg^{-1} (dry basis)
Cadmium	2	2	1
Zinc	1020	138	85
Copper	101	20	14
Lead	522	67	61
Nickel	42	25	7

accepted AD composted material are taken from Robinson *et al.* [18]. The leachate was very similar to a methanogenic leachate albeit that the ammoniacal N concentration was less than 200 mg l^{-1}. There was a low, but detectable, concentration (0.47 μg l^{-1}) of mecoprop although there was a near absence of other identifiable trace organic contaminants.

Refuse derived fuel (RDF)

RDF (alternatively known as solid recovered fuel or SRF) has different meanings in different member states of the EU. It is well-established in Austria, Finland, Germany, Italy, the Netherlands and Sweden whilst in Belgium and the UK RDF production is still developing [25]. RDF generally encompasses a residue that is produced from waste with the intent of being traded and co-burnt in installations for power generation or in a manufacturing process where heat is required (*e.g.* cement production). The principal purpose for developing RDF from MSW is to arrive at a dry, high-calorific value (15->18 MJ kg^{-1} [26]) product of improved homogeneity compared with raw MSW. In some cases, purpose-built incinerators have been developed to receive only RDF from MSW. The European standards organization (CEN) is classifying fuel according to net calorific value, chlorine and mercury content. However, the particle size, moisture content and fuel composition are also important.

There is a high likelihood that not all RDF will be utilised continuously in co-incineration plants. Historically, considerable amounts of RDF have been stored or landfilled for a variety of reasons such as lack of demand or poor quality. Hence, this study considered that one potential process flow will result in RDF being landfilled directly.

The composition of RDF from MSW will vary according to the origin of waste material and the sorting/separation process. This will in turn greatly influence the properties of RDF such as the calorific value. A typical composition for RDF from MSW originating from the UK is plastic (20%), paper/cardboard (58%), wood (5%), textile (15%), non-combustibles *e.g.* glass and metals (2%) [26].

The important characteristics for RDF as a fuel are the calorific value (20-23 MJ kg^{-1} for source-separated MSW; 13 MJ kg^{-1} for mixed MSW), water (10-35%), ash (10-16%), sulphur (0.2%) and chlorine (0.3-0.7%) contents [25]. These values are indicative and also vary according to the sources, the collection system (mixed or source separated) and the treatment applied (screening, sorting, grinding, drying etc.) [25]. RDF tends to affect the concentrations of cadmium, lead, copper and zinc when co-incinerated with other material. No specific information could be obtained on leachate quality from landfilling 100% RDF incineration residues.

Wet flock-type RDF is prepared by shredding, screening, magnetic separation, eddy current separation and possibly air classification to remove the non-combustible fraction (*e.g.* ferrous materials, glass and grit). The output tends to be dry and odour-free, with an enhanced calorific value, as both the moisture content and non-combustible fraction have been substantially reduced.

No specific information could be obtained from RDF/MBT where RDF results from a more sophisticated MBT process. However, if the material is incinerated, it is unlikely to differ significantly from RDF ash. If, because of lack of markets, it is not burnt, then it is likely to be similar to MBT residues that have been sent to landfill.

Mass Burn Incineration

In mass burn incineration the volume of waste is reduced by around 90% and its weight by 75% [27]. Generally up to three different types of waste are produced: bottom ash, fly ash and air pollution control (APC) residues. Bottom ash arises from high temperature oxidative processes acting on the waste. Fly ash is the fine particulate matter (typically 1 to 500 μm) which is carried over from the combustion chamber and can be collected separately from other air pollution control residues. APC residues result from the collection of other air pollutants from incinerator flue gases, especially acid gases, volatilised heavy metals and other micro pollutants. The three wastes have different compositions and will produce different emissions when landfilled. Fly ash and APC residues are unlikely to meet the hazardous waste acceptance criteria for acceptance at a landfill site, without treatment.

The Environment Agency reports that incinerator bottom ash (IBA) is approximately 25% to 30% by weight and 10% by volume of input, and APC residues are approximately 3% by weight of waste input [28]. These data depend on

factors which include quantity, composition of waste burnt, any recycling schemes and the design and operation of the plant. MSW IBA will have a density of about 1.5 tonnes m^{-3}.

Chemical analysis and characterisation of bottom ash and APC residues from three UK incinerators has been undertaken [18]. An example of the chemical composition of fresh bottom ash is presented in Polettini *et al.* [29].

Pre-treatment processes such as carbonation and acid treatment have been demonstrated to influence the pH of the waste and hence affect the waste emissions (via leachate). Williams [30] presented typical composition of bottom ash, fly ash, and APC residues from a dry/semi-dry system and a wet control system.

For leachate produced from incinerator bottom ash and APC residues, Robinson et al. [18] reported that the trace elements and some of the major ions in leachates are strongly influenced by several chemical, and occasionally biological reactions that begin as soon as the ash reaches the quench tank and continue, often for many decades, within the landfill. They reported that variations in ash leachates are more likely to occur as a result of site topography and water regime than any variation in reactions occurring after landfilling. Leaching test data are therefore valued as a good guide to actual leaching quality. Concentration ranges for maximum levels observed in leaching tests on bottom ashes at liquid/solid ratios below 0.5 are provided by Hjelmar [31].

Inorganic components from a lysimeter study of bottom ash leached to a liquid/solid (L/S) ratio of 1.4 have been reported by Stegmann *et al.* [32]. Throughout this lysimeter study, chloride exhibited a washout pattern, falling to a L/S ratio of ~0.7, then continued at a lower concentration for the remainder of the experiment. The pH remained high throughout due to the lime content, although sub-sampling at the end showed that lower pH values had developed in the upper (exposed) surface, indicating partial carbonation.

Sulphate concentrations were initially low, presumably because of very high calcium concentrations. Sulphate then fell further, before rising during the second half of the study, as carbonation began to remove calcium from solution. This is consistent with a long-term decrease in alkalinity. At the end of the test only 2% of the sulphate content had been leached.

Leachate quality data are available from a bottom ash landfill in Switzerland [33, 34]. L/S ratios at the time of the study were reported to be 0.2 – 0.25. Dry weather concentrations of Cl, SO_4 and Na were consistent with published eluate values for low L/S ratios [31], while Total Organic Carbon (TOC), K, Ca and most of the heavy metals were generally at lower concentrations than indicated in eluate concentrations.

A long-term dataset of leachate quality (1973 to 1998) is available for a PVC lined landfill [3]. The site accepted ~85% bottom ash and ~15% fly ash. It was noted by Robinson *et al.* [18] that copper concentrations correlated strongly with dissolved organic carbon (DOC) indicating the presence of strong organic complexes. This is an issue raised by a number of researchers working with IBA leaching studies. It is possible that a number of other metals also exhibit similar relations with DOC, but to a lower degree. The mobility of copper as a complex is likely to be far higher than its mobility as a metal ion and could have implications for groundwater contamination from sites accepting IBA.

Bottom ash, while having virtually no dioxins, contained large numbers of other trace organics including halogenated aliphatic and aromatic hydrocarbons, BTEX compounds, alkenes and PAHs. Concentrations of trace organics were found to vary by up to three orders of magnitude in bottom ash from three different sites [18].

Carbonation is an important process that affects the physical and chemical nature of bottom ashes. It is formed by the reaction of atmospheric carbon dioxide with lime in the wastes, forming calcium carbonate. Carbonation of the bottom ash increases leachate concentrations of calcium and sulphate ions, but has no significant impact on the leaching of most other ions, DOC, organic nitrogen, and trace organics. However, it lowers pH significantly and the concentrations of certain heavy metals in the leachate by orders of magnitude, while some trace metals increase [18]. Insolubility of lead (in the short-term) can be ensured through accelerated aging of the fly ash by effective contact between wet fly ash and exhaust gas of the incineration plant [35].

Fluidised Bed Incineration

This type of thermal treatment (a simple modification to mass burn) involves the waste being used as a fuel, suspended by an updraft supply of air, and kept 'fluidised' on a base of small inert particles such as sand or dolomite. Pre-processing essentially involves the removal of large items such as white goods and ferrous and non-ferrous metals and may be extended to include the recovery of other materials such as recyclables. However, it is noted that savings are made when compared with basic incineration systems because of the possibility of including lime in the combustor material to inhibit the production of acid pollutants. Furthermore, there is no need for the expensive bolt-on air pollution control systems typical of mass burn incinerators to clean up the flue gases. Fluidised bed incineration ensures a high level of waste destruction due to both the preparation of the waste and the method of combustion.

The incineration of MSW using a fluidised bed system is best achieved with some form of pre-screening and shredding, or the production of RDF pellets. Fluidised bed incinerators also have the potential for burning organic liquids, acid tars and sludges.

Pyrolysis

Pyrolysis is the indirect heating of material in the absence of oxygen such that the organic material is gasified and the resultant solid residues are inert and mainly contain carbon. Pyrolysis can be used to treat organic wastes, rendering the residues biologically inert while extracting a

fuel as an energy source for later use. Organic waste is transformed to a medium calorific gas, liquid and a char fraction. These contain hydrocarbons (gas and oils/tars) and solid residue (char/pyrolysis coke) containing carbon, ash, glass and non-oxidised metals. The pyrolysis process occurs without the release of polluting dust containing dioxins and/or nitrogen oxides (combustible gases are released). These combustible gases can be used in any industrial application requiring heat or energy.

Studies have shown that increasing the temperature of pyrolysis decreases char production and increases oil and water production. Gas production increases between 300 and 420°C, but then stays constant. For flash pyrolysis at temperatures less than 600°C, the production of oil is very high; moreover, at temperatures above 700°C gas production is very high.

The Plasma Pyrolysis/Vitrification (PP/V) system produces a solid vitrified residue which presents a low leachability of pollutants and low toxicity levels in leachates [36]. A number of waste streams have been processed at the pyrolysis plant in Bristol including a batch of RDF. Subsequent analysis of the ash (char) is shown in Table 5 [37].

Gasification

Gasification is a similar process to pyrolysis but takes place with the addition of some oxygen as air or steam. The process produces a mixture of combustible gases (primarily methane, complex hydrocarbons, hydrogen and carbon monoxide), ash and a tar. The major environmental benefit of this process is that it retains pollutants (the sulphur, heavy metals etc.) in the ash instead of the gas phase and prevents subsequent discharge to the atmosphere. The emissions from this technology may be lower than produced by conventional incineration and will require less flue gas treatment. There is little data available in the public domain regarding the contaminant concentration of the char. Initial indications [37] are that the char may have similar leaching properties to incinerator bottom ash.

CONCLUSIONS

During the last two decades the estimated timescale for the potential polluting life of a large modern landfill has increased from early estimates of 20-40 years to greater than 500-1000 years. Currently, technical and financial provision for post-closure liabilities is usually made for a 30-60 year period. Modelling results suggest that this period may be inadequate if measures are not taken to increase the rate of waste stabilisation.

Initial benchmark study results for pre-Landfill Directive landfills suggest that two key contaminants (lead and chloride) are likely to control the achievement of equilibrium status. A second scenario run with leachate concentrations set for stable non reactive hazardous waste going to a non-hazardous waste landfill (Landfill Directive)

Table 5. Results of ash analysis for RDF (EUS Laboratories Ltd, 22nd Feb. 2002).

Element	Solid mg kg^{-1}	Leachate μg kg^{-1}
Total organic carbon	455	Na
Total hydrocarbon	76	na
Cadmium	36	0.8
Thallium	<0.5	1.3
Mercury	<0.1	<0.1
Lead	8	8
Chromium	650	9
Copper	720	143
Manganese	830	12
Nickel	120	4
Arsenic	23	12
Antimony	48	4
Cobalt	12	8
Vanadium	16	9
Tin	870	10
Dioxin / furan	22.5 ng kg^{-1}	0.0063 ng l^{-1}

suggests that the post-closure management period is likely to be >1000 years for most contaminants with 50% of contaminants requiring >2000 years to achieve equilibrium. The predicted timescales of centuries rather than decades suggest that a reappraisal of the role of accelerated landfill stabilisation techniques such as aerobic and bioreactor landfilling is required. The benchmarking results presented here are a starting point and the next stage was to model the most likely options that may contribute towards meeting the Landfill Directive diversion and pre-treatment targets. This forms a second manuscript that presents the full modelling methodology and results.

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ESTIMATING POLLUTANT REMOVAL REQUIREMENTS FOR LANDFILLS IN THE UK: II. MODEL DEVELOPMENT

D. H. HALL[1], D. DRURY[1], J. R. GRONOW[2], A. ROSEVEAR[3], S. J. T. POLLARD[2] AND R. SMITH[2*]

[1]Golder Associates (UK) Ltd., Attenborough House, Browns Lane Business Park, Stanton-on-the-Wolds, NG12 5BL, UK
[2]Integrated Waste Management Centre, Sustainable Systems Department, School of Applied Sciences, Cranfield University, MK43 0AL, UK
[3]Environment Agency, Kings Meadow House, Kings Meadow Road, Reading, RG1 8DQ, UK

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ABSTRACT

A modelling methodology using a leachate source term has been produced for estimating the timescales for achieving environmental equilibrium status for landfilled waste. Results are reported as the period of active management required for modelled scenarios of non-flushed and flushed sites for a range of pre-filling treatments. The base scenario against which results were evaluated was raw municipal solid waste (MSW) for which only cadmium failed to reach equilibrium. Flushed raw MSW met our criteria for stabilisation with active leachate management for 40 years, subject to each of the leachate species being present at or below their average UK concentrations. Stable non-reactive wastes, meeting EU waste acceptance criteria, fared badly in the non-flushed scenario, with only two species stabilising after a management period within 1000 years and the majority requiring >2000 years of active leachate management. The flushing scenarios showed only a marginal improvement, with arsenic still persisting beyond 2000 years management even with an additional 500 mm y^{-1} of infiltration. The stabilisation time for mechanically sorted organic residues (without flushing) was high, and even with flushing, arsenic and chromium appeared to remain a problem. Two mechanical biological treatment (MBT) scenarios were examined, with medium and high intensity composting. Both were subjected to the non-flushing and flushing scenarios. The non-flushing case of both options fell short of the basic requirements of achieving equilibrium within decades. The intense composting option with minimal flushing appeared to create a scenario where equilibrium could be achieved. For incinerator bottom ash (raw and subjected to various treatments), antimony, copper, chloride and sulphate were the main controls on achieving equilibrium, irrespective of treatment type. Flushing at higher flushing rates (500 mm y^{-1}) failed to demonstrate a significant reduction in the management period required.

Keywords: Equilibrium, completion, emissions, municipal solid waste

INTRODUCTION

This work presents the second of a series of three companion papers. The first manuscript presented a leachate modelling benchmark study and review of treatment technologies [1] in relation to removing landfill pollutants and achieving environmental equilibrium status. Equilibrium is defined here as that state when emissions from a landfill site occur at a rate that allows sufficient natural attenuation in the surrounding environment to prevent environmental harm, so management is no longer required. To embody the principles of sustainability, equilibrium can only be achieved when the management period (post-closure when the site has ceased accepting waste for disposal) is measured in decades rather than centuries. The hydrogeological scenario used as a basis for calculations is depicted in Figure 1.

MODELLING METHODOLOGY

Modelling Approach and Objectives

This section provides further information on the methodology; the details have been provided in the review of treatment technologies provided in the first manuscript. The post processing capabilities of GoldSim [2] allowed multivariate analysis of the results, which is essential in order to correlate the length of aftercare period with long-term groundwater impacts. Apart from the aftercare period, all other inputs to the model were set as single values only.

Essentially the aftercare period was defined as a variable and the model was run allowing this period to vary between 3 years and 2000 years. During each iteration (each using a different aftercare period) the maximum groundwater concentration for each of the contaminants modelled was

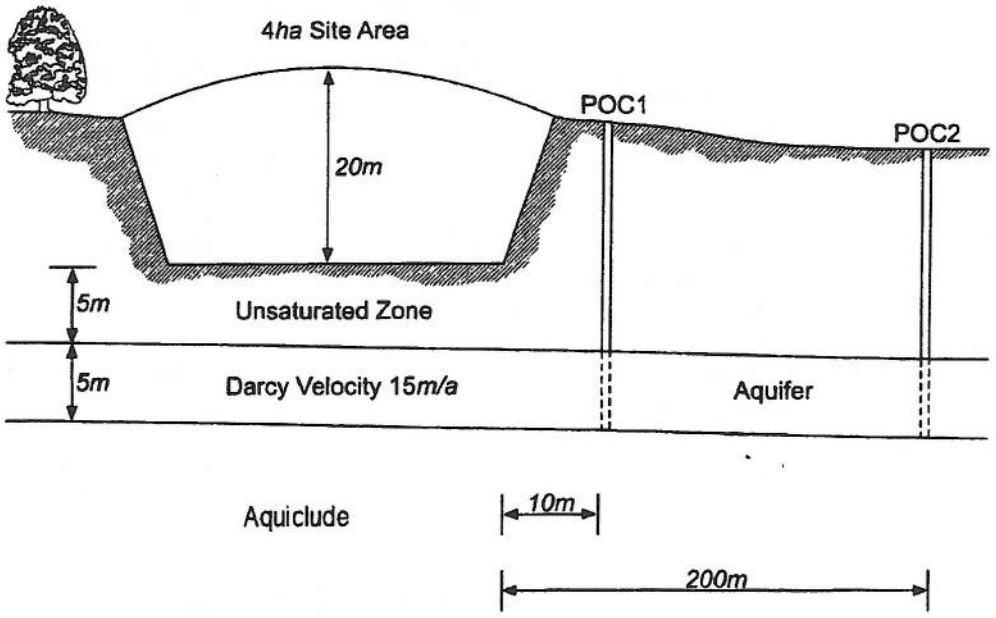


Figure 1. The basic hydrogeological scenario for the basis of calculations.

recorded and then plotted against aftercare time. In this way, the management time period needed to achieve the water quality standard could be estimated. Any model run that resulted in a contaminant requiring a management period greater than 2000 years was simply recorded as >2000.

In the model it was assumed that leachate pumping at the site continued throughout the aftercare period maintaining leachate heads at 1 m. Once management ceases, leachate heads were allowed to vary. The methodology for this was based on the water balance model incorporated in LandSim 2.5 [3]. Leachate levels were expected to increase as a result of cap infiltration and cap deterioration despite the fact that the leakage rate was likely to increase markedly as a result of degradation of the liner system. No account was taken of the prospect of cap breakout of leachate as a result of a build-up of leachate head after the end of management control. It was assumed that this possibility was likely to be a further and semi-independent site-specific control on the duration of site management.

The European Landfill Directive [4] seeks to minimise leachate production by limiting rainfall infiltration and groundwater inflow. It has been shown that appreciable flushing rates are important for achieving landfill stabilisation [5]. Therefore, simulations were also run as flushing systems with 200 or 500 mm of additional infiltration, to determine the implications for aftercare periods. This recirculation ceases at the time management control ends. The receptors for the various contaminants were selected as the downgradient boundary of the site for List II or non-listed substances [6] and the base of the unsaturated zone for List I substances.

Note that, on a site-specific basis, the water quality standards used may not be appropriate, as they may be too high (e.g. if the site is in a sensitive location) or too low (e.g. where background levels already exceed these values and the location is not sensitive). Also, certain species, such as zinc, are only found in high concentrations in leachates that are acetogenic; concentrations often fall below the relevant water quality standards once the waste becomes fully anaerobic. In this instance, the concentration was modelled at its higher aerobic concentration. It must be stressed that there will be situations where the leachate strengths will be higher than those used in the model, and where less attenuating capacity is available. However, the modelling was undertaken on the basis of mean leachate concentrations (not ranges) and is based on a 50th percentile result and not a 95th percentile (which would be the typical percentile used for a risk assessment). For each scenario and each contaminant, the modelling approach allowed for an estimation of the leachate strength when management control can end and groundwater impacts are acceptable (i.e. less than the Water Quality Standard (WQS)).

Model Inputs

In all cases the landfill was assumed to be composite lined with a HDPE capping system. Infiltration into the open waste mass prior to capping was assumed to be 250 mm y^{-1} (taken over a ten year period) reducing to 50 mm y^{-1} on capping. Infiltration was then allowed to increase from 50 mm y^{-1} to 140 mm y^{-1} between 250 and 1000 years to simulate degradation of the cap. Single value inputs for the generic site modelled are provided in Tables 1 to 6 below.

Table 1. Values describing basal lining system.

Parameter – Flexible membrane liner	Parameter value
Area of pinholes	2.55 mm^2
Area of holes	52.5 mm^2
Area of tears	5050 mm^2
Number of pinholes	start = 0, end = 25
Number of holes	start = 0, end = 5
Number of tears	start = 0, end = 0.1
Contact coefficient for leakage calculations	0.68
Contact coefficient for calculation of radius of wetted area	0.435
Mineral component	
Clay permeability	1E-9 m s^{-1}
Mineral liner porosity	0.3
Mineral liner density	1800 kg m^3
Liner thickness	1 m

Table 2. Physical waste properties used in modelling.

Parameter	Parameter value
Waste density	Dependent on waste type.
Waste porosity	0.3
Waste field capacity	0.3

Table 3. Kappa values defining the rate of source term concentration decline.

Contaminant species	Kappa value (kg l^{-1})
Antimony (Sb)	0.11
Arsenic (As)	0.03
Barium (Ba)	0.15
Cadmium (Cd)	0.35
Chromium (Cr)	0.18
Copper (Cu)	0.57
Mercury (Hg)	0.05
Lead (Pb)	0.27
Molybdenum (Mo)	0.35
Nickel (Ni)	0.29
Zinc (Zn)	0.28
Selenium (Se)	0.38
Fluoride (F)	0.22
Sulphate (SO_4)	0.33
Chloride (Cl)	0.57
NH_4	0.59

Source: Data used for EU WAC modelling [10]

Table 4. Values describing unsaturated and saturated zones.

Parameter	Parameter value
Thickness of the unsaturated zone	5 m
Distance from edge of landfill to first saturated zone point of compliance (POC1)	10 m
Distance from edge of landfill to second saturated zone point of compliance (POC2)	200 m
Darcy flux	15 m yr^{-1}
Aquifer porosity	0.3
Aquifer thickness	5 m
Aquifer density	2000 kg m^3

Table 5. Values of contaminant species specific parameters.

Contaminant species	Liner, unsaturated zone and saturated zone partition coefficient (l kg^{-1})	Water quality standard (mg l^{-1})	Location of receptor where water quality standard must be achieved
Antimony (Sb)	5	0.005	Receptor 1
Arsenic (As)	50	0.01	Receptor 1
Barium (Ba)	2	0.7	Receptor 1
Cadmium (Cd)	20	0.005	Base of unsaturated zone
Chromium (Cr)	100	0.05	Receptor 1
Copper (Cu)	14	0.05	Receptor 1
Mercury (Hg)	100	0.001	Base of unsaturated zone
Lead (Pb)	50	0.01	Receptor 1
Molybdenum (Mo)	10	0.07	Receptor 1
Nickel (Ni)	50	0.02	Receptor 1
Zinc (Zn)	30	0.1	Receptor 1
Selenium (Se)	5	0.01	Receptor 1
Fluoride (F)	0	1.5	Receptor 2
Sulphate (SO_4)	0	250	Receptor 2
Chloride (Cl)	0	250	Receptor 2
NH_4	0.5	0.5	Receptor 2

Table 6. Initial leachate concentrations for MSW and allied waste streams (mg l^{-1}).

Waste Stream	MSOR	MBT	MBT	MSW	Stable non-reactive
Treatment		Intensive	Medium	Raw	None
Reference	[8]	[8]	[8]	LandSim [10]	WAC [11]
Species					
Sb	X	X	X	X	0.15
As	0.1	0.006	0.05	0.013	0.3
Ba	X	X	X	X	20
Cd	0.0005	0.003	0.02	0.01	0.3
Cr	5	0.1	0.3	0.18	2.5
Cu	0.5	0.2	0.35	0.1	30
Hg	0.0001	0.0001	0.0001	0.00009	0.03
Pb	0.05	0.04	0.3	0.17	3
Mo	X	X	X	X	3.5
Ni	0.5	0.1	0.4	0.24	3
Zn	0.5	0.2	1.5	5.09	15
Se	X	X	X	X	0.2
F	X	X	X	X	40
SO_4	400	500	3000	263	7000
Cl	6000	2000	6000	1466	8500
NH_4	4000	200	550	495	2000

Notes to Table
X - No reliable data from UK MSW sites or literature.
Data derived from LandSim 2.5.
MSOR - Mechanically Sorted Organic Residues.
MBT - Mechanical Biological Treatment.
MSW - Raw Municipal Solid Waste.
WAC - Waste Acceptance Criteria C_0 values.

Conservative retardation factors (identical to those used for the UK contribution to the derivation of EU Waste Acceptance Criteria (WAC) were used [7]. Ammoniacal nitrogen was not included in the WAC, so a typical value of 0.5 l kg^{-1} was chosen. It was assumed that biodegradation of ammoniacal nitrogen did not occur.

There is some uncertainty about the long term viability of kappa values (first order decay constants) as an input variable to the modelling that has been undertaken. Work is currently underway in the UK to derive additional waste characterisation information that will help to understand the short-term variability of kappa for some of the contaminants of interest. Only by looking at long-term leachate quality data from landfills where some realistic estimate of the liquid/solid (L/S) ratio can be made, will any real advance in our understanding of this variable be achieved. We consider that it remains, at this time, the best method of estimating long-term leaching behaviour, but it is unlikely to represent the perfect solution and further advances in this area should be made over coming years as more data become available.

Leachate Source Term

The main contaminants modelled were those that are included in the EU WAC, although the inclusion of ammoniacal nitrogen was necessary, as for some waste streams it will represent one of the key contaminants in relation to its concentration in leachate and its various water quality standards. The inclusion of ammoniacal nitrogen within the list of contaminants modelled required the derivation of a nominal (and non-statutory) WAC for ammonia.

Data relating to initial leachate concentrations came from a variety of sources. For the Mechanical Biological Treatment (MBT) residues and incinerator bottom ash, data were derived from published research [8]. For those model runs relating to WAC values, C_0 was taken to be the initial flush from a standard column test equating to a L/S ratio of approximately 0.05 l kg^{-1} back calculated from the published WAC. Additional data were drawn from corporate knowledge and judgement.

The initial leachate concentrations used for the modelling of municipal solid waste (MSW) and treated MSW (or closely allied wastes) are shown in Table 6, and those for incinerator bottom ash (both raw and treated) are shown in Table 7. It should be noted that suitable leachate source terms were not identified for all of the ten processes discussed.

The column in Table 6 entitled 'Stable Non-Reactive' relates solely to the C_0 values derived from the WAC for that waste that could be placed in a non-hazardous landfill in a separate cell. The implied assumption was that the entire waste was deposited at the maximum concentration of each species. The likelihood of this occurring is very low, but given that individual species were being examined it did provide an insight into which species are likely to result in the need to extend aftercare periods from the processes included.

Table 7. Initial leachate concentrations for MSW incinerator ash (mg l^{-1}).

Waste stream	Incinerator bottom ash		
Treatment	Raw	Carbonated	Acid treated
Reference	[8]	[8]	[8]
Species			
Sb	0.025	0.1	0.2
As	0.001	0.001	0.001
Ba	1	0.1	0.25
Cd	0.01	0.01	0.01
Cr	0.01	0.2	0.03
Cu	5	5	10
Hg	0	0	0
Pb	5	0.005	0.015
Mo	0.3	0.4	0.5
Ni	0.075	0.05	0.05
Zn	0.001	0.001	0.002
Se	1	0.05	0.02
F	0	0	0
SO_4	500	2000	2000
Cl	1700	1700	1700
NH_4	10	10	15

Model Results

Tables 8, 9 and 10 show a summary of the results of the modelling exercise simply indicating, for each waste stream, each landfill management option and each species with the number of years required to achieve equilibrium status. For each scenario the model was run using what might be regarded as a standard management option (i.e. the waste remains uncapped during the filling sequence and is then capped). In addition, a flushing scenario where infiltration is increased during the management period has been modelled. Whether this is achieved by irrigation beneath the cap, by not having a cap, by removing the cap, or via treated leachate recirculation is, to an extent, incidental for modelling purposes.

True equilibrium status for a landfill is only achieved after every contaminant has reached equilibrium status. The final row in each table picks up the longest period defined by any species within the landfill and therefore highlights the one that equilibrium status is dependent upon.

Table 8 examines raw MSW and a synthetic leachate derived to represent a site filled with waste at its maximum WAC for stable non-reactive waste. This is a slightly fictitious scenario as it is highly unlikely that wastes infilling a site would all equal the relevant WAC. However, it is conceivable that a process waste might be consistently close to the limit for one of the WAC species.

The raw MSW waste in the basic scenario (i.e. one where the waste is placed, capped and leachate generation minimised) formed the base case. Somewhat surprisingly this scenario contained only one contaminant that failed the general criteria of equilibrium status. It must be noted however that the compliance concentration for cadmium was taken as the drinking water standard and not the Minimum Reporting Value (MRV), albeit that the compliance point was taken as the base of the unsaturated zone. The MRV is the value that is normally applied to List 1 Substances to determine whether their presence is discernible or not, and is enshrined in the UK groundwater risk assessment methodology [9]. If the compliance water quality standard is taken as the MRV, the time for cadmium to reach equilibrium status increases to slightly over 2000 years. The option of disposing of raw MSW to landfill is unlikely to remain as the Landfill Directive seeks to reduce the volume of

Table 8. Results of the modelling management time for MSW and stable non-reactive wastes.

Waste Type	Raw MSW	Raw MSW	Stable non-reactive	Stable non-reactive	Stable non-reactive
Treatment	None	None	None	None	None
Scenario	Basic	Additional 200 mm y^{-1} infiltration	Basic	Additional 200 mm y^{-1} infiltration	Additional 500 mm y^{-1} infiltration
Contaminant	Years to achieve equilibrium status				
Antimony (Sb)	X	X	>2000	1350	700
Arsenic (As)	<3	<3	>2000	>2000	>2000
Barium (Ba)	X	X	>2000	1050	490
Cadmium (Cd)	<3	<3	>2000	533	240
Chromium (Cr)	<3	<3	1200	1200	185
Copper (Cu)	<3	<3	>2000	500	219
Mercury (Hg)	<3	<3	>2000	>2000	1300
Lead (Pb)	400	40	>2000	750	350
Molybdenum (Mo)	X	X	1375	440	200
Nickel (Ni)	<3	<3	1750	533	240
Zinc (Zn)	<3	<3	>2000	670	300
Selenium (Se)	X	X	965	275	115
Fluoride (F)	X	X	1700	665	250
Sulphate (SO_4)	<3	<3	1375	390	150
Chloride (Cl)	40	4	965	200	75
Ammoniacal Nitrogen (NH_4)	<3	<3	1100	130	50
Maximum management period required in scenario	400	40	>2000	>2000	>2000

X - No reliable data from UK MSW sites or literature.

Table 9. Results of the modelling management time for mechanically and biologically treated wastes.

Waste Type	MSOR	MSOR	MBT	MBT	MBT	MBT
Treatment	None	None	Medium	Medium	Intense	Intense
Scenario	Basic	Additional 500 mm y^{-1} infiltration	Basic	Additional 200 mm y^{-1} infiltration	Basic	Additional 200 mm y^{-1} infiltration
Contaminant	Years to achieve equilibrium status					
Antimony (Sb)	X	X	X	X	X	X
Arsenic (As)	>2000	1100	<3	<3	<3	<3
Barium (Ba)	X	X	X	X	X	X
Cadmium (Cd)	<3	<3	41	<3	<3	<3
Chromium (Cr)	1600	300	<3	<3	<3	<3
Copper (Cu)	50	<3	<3	<3	<3	<3
Mercury (Hg)	<3	<3	<3	<3	<3	<3
Lead (Pb)	<3	<3	780	206	<3	<3
Molybdenum (Mo)	X	X	X	X	X	X
Nickel (Ni)	580	50	410	76	<3	<3
Zinc (Zn)	<3	<3	550	125	<3	<3
Selenium (Se)	X	X	X	X	X	X
Fluoride (F)	X	X	X	X	X	X
Sulphate (SO_4)	<3	<3	1050	184	<3	<3
Chloride (Cl)	900	70	900	157	367	40
Ammoniacal Nitrogen (NH_4)	1275	85	<3	<3	<3	<3
Maximum management period required in scenario	>2000	1100	1050	206	367	40

Notes
MSOR – Mechanically sorted organic residues (generally the fines)
MBT - Mechanical and Biological Treatment (Separation and composting)
Treatment – in this table it relates to the amount or intensity of the composting process.
X - No reliable data from UK sites or literature.

biodegradable MSW being disposed of to landfill.

The flushed raw MSW met the criteria of stabilisation at 40 years, subject to each of the leachate species being present at or below their average UK concentrations. After this time it is interesting to note that landfill gas generation would also have ceased (or at least be below the point at which meaningful management could be applied), so the requirements of equilibrium status would have been met.

Stable non-reactive wastes meeting the WAC performed badly in the non-flushing scenario, with only two species stabilising within 1000 years and the majority taking in excess of 2000 years. The flushing scenarios showed only a marginal improvement, with arsenic still persisting beyond 2000 years with an additional 500 mm y^{-1} of infiltration.

Table 9 shows the results for mechanically and biologically treated waste. Mechanically Sorted Organic Residues (MSOR) generates a waste that is high in contaminants and has high ammonia loading. As such, its stabilisation time (without flushing) was high, and even with flushing, arsenic and chromium remained a problem. In this case cadmium did not appear to be an issue at either of its WQSs.

Two MBT cases were examined, one with medium intensity composting and one with highly intensive composting. Both were subjected to the non-flushing and flushing scenarios. The non-flushing case of both fell short of the basic requirements of equilibrium status within decades. However, the intense composting option with some minimal flushing appeared to create a scenario where equilibrium status could be achieved. Cadmium met the MRV at around 400 years in the flushed scenario.

The final set of results (Table 10) relate to incinerator bottom ash (raw and subjected to various treatments). Antimony, copper, chloride and sulphate appeared to be the

Table 10. Results of the modelling management time for incinerator bottom ash.

Waste Type	Raw bottom ash	Raw bottom ash	Bottom ash	Bottom ash	Bottom ash	Bottom ash
Treatment	None	None	Carbonated	Carbonated	Acid treated	Acid treated
Scenario	Basic	Additional 500 mm y^{-1} infiltration	Basic	Additional 500 mm y^{-1} infiltration	Basic	Additional 500 mm y^{-1} infiltration
Contaminant	Years to achieve equilibrium status					
Antimony (Sb)	1950	310	>2000	900	>2000	1150
Arsenic (As)	<3	<3	<3	<3	<3	<3
Barium (Ba)	<3	<3	<3	<3	<3	<3
Cadmium (Cd)	140	<3	150	<3	150	<3
Chromium (Cr)	<3	<3	<3	<3	<3	<3
Copper (Cu)	600	240	1750	240	2050	870
Mercury (Hg)	N/a	N/a	N/a	N/a	N/a	N/a
Lead (Pb)	2000	750	<3	<3	<3	<3
Molybdenum (Mo)	410	20	710	55	860	85
Zinc (Zn)	950	130	<3	<3	<3	<3
Selenium (Se)	<3	<3	<3	<3	<3	<3
Fluoride (F)	<3	<3	N/a	N/a	N/a	N/a
Sulphate (SO_4)	<3	<3	1190	75	1180	75
Chloride (Cl)	580	90	570	75	570	20
Ammoniacal Nitrogen (NH_4)	<3	<3	<3	<3	<3	<3
Maximum management period required in scenario	2000	750	>2000	900	>2000	1150

Table 11. Leachate concentrations at equilibrium status for MSW and stable non-reactive wastes.

Waste type	Raw MSW	Raw MSW	Stable non-reactive	Stable non-reactive	Stable non-reactive
Treatment	None	None	None	None	None
Scenario	Basic	Additional 200 mm y^{-1} infiltration	Basic	Additional 200 mm y^{-1} infiltration	Additional 500 mm y^{-1} infiltration
Contaminant	Leachate concentration when equilibrium status is attained				
Antimony (Sb)	X	X	AA	0.0082	0.01
Arsenic (As)	AB	AB	AA	AA	AA
Barium (Ba)	X	X	AA	1.1	1.6
Cadmium (Cd)	AB	AB	0.002	0.02	0.02
Chromium (Cr)	AB	AB	0.61	0.8	0.824
Copper (Cu)	AB	AB	AA	0.3	0.3
Mercury (Hg)	AB	AB	AA	AA	0.0022
Lead (Pb)	0.121	0.125	AA	0.1	0.109
Molybdenum (Mo)	X	X	0.153	0.3	0.309
Nickel (Ni)	AB	AB	0.051	2.4	0.248
Zinc (Zn)	AB	AB	AA	0.8	0.73
Selenium (Se)	X	X	0.0281	0.04	0.04
Fluoride (F)	X	X	1.8	3.5	5.28
Sulphate (SO_4)	AB	AB	365.5	860	1231.5
Chloride (Cl)	1224.2	1401.5	442.4	1230	1182.5
NH_4	AB	AB	49.5	533.9	504.4

Notes

AA = Groundwater concentration always exceeded WQS hence leachate concentration always above equilibrium status.

AB = Groundwater always below WQS hence leachate always below equilibrium status.

X - No reliable data from UK MSW sites or literature.

main controls in achieving equilibrium status of this waste stream, irrespective of the treatment type. Flushing at higher rates (500 mm y^{-1}) failed to make a significant reduction in the management period required. It may be that the source term used was selected with conservatism and that a greater familiarity with the material would generate lower mean values of the key contaminants. What is clear is that bottom ash on its own will remain a challenge.

Leachate Source Concentrations at Time of Equilibrium

One of the objectives of this work was to determine a test to assist in defining when waste has reached equilibrium status. Leachate quality itself should give an indication of the status of the waste, and it was originally thought that a series of leachate quality criteria could be developed that could be used to define equilibrium status (with respect to leachate). Leachate source concentrations when equilibrium status was attained (based on the results presented in Tables 8, 9, and 10) were extracted from the data and are presented in Tables 11, 12 and 13. It is clear that there is no single leachate value that dictates equilibrium. Degradation of the liner and capping systems causes considerable complexity of the relationship between leachate quality with time, transient groundwater quality, and equilibrium.

Overall it would appear from the work undertaken that intensively composted MBT residues that undergo flushing within a landfill will provide one means of achieving equilibrium status. MBT is gaining in popularity in the UK and Europe. Reports that MBT residues have a low permeability do raise some concern. It would not be feasible to irrigate a material with a permeability value of 1×10^{-10} m s^{-1} at a rate of more than 3 mm y^{-1}. A permeability value of greater than 6×10^{-9} m s^{-1} would be required to allow intensively composted MBT residues to meet the requirements of our definition of sustainable landfill (in relation to leachate).

The result of this is that rather than generating a specific time to achieve equilibrium status, the best that can be achieved is the definition of a broad time scale over which equilibrium status may be achieved. It is further cautioned that there remains some considerable uncertainty with these results and they must be regarded as tentative.

Table 12. Leachate concentrations at equilibrium status for mechanically and biologically treated wastes.

Waste type	MSOR	MSOR	MBT	MBT	MBT	MBT
Treatment	None	None	Medium	Medium	Intense	Intense
Scenario	Basic	Additional 500 mm y^{-1} infiltration	Basic	Additional 200 mm y^{-1} infiltration	Basic	Additional 200 mm y^{-1} infiltration
Contaminant	Leachate concentration when equilibrium status is attained					
Antimony (Sb)	X	X	X	X	X	X
Arsenic (As)	AA	0.0299	AB	AB	AB	AB
Barium (Ba)	X	X	X	X	X	X
Cadmium (Cd)	AB	AB	0.0183	AB	AB	AB
Chromium (Cr)	0.4	0.802	AB	AB	AB	AB
Copper (Cu)	0.417	AB	AB	AB	AB	AB
Mercury (Hg)	AB	AB	AB	AB	AB	AB
Lead (Pb)	AB	AB	0.112	0.126	AB	AB
Molybdenum (Mo)	X	X	X	X	X	X
Nickel (Ni)	0.255	0.254	0.256	0.267	AB	AB
Zinc (Zn)	AB	AB	0.799	0.859	AB	AB
Selenium (Se)	X	X	X	X	X	X
Fluoride (F)	X	X	X	X	X	X
Sulphate (SO_4)	AB	AB	418.6	1098.8	AB	AB
Chloride (Cl)	437.1	1139.8	433	1478.1	970.3	1381
NH_4	39.85	529.3	AB	AB	AB	AB

Notes
MSOR – Mechanically sorted organic residues (generally the fines).
MBT - Mechanical and Biological Treatment (Separation and composting).
Treatment – in this table it relates to the amount or intensity of the composting process.
AA - Groundwater concentration always exceeded WQS hence leachate concentration always above equilibrium status.
AB - Groundwater always below WQS hence leachate always below equilibrium status.
X - No reliable data from UK sites or literature.

Table 13. Leachate concentrations at equilibrium status for incinerator bottom ash.

Waste type	Raw bottom ash	Raw bottom ash	Bottom ash	Bottom ash	Bottom ash	Bottom ash
Treatment	None	None	Carbonated	Carbonated	Acid treated	Acid treated
Scenario	Basic	Additional 500 mm y^{-1} infiltration	Basic	Additional 500 mm y^{-1} infiltration	Basic	Additional 500 mm y^{-1} infiltration
Contaminant	Leachate concentration when equilibrium status is attained					
Antimony (Sb)	0.009	0.0113	AA	0.0092	AA	0.006
Arsenic (As)	AB	AB	AB	AB	AB	AB
Barium (Ba)	AB	AB	AB	AB	AB	AB
Cadmium (Cd)	0.0087	AB	0.0087	AB	0.0087	AB
Chromium (Cr)	AB	AB	AB	AB	AB	AB
Copper (Cu)	0.024	0.239	0.024	0.238	AB	0.212
Mercury (Hg)	X	X	X	X	X	X
Lead (Pb)	AA	0.0342	AB	AB	AB	AB
Molybdenum (Mo)	0.209	0.213	0.193	0.232	0.197	0.251
Nickel (Ni)	AB	AB	AB	AB	AB	AB
Zinc (Zn)	AB	AB	AB	AB	AB	AB
Selenium (Se)	AA	AA	0.025	0.034	AB	AB
Fluoride (F)	X	X	X	X	X	X
Sulphate (SO_4)	AB	AB	357	1052	357	1052
Chloride (Cl)	722.5	985	723	973.1	722.5	973.1
NH_4	AB	AB	AB	AB	AB	AB

Notes
AA - Groundwater concentration always exceeded WQS hence leachate concentration always above equilibrium status.
AB - Groundwater always below WQS hence leachate always below equilibrium status.
X - No reliable data from UK sites or literature.

CONCLUSIONS

This work has demonstrated that there is no simple relationship between landfill leachate quality and equilibrium status. Equilibrium status is achievable for MBT treated waste with intensive composting, the residues from which are then landfilled. There is a wide range of reported literature values for the permeability of these waste streams and further work is required to assess their actual permeability which is likely to be the limiting factor for achieving equilibrium status.

Further work is also needed on the composition and leaching potential of treated waste streams. Data for pyrolysis and gasification processes in particular is lacking, though these are not likely to become dominant strategic options for waste management in the foreseeable future. Data is also lacking for the anaerobic digestion of specific waste streams and there are a growing number of these facilities in the UK in common with Europe.

The achievement of equilibrium status for an entire landfill is site-specific and ultimately factors such as size of site and depth of waste are likely to be important. The behaviour of wastes at deep (>50m) landfills is uncertain and appropriate L/S ratios may not be achieved even with leachate recirculation. Robust leachate collection systems in such sites will be essential.

This requires an evaluation of landfill management practice at current landfills so as to promote the achievability of equilibrium. For pre-Landfill Directive sites there is likely to be a legacy of long active management periods taking centuries rather than decades. Some of these sites may ultimately fall under the contaminated land legislative regime. A third manuscript [9] considers the policy and operational implications of this work.

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European household waste management schemes: Their effectiveness and applicability in England

I.G. Husaini [a], A. Garg [a], K.H. Kim [b], J. Marchant [c], S.J.T. Pollard [a], R. Smith [a,*]

[a] *Centre for Resource Management & Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire MK43 0AL, United Kingdom*
[b] *Department of Environmental Horticulture, The University of Seoul, 90 Jeonnong-Dong, 130-743 Seoul, Republic of Korea*
[c] *Environment Agency, Waste & Remediation Science Group, Kings Meadow House, Kings Meadow Road, Reading RG1 8DQ, United Kingdom*

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Abstract

This paper reviews European household waste management schemes and provides an insight into their effectiveness in reducing or diverting household waste. The paper also considers the feasibility of replicating such schemes in England. Selected case studies include those implemented using variable charging schemes, direct regulation and household incentivisation (reduced disposal charges). A total of 15 case studies were selected from developed countries in the EU where some schemes have operated for more than a decade. Criteria for assessing the effectiveness and replicability of schemes were developed using scheme progress towards targets, response time, compatibility with government policy, ease of administration and operation, and public acceptance as attributes. The study demonstrates the capability of these schemes to significantly reduce household waste and suggests changes to allow their possible adoption in England. One of the main barriers to their adoption is the Environmental Protection Act, 1990 that prevents English local authorities (LAs) from implementing the variable charging method for household waste management. This barrier could be removed through

* Corresponding author. Tel.: +44 1234 754963; fax: +44 1234 751671.
E-mail address: r.smith1@cranfield.ac.uk (R. Smith).

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a change in legislation. The need to derive consistent data and standardise the method of measuring the effectiveness of schemes is also highlighted.
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Keywords: Household waste; Waste reduction; Waste diversion; Economic instruments; Regulatory instruments; Incentivisation

1. Introduction

Waste is generated by activities in all economic sectors and often indicates the inefficient use of natural resources (Phillips et al., 2001), loss of materials and energy in production processes and unsustainable consumption patterns (EEA, 2002). Currently in England 67% of municipal solid waste (MSW) generated is landfilled, 9% incinerated and 23.5% recycled or composted (DEFRA, 2006). Results of the latest survey show that in England 29.7 million tonnes of MSW was produced during 2004/2005, which was 2.1% more than that produced in 2003/2004. However, the average annual MSW increase in England is 1.5% from 2000/2001 to 2004/2005. Out of this, 25.7 million tonnes (about 86%) was from households alone (DEFRA, 2006). It has been reported that the amount of total household waste and per capita waste increased by around 15% and 12%, respectively, between 1996/1997 and 2002/2003 (EEA, 2005). However, no further increase in the household waste production was observed until 2004/2005 (DEFRA, 2006). Household waste is mainly comprised of paper and card, kitchen and garden waste. The Waste Strategy 2000, which is currently under review by government, set MSW recycling or composting targets at 33% by 2015 (DETR, 2000). Also, in the UK, the EU Landfill Directive (1999/31/EC) requires the progressive reduction in biodegradable municipal waste to 75% of the 1995 disposal level by year 2010 and 35% reduction by 2020. Therefore, England requires more sustainable and practicable waste management methods to comply with the EU Landfill Directive. Originating in the Waste Framework Directive, a universal waste hierarchy is suggested for developing a sustainable waste management strategy, the elements of which include prevention, reuse, recycling, recovery and disposal (Fiorucci et al., 2003).

Continuous growth in waste quantities is imposing economic and environmental costs on society in most of the European countries for its management (EEA, 2000). The increase in the amount of waste is mainly attributed to the inability of member states to decouple economic growth from waste growth. According to the European Environment Agency (EEA, 2002), only Germany, the Netherlands, Iceland, and to a lesser extent Sweden and Denmark, have been successful in decoupling economic growth and growth in waste production. This decoupling is an objective of the sixth EU Environment Action Programme (2001–2010) (Gervais, 2002).

In Europe, the implementation of the waste hierarchy has become difficult due to complexity and multidisciplinary problems involving social, economic, environmental and technical aspects (Phillips et al., 2001). However, laws have been established by governments at international, national, regional and local levels to facilitate the establishment of challenging targets and to ensure a more sustainable approach to waste management in which less waste is produced and more waste is either reused or value recovered from it. As

a result, the use of household waste management schemes has become widely acceptable for effective waste management towards the top of the waste management hierarchy, i.e. waste reduction.

Several schemes based on economic, regulatory and incentive instruments have been successfully used in Europe to manage municipal waste (Dungan, 2003; Eunomia, 2002, 2003; Green Alliance, 2002; INFORM, 2005). Economic instruments refer to schemes established based on variable charging in order to implement the polluter pays principle. In these schemes, the local authorities (LAs) charge fees from householders for managing their waste. Regulatory instruments refer to the laws or regulations that are introduced by governments in order to enable the LAs to use them in the establishment of schemes. Incentive based instruments refer to schemes in which LAs provide some financial assistance or other ways to encourage householders to participate in waste management. The performance of the schemes in different countries varies depending on the social, economic, political and physical conditions of the areas.

In the present study, the focus is on the reduction of household waste in England using economic, regulatory and incentive based instruments that have already been used in Europe to implement strategies by LAs in order to address the waste issue. So this paper reviews household waste management schemes implemented in Europe, assesses their effectiveness in achieving the set targets and considers their replicability in England.

2. Materials and methods

2.1. Procedure and selection of selected schemes

To review household waste reduction schemes, a method for selecting the schemes was required. Schemes were selected after extensive literature review and consultation with the Environment Agency (EA). However, most of the studies were taken from two Eunomia reports (Eunomia, 2002, 2003). The most relevant schemes from Europe were chosen as they share a number of common features. For example, EU Member States have to comply with common legislation on waste management such as the packaging directive. It was expected that Member States would provide a wide range of credible data for good analysis and comparison. It was ensured that selected schemes cut across the principal instruments (economic, regulatory and incentivised) used for the implementation of waste management schemes.

After a comprehensive literature review, the following 15 household waste management schemes were selected for our study:

1. Belgium: Pay-Per-Bag scheme (Eunomia, 2002, 2003);
2. Denmark: weight-based charging scheme (Eunomia, 2002, 2003);
3. Germany: weight-and volume-based system (Eunomia, 2002);
4. Italy: tagged bag scheme (Eunomia, 2003);
5. Luxemburg: combined volume and weight-based scheme (Eunomia, 2002, 2003);
6. Sweden: weight-based scheme (Eunomia, 2002);
7. Ireland: plastic bag environmental levy (Dungan, 2003);
8. Germany: MSW management scheme (INFORM, 2005);

9. Belgium: BEBAT scheme for battery collection (Eunomia, 2003);
10. Finland: paper collection scheme (Eunomia, 2002);
11. Belgium: brussels scheme for the management of waste paper and board (Eunomia, 2002);
12. Netherlands: paper and fibre collection (Eunomia, 2002);
13. Belgium: flanders MSW management (Eunomia, 2002; Green Alliance, 2002);
14. Sweden: home composting scheme (Eunomia, 2002);
15. United Kingdom: West Sussex 'Real Nappy' initiative (Eunomia, 2003).

2.2. Review of schemes

A preliminary review was performed during an extensive literature survey for all 15 selected schemes. During the survey, the important issues in the schemes were identified and critically examined. These include the methodology of establishing the scheme (i.e., data gathering on waste arising, quantities, number of households to be served, etc.), the operational and administrative requirements of the scheme, the targets set to be achieved, the level of target actually achieved and the time period within which the achievement of the set target was desired. The limitations of each scheme were highlighted, and the effectiveness and replicability of each scheme were considered on the basis of observations.

For a more detailed review of the 15 schemes, the data was normalised in order to compare and assess the effectiveness of the schemes.

2.3. Assessing the effectiveness of schemes

The effectiveness of schemes is an essential aspect of this study. To appropriately comment on the effectiveness of the schemes, criteria were developed using achievement, time and costs as basic parameters.

Achievement of each scheme was judged based on the total quantity of waste reduced or diverted. Figures provided were normalised to waste kg/cap year for better understanding and ease of analysis and comparison. Waste reduction or diversion was scored based on performance as presented in Table 1. The quantities of waste for diversion are higher than those of reduction because household waste diversion, which is largely achieved through recycling and composting, is more easily achieved than reduction at source. Skumatz (2000)

Table 1
Assessment for achievement of the schemes based on the total quantity of waste reduced or diverted

Criteria	Scale (kg/cap year)	Points
Reduction	<3.9	2
	4–7.9	4
	8–11.9	6
	>12	8
Diversion	<19	2
	20–39	4
	40–79	6
	>79	8

Table 2
Assessment of time taken to achieve the set target by the scheme

Criteria	Time (year)	Points
Reduction	3	12
	6	9
	9	6
	12	3
Diversion	1	12
	2	9
	3	6
	4	3

observed that source reduction schemes have attracted less attention than recycling because source reduction is difficult to achieve, difficult to quantify, can be tedious and can be data intensive.

Time refers to the period expected to achieve the set targets by the scheme. This is considered an important parameter for assessing the effectiveness of schemes because programmes are time bound, otherwise they could be unnecessarily expensive to achieve the goals. Therefore, weighted scores were also allotted to time taken to reduce or divert a certain quantity of waste, which is shown in Table 2. For the 15 case studies, the score points also differ in respect of reduction and diversion due to similar reasons as for the case of achievement.

The cost of schemes (capital and operational) is the third parameter considered for assessing the effectiveness of a scheme. Although this parameter is important in assessing effectiveness, it was not possible to develop a criterion for costing the schemes due to the following reasons: (a) great variations amongst countries in the ways household waste management schemes are designed and managed. For instance, costs for kerbside waste collection will greatly differ from drop off or take back methods for recycling schemes, (b) the administrative and operational costs for running schemes could be vastly different from one country to another due to the technical requirements for operating the schemes, for example, the lock gate scheme in Germany, which was described as technically cumbersome and (c) lack of data on the cost of schemes; of the 15 schemes only the German lock gate scheme provided any cost data, in the form of total equipment cost without regard to operational and administrative costs.

Due to the constraints above, the assessment of selected schemes on a cost basis was not viable. This is a limitation of the assessment. The assessment of the effectiveness of the scheme was therefore limited to two parameters, that is, achievement for both the quantity of waste reduced or diverted and the time it takes to achieve set targets. The criteria for ranking the schemes are shown in Table 3.

2.4. *Applicability of schemes to England*

To determine the replicability of the schemes reviewed in England, a criterion was developed using effectiveness of schemes, ease of operation, compatibility with government policies and public acceptability as key parameters. Each parameter was scored with a

Table 3
Criteria for ranking the schemes

Category	Points
Poor	1–7
Fair	8–14
Good	15–20

maximum of five points. The following three categories of replicability were proposed: (a) readily replicable (R) schemes, that are in harmony with the above parameters, which do not require any modifications to be implemented (16–20), (b) modified (M) schemes, that will require some modification to enable them to be replicated, due to non-conformity with some of the parameters (11–15) and (c) difficult (D) scheme, which refers to schemes that will be extremely difficult to be adopted with respect to the scheme's non-conformity with government policy and effectiveness parameters (5–10).

3. Results

3.1. Detailed review

A summary of the selected 15 schemes reviewed is presented in Table 4. It essentially indicates that three instruments (economic, regulatory and incentive based) are widely used in establishing household waste management schemes. Out of the 15 schemes, 7 schemes were established using economic instruments, 6 using regulatory instruments and 2 schemes were established based on householder incentivisation.

Table 4
Category and goal of the 15 schemes reviewed

Country	Instrument used			Goal of scheme	
	Economic	Regulatory	Incentive based	Reduction	Diversion
Belgium (F. B. MSW)	X				X
Denmark	X				X
Germany (MSW)	X				X
Italy	X				X
Luxemburg	X				X
Sweden (MSW)	X				X
Ireland	X			X	
Germany (green dot)		X			X
Belgium (battery)		X			X
Finland		X			X
Belgium (waste paper and board)		X		X	
Netherlands		X			X
Belgium (Flanders MSW)		X			
Sweden (home composting)			X		X
UK (real nappy)			X	X	

3.1.1. Performance of schemes based on amount of waste reduced or diverted

Assessing the performance of the schemes with regards to the amount of waste reduction or diversion was one of the key objectives of this study. However, only 4 out of the 15 schemes could be compared based on performance because the four schemes provided data on clear targets and achievements in similar units or in units that were agreeable after conversion. In the remaining schemes data were either provided for achievements or targets only, and in some instances, in percentages without actual values to allow conversions. The results presented in Fig. 1 indicate that a waste reduction/diversion rate of up to 95 kg/cap year was achieved in the case of a paper recovery scheme in Finland. The results also indicate that set targets were actually exceeded by two schemes, the Belgian MSW diversion scheme (target 35 kg/cap year; achieved 40 kg/cap year) and the Irish plastic bag scheme (target 2 kg/cap year; achieved 4 kg/cap year). In the remaining schemes although targets were not fully achieved, performances ranged from 53 to 67%. The actual quantity of waste reduced or diverted/kg/cap year is shown in Table 5. The results also showed that the quantities of wastes reduced or diverted by the schemes range from 4 kg/cap year in the Irish plastic bag scheme to 1600 kg/family year in the West Sussex real nappy scheme. The amount seems small after normalisation by comparing the quantity achieved by the scheme with various per capita waste generation of the country where the schemes are implemented. Thus performances after normalisation range between 0.01 and 5 kg/cap year.

It is observed that the performances differ greatly between schemes due to the different waste streams handled by schemes and whether the goal of the scheme was waste reduction or diversion.

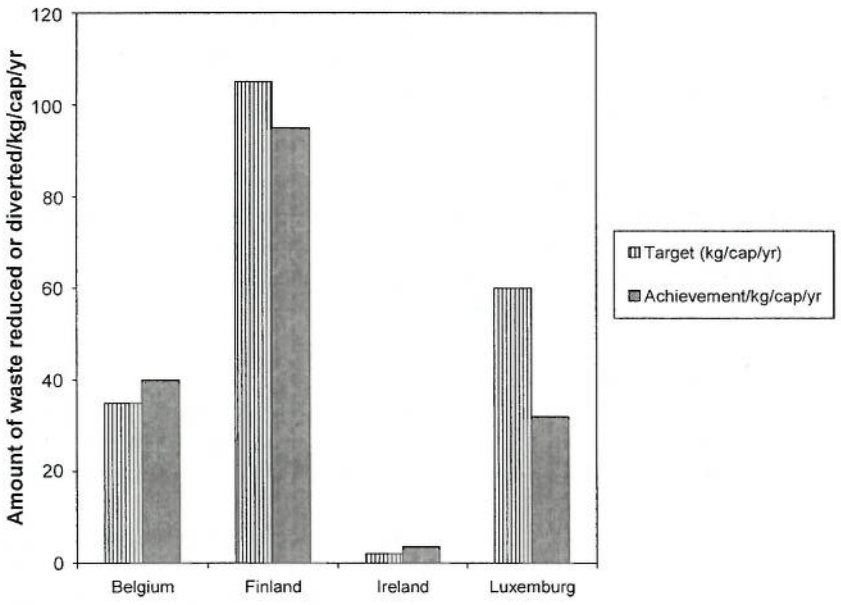


Fig. 1. Performance of waste management schemes based on economic instruments in four EU Member States (amount of waste reduction/diversion against set targets).

Table 5
Normalised performance of the 15 schemes

Country	Amount of waste reduced or diverted (kg/cap year)	Normalised amount of waste reduced or diverted (kg/cap year)
Belgium (F. B. MSW)	47	0.1
Denmark	120	0.2
Germany (MSW)	236	0.7
Italy	17	0.04
Luxemburg	32	0.07
Sweden (MSW)	37	0.08
Ireland	4	0.01
Germany (green dot)	ND	ND
Belgium (battery)	ND	ND
Finland	95	0.5
Belgium (waste paper and board)	ND	ND
Netherlands	ND	ND
Belgium (Flanders MSW)	40	0.03
Sweden (home composting)	6	0.01
UK	1600	5

ND: not determined.

3.1.2. Performance of economic instruments based schemes

The performance of six out of the seven schemes based on economic instruments was compared. The results obtained are presented in Table 5. The Danish weight-based MSW scheme achieved a diversion rate of up to 120 kg/cap year (0.2 kg/cap year, normalised) whilst the Irish plastic bag levy scheme achieved a 4 kg/cap year (0.01 kg/cap year, normalised) reduction rate. On average, the economic instrument based schemes achieved reduction/diversion rates of 43 kg/cap year of the targets they were set to achieve. However, the average achieved in terms of actual waste reduction was not normalised because of the differences in the per capita waste production of the countries.

3.1.3. Performance of regulatory instruments based schemes

Achievement results of the schemes established using regulatory instruments indicate that the amount of waste reduced or diverted by the schemes are 40 and 95 kg/cap year for Belgium (MSW Flanders scheme) and Finland, respectively. Table 5 shows the achievement of these two schemes that provided data on their targets.

3.1.4. Performance of incentivised schemes

Two schemes in the 15 case studies were based on provision of incentives to householders in order to encourage them to participate in waste management schemes. The schemes include the Swedish household composting and the West Sussex real nappy scheme in the UK.

The Swedish households using the scheme, composted an estimated quantity of 1600 tonnes/year of food wastes, this reduced the amount of waste going to landfill by about 6 kg/cap year (0.01 kg/cap year, normalised) in communities where the scheme was used (Table 5). Households that had installed composting facilities within their area were qualified to apply for a reduction in waste fees. In the year 2000, the total fee

Table 6
Assessment of the effectiveness of economic instrument schemes

Country	Achievement	Time	Total points	Effectiveness
Belgium (F. B. MSW)	6	6	12	Fair
Denmark	6	9	15	Good
Ireland	4	12	16	Good
Italy	2	9	11	Fair
Luxemburg	4	6	10	Fair
Sweden (MSW)	2	6	8	Fair

reduction (incentive) to households corresponds to €211,111 $year^{-1}$ (~ £131,944) or €133.3 $household^{-1}$ $year^{-1}$ (~ £83.30). The West Sussex real nappy scheme provides free laundry services for families using the scheme. The results of the scheme show that 500 families participated in the scheme between 1999 and 2000 and this saved the production of 800 tonnes of disposable nappies as well as cost savings of €32,000 (~ £20,000) for the local authority. The waste reduction per family that used the scheme translated to 1600 kg/family year and the incentive provided amounted to €48 $family^{-1}$ $year^{-1}$ (~ £30).

3.2. Assessment of the effectiveness of schemes

Assessment of the effectiveness of schemes was the major objective of the present study. Three parameters considered for developing the criterion for assessing the effectiveness of the schemes were achievement, time and total costs of schemes as explained in Section 2.3. The schemes were categorised in to three groups based on the instruments used for establishing them to allow for comparison of the effectiveness between the schemes and to explain the differences observed in Section 4. The assessment was categorised as good, fair or poor based on their scores. The results of the effectiveness are presented in the following sections.

3.2.1. Effectiveness of economic instrument schemes

The results of the assessment of the effectiveness of the economic instrument based schemes is presented in Table 6. Within the confines of the assessment criterion used, the results indicate that two of the schemes (Ireland and Denmark) were ranked as good, and the remaining four were rated as fair (Belgium, Luxemburg, Italy and Sweden). The remaining scheme from Germany in this category was not rated due to a lack of data.

3.2.2. Effectiveness of regulatory instrument schemes

The results of the assessment of the effectiveness of the schemes established based on regulatory instruments are presented in Table 7. Within the limits of the criterion used, the results indicate that the paper recovery scheme from Finland was the most effective and ranked as good. Three other schemes were rated as fairly effective whilst two schemes were not rated due to insufficient information.

welcome the variable charging method because of the general belief that waste collection is already paid for through the council tax (Price, 2001; Rayner, 2003). Government has ruled out charging schemes for the foreseeable future despite considerable analysis (Ernst and Young, 2002) but such schemes have not been ruled out altogether. The Government has however ruled out a separate national tax on household waste (HM Treasury, 2003) which is an alternative option. The Local Government Association (2004) is lobbying Government to give power to councils to implement direct and variable charging schemes. Despite existing legislation, LAs are able to charge for excess waste by restricting the size of containers they provide. In this manner, home composting can also be encouraged and waste production can be significantly reduced. The House of Commons Environment Food and Rural Affairs Committee (2003, 2005) is strongly in favour of LAs being given the ability to introduce variable charging schemes if they so wish but argues that they should only be introduced if they do not have an unfair impact, especially on low income families. Potentially, direct charging could reward those households that produce less waste.

However, in England, kerbside collection is increasing under the provisions of the Household Waste Recycling Act 2003 that aims to increase the amount of recyclables to meet the prescribed targets (DEFRA, 2005). English waste collection authorities are to collect separately at least two types of recyclables at the kerbside from all households by 2015 at reasonable cost. Under the act, materials recycling facilities (MRFs) are not an acceptable alternative for the separate collection of two different types of recyclables. In order to comply with the act, direct charging can be implemented for excess waste. Some EU member states are already performing significantly better than England, for example Austria collected >65% and the Netherlands and Germany both around 40% of all MSW as separate waste fractions in 1999 (European Commission, 2003). Householder charging is much the most widely used instrument to influence waste generation and reductions in residual waste (Resource Recovery Forum, 2004).

4.2. *Performance of regulatory instrument schemes*

Regulatory policy is an instrument based on legislation introduced by countries in order to address waste problems. In most cases, some form of legislation is required to force the implementation of a waste management scheme. The result of this study shows (in Table 4) that six of the schemes reviewed were established using regulatory instruments. It is evident from the study that regulatory instruments can successfully be used to address the generic MSW problem. However, most of the regulatory instrument schemes were assessed for specific waste streams.

Within the limitations of the criterion used for assessing the effectiveness of the schemes, there seems to be no significant difference in achievements between the regulatory-based schemes.

All six regulatory-based schemes were established through producer responsibility with respect to household wastes. For instance, the 1993 Belgian law of ecotaxes aimed to give incentives to consumers to change their behaviour towards product consumption in an environmentally friendly way. In order to achieve this, a tax was imposed on a range of products to be sold. Therefore, the BEBAT scheme was introduced to collect used dry

batteries for subsequent recycling. The batteries are exempt from ecotax if the manufacturers agree to set up a recycling and collection scheme. The paper schemes of Finland and the Netherlands targeted waste paper collection from households. In the Netherlands scheme, local authorities are responsible for collecting paper and board from the household. The paper industry then purchases this material from LAs and it pays for further processing and disposal. All the schemes were implemented through producer responsibility. The main reason for the participation of industries in household waste schemes may be attributed to the imposition of tax on certain products. An increased price due to tax might bring a change in public perception towards the use of products. This may eventually reduce the market of such products.

Good performance of most regulatory schemes is observed as it is easier to identify, separate and collect the specific waste streams. Also, breach of legislation may result in prosecution to the waste collectors and producers (Green Alliance, 2002).

4.3. Incentivised schemes

Incentivised instruments are essentially based on the provision of incentives in cash or kind by waste management authorities to householders who participate in schemes. Two of the reviewed case studies were established based on the provision of incentives to householders who wish to participate in waste management schemes implemented by LAs. The results of the use of incentives to address household waste show a dramatic performance by the West Sussex real nappy scheme, which reduced at source 1600 kg/family year (Eunomia, 2003). The use of incentive schemes also achieved some diversion of *ca.* 6 kg/cap year of household waste to landfill in Sweden, which translates to 0.01 kg/cap year, when compared to the Swedish 530 kg per capita waste generation. The performance of the two schemes was surprising because incentivised schemes do not seem to perform so well in reality. This is because the choice to participate in the scheme is entirely the decision of the householders, who despite the incentives on offer, may not feel comfortable to participate in recycling or composting of their waste. This is supported by Rayner (2003), who demonstrated in a newspaper survey report that some UK residents "avoided the recycling route by continuing to put everything in one bin for the general rubbish", their argument being that they have paid for waste management and could not understand why they should be involved.

The reason for the good performance of the two incentive-based schemes in West Sussex could be because they targeted specific waste streams combined with the wide publicity enjoyed by the scheme. This is supported by the fact that most of the schemes that addressed specific waste streams have significantly reduced or diverted waste, for example as seen in the case of plastic bags in Ireland, battery collection and recycling in Belgium and paper recovery in Finland.

4.4. Effectiveness of schemes

The criteria used for assessing the effectiveness of the schemes have already been presented in detail in Section 2.3.

4.4.1. Effectiveness of the economic instruments based schemes

The results of the assessment of the effectiveness of schemes based on economic instruments are presented in Table 6. The reason for the good performance of the Irish and Danish schemes is that both targeted specific waste streams (plastic bags and household composting) which make it easier for the householders and the operators to manage than total MSW that might require sorting before treatment or disposal. An additional reason for the effectiveness of the Irish plastic bag scheme is probably the charge of €6.7 kg^{-1} (~£4.20) which is higher than all other charging schemes reviewed. This cost might have been responsible for the change of people's behaviour, which is a greater challenge to waste reduction (Grigg and Read, 2001).

4.4.2. Effectiveness of the regulatory instruments

The results of the effectiveness of the regulatory instrument based schemes are presented in Table 7. Using our criteria, only the Finland paper recovery scheme was rated as effectively good. The reason for this is probably two-fold; firstly there is a long demand-lead history of paper recycling in Finland dating back to the 1940s; and secondly due to the involvement of the most experienced paper company in Finland (Paperinkerays Ltd.), in the scheme, whose responsibility is to collect and recover waste paper from households and offices. Paperinkerays maintains an information system pertaining to waste paper operations. The success of the scheme is also attributable to involvement of property owners in waste paper collection. Property owners were responsible for the provision of containers and collection of waste paper. Three of the schemes were rated as fairly effective and the other two could not be assessed due to lack of data. The effectiveness of the schemes could be attributable to being waste stream specific, e.g. the battery and waste paper and board schemes in Belgium and the paper recovery schemes in Finland and the Netherlands, possibly due to ease of identification and handling. Another reason is that under producer responsibility, there do not seem to be financial constraints for the operation of schemes and possible monitoring by government to ensure compliance. In the producer responsibility schemes reported in the literature, there are proper arrangements for financing the schemes by the stakeholders and all of them become obliged.

4.4.3. Effectiveness of incentivised schemes

The Swedish household food composting scheme was rated as fairly effective whilst the West Sussex real nappy scheme was rated as good. The reason for the effectiveness of the West Sussex real nappy scheme is the intensive campaigning and the assistance by hospitals, health officers, the local media, and increasing support from householders. Another possible reason for effectiveness could be the need to protect babies from rashes due to poor ventilation caused by the plastic content of non-real nappies.

4.5. Applicability of schemes in England

The result of the assessment of the potential replicability of schemes in England shows that only six of the reviewed schemes could be directly replicated in England (Table 9). This is because the schemes were implemented using the producer responsibility that is already well established in the UK through the Environment Act 1995. The two other schemes that

could be readily replicated were established based on the provision of incentives, which is a widely accepted method of implementing schemes in the UK. The real nappy scheme is a good example of an incentive-based scheme in the UK.

The results further suggest that 10 of the 15 schemes could be replicated in England with some modification. Most of these schemes were based on the variable charging system, which is not currently permitted in England. Some schemes, although not based on variable charging, would need modification because they employ fines of up to $10,000 per day (~ £5600) on any county that fails to comply with the recycling targets (Green Alliance, 2002). These measures are not popular in Europe and would not be readily accepted in England.

5. Conclusions

Household waste management schemes adopt economic, regulatory or incentive based instruments that are widely acceptable across Europe. Many such schemes have been successful in achieving waste reduction. In the absence of a standardised method of measuring effectiveness of schemes, the quality of assessing the effectiveness of schemes is within the constraints of our criterion developed. This emphasises the need for consistent data and in particular the need to standardise the measurement of effectiveness. Furthermore, whilst the success of some individual schemes can be highlighted, there is a lack of transparent data on the costs of commissioning, operating and monitoring household waste management schemes in relation to their waste reduction or diversion achievements. Schemes that are designed to manage specific waste streams achieve the greatest reduction or diversion, rather than the general MSW stream.

Although some schemes were found to be highly effective, many cannot be replicated in England due to the policy barrier created by the Environmental Protection Act 1990 which prohibits variable charging by LAs to implement waste management schemes. This suggests the need for central government to review policy with respect to that Act.

The waste paper and board, real nappy and BEBAT schemes provide good potential for achieving waste reduction at household levels. In addition to these, the Belgian and German MSW schemes, Irish plastic bag environmental levy scheme, Netherlands waste paper scheme and Swedish home composting schemes would require modifications before possible implementation.

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Short communication

Enumerating actinomycetes in compost bioaerosols at source—Use of soil compost agar to address plate 'masking'

M.P.M. Taha[a], G.H. Drew[a], A. Tamer Vestlund[a], D. Aldred[b], P.J. Longhurst[a], S.J.T Pollard[a,*]

[a]*Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Building 61, Cranfield, Bedfordshire MK43 0AL, UK*
[b]*Cranfield Health, Cranfield University, Silsoe, Bedfordshire MK45 4DT, UK*

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Abstract

Actinomycetes are the dominant bacteria isolated from bioaerosols sampled at composting facilities. Here, a novel method for the isolation of actinomycetes is reported, overcoming masking of conventional agar plates, as well as reducing analysis time and costs. Repeatable and reliable actinomycetes growth was best achieved using a soil compost media at an incubation temperature of 44 °C and 7 days' incubation. The results are of particular value to waste management operators and their advisors undertaking regulatory risk assessments that support environmental approvals for compost facilities.
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Keywords: Actinomycetes; Bioaerosols; Compost; Enumeration; Risk assessment

1. Introduction

Actinomycetes are a heterogeneous group of filamentous bacteria resembling fungi. They are a major component of bioaerosols emitted from composting facilities (Strom, 1985; Lacey, 1997; Niemi et al., 1982; Swan et al., 2003). Mesophilic and thermophilic actinomycetes have growth profiles of 20–50 and 30–60 °C, respectively. They grow as branching microorganisms with short chains of spherical spores, 0.7–1.3 μm in diameter. Prolonged inhalation of actinomycetes is linked to adverse human health effects (Douwes et al., 2003), including allergic alveolitis and other respiratory responses (Millner, 1982; Lacey and Crook, 1988; Lacey and Dutkiewicz, 1994; Reboux et al., 2001; Herr et al., 2003), in which inflammation of the lung is believed to be caused by glycopeptides and protein allergens released from spores, as is the case for 'farmer's lung disease' (Edwards, 1972).

Actinomycetes concentrations, reported in colony forming units per cubic metre of air (cfu m^{-3}), are among the microorganisms that comprise the atmospheric bioaerosol burden emitted from composting facilities (Composting Association, 1999; Taha et al., 2005, 2006). In the UK, a quantitative estimation of bioaerosol load is expected as part of risk assessments for composting facilities within 250 m of sensitive receptors, prior to the development or extension of such facilities and to inform

*Corresponding author. Tel.: +44 0 1234 754101; fax: +44 0 1234 751671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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the permitting of waste licences (Environment Agency, 2001). Meaningful risk assessments rely on quality source term data (Pollard et al., 2006); particularly at source, so that downwind concentrations may be reliably approximated.

In bioaerosol sampling methods based on the capture of culturable microorganisms, problems associated with the identification and quantification of microorganisms include colony 'masking', where colonies overlap (Chang et al., 1994, 1995; Chen et al., 1998; Kalogerakis et al., 2005). Masking impedes the visual inspection of the media plate and enumeration of individual species, which may lead to colony counting errors. Lacey (1997) suggests that the method used to collect samples may influence the growth of other bacteria, and that this problem is particularly associated with isolating actinomycetes from compost samples. Researchers have also commented that selecting the appropriate media for the environment in which the sample is collected may also improve the enumeration results (Balestra and Misaghi, 1997).

Here, we introduce an alternative media, soil compost agar (SCA), for the improved enumeration of actinomycetes from bioaerosols sampled close to source at two green waste composting facilities. Source term samples, we have found, are especially prone to masking and yet are most relevant to estimating the bioaerosol flux from compost facilities and so a reliable enumeration method must be established. We believe that the method proposed here is of timely importance due to the current regulatory interest in occupational and public exposures to bioaerosol emissions (Swan et al., 2003; Herr et al., 2003).

2. Materials and methods

2.1. Bioaerosol and compost sampling

Bioaerosol sampling was performed at two green waste windrow composting facilities, with capacities of 2000 and 1000 m^3 per annum, respectively. Air and compost samples were taken on nine separate occasions between October 2003 and March 2005, covering the winter, spring and autumn seasons. The samples were taken (i) >15 m upwind of the facility boundary, (ii) within the site, and (iii) at 15, 100 and 200 m downwind of the composting facility site boundary. Further details and the background context for our bioaerosols studies at these composting facilities have previously been reported (Taha et al., 2005, 2006, 2007).

Sampling employed medium flow, personal aerosol filter samplers (SKC Universal dust and vapour sampling pump; models SKC Aircheck^{TM} 224-PCXR8 and 224-PCTX8). Pumps operated at 2.0 ± 0.1 l min^{-1} and were fitted with SKC dust sampling IOM (Institute of Occupational Medicine) heads connected using 10 mm i.d. Tygon^{TM} tube. IOM heads were loaded with 25 mm diameter, 0.8 μm MCE (mixed cellulose ester, SKC) filters. The IOM samplers were attached to a stand, 1.8 m above ground, similar to the method used by Wheeler et al. (2001) and Environment Agency (2007). The sampling time was 30 min, reduced to 10 min where the expected bioaerosol concentration was high. Two air samples were taken simultaneously in each case using two samplers, with one pump kept as a standby, as recommended by the Composting Association (1999). Both samples were treated identically in further analyses and the collection of simultaneous samples was used to increase the statistical significance of the results. All pumps were calibrated before use.

Compost grab samples (ca. 30 g) were also taken from the windrows associated with bioaerosol release. The grab samples were taken from as close to the area where the air samples were taken as possible, usually at a depth of 0–10 cm into the compost pile, which had already been shredded and turned so that there was homogenisation of the material. This procedure was adopted so as to sample the area most closely representing the area where the air samples were collected.

2.2. Isolation

Microorganisms were quantified using the plate count analysis steps of the CAMNEA-method (collection of airborne microorganisms on nuclepore filters, estimation and analysis; Palmgren et al., 1986) with subsequent visual enumeration. Filters and compost grab samples were placed, whilst at the site, into 30 ml vials containing 10 ml 0.05% v/v Tween-80^{TM} mixed with 0.1% w/v NaCl to prevent osmosis. Samples were transported at <4 °C and, on return to the laboratory, re-suspended by separating the filter from the head and shaking in a vial for 2 min. The solution was diluted to a common logarithm order (10^{-1}, 10^{-2} and 10^{-3}) and inoculated onto both media plates. All equipment was sterilized before use.

2.3. Enumeration

Media preparation, inoculation, dilution and sterilization were performed in accordance with BS 5763: Part 0:1996 (British Standards Institution, 1996). Two media were used: (a) half strength nutrient agar (NA) (Oxoid CM3 nutrient agar); $14\,g\,l^{-1}$, in ionised water; and (b) SCA; a supernatant of 100 g loam compost (John Innes^{TM} No. 1) with 1000 ml deionised water was vigorously shaken for 2 min and centrifuged at 500 rpm for 5 min. The SCA agar was prepared using 7 g of agar–agar powder with 500 ml deionised water, with no need for pH adjustment. After preparation, both media were autoclaved (121 °C for 15 min), left to cool to below 47 °C and treated with 1% w/v

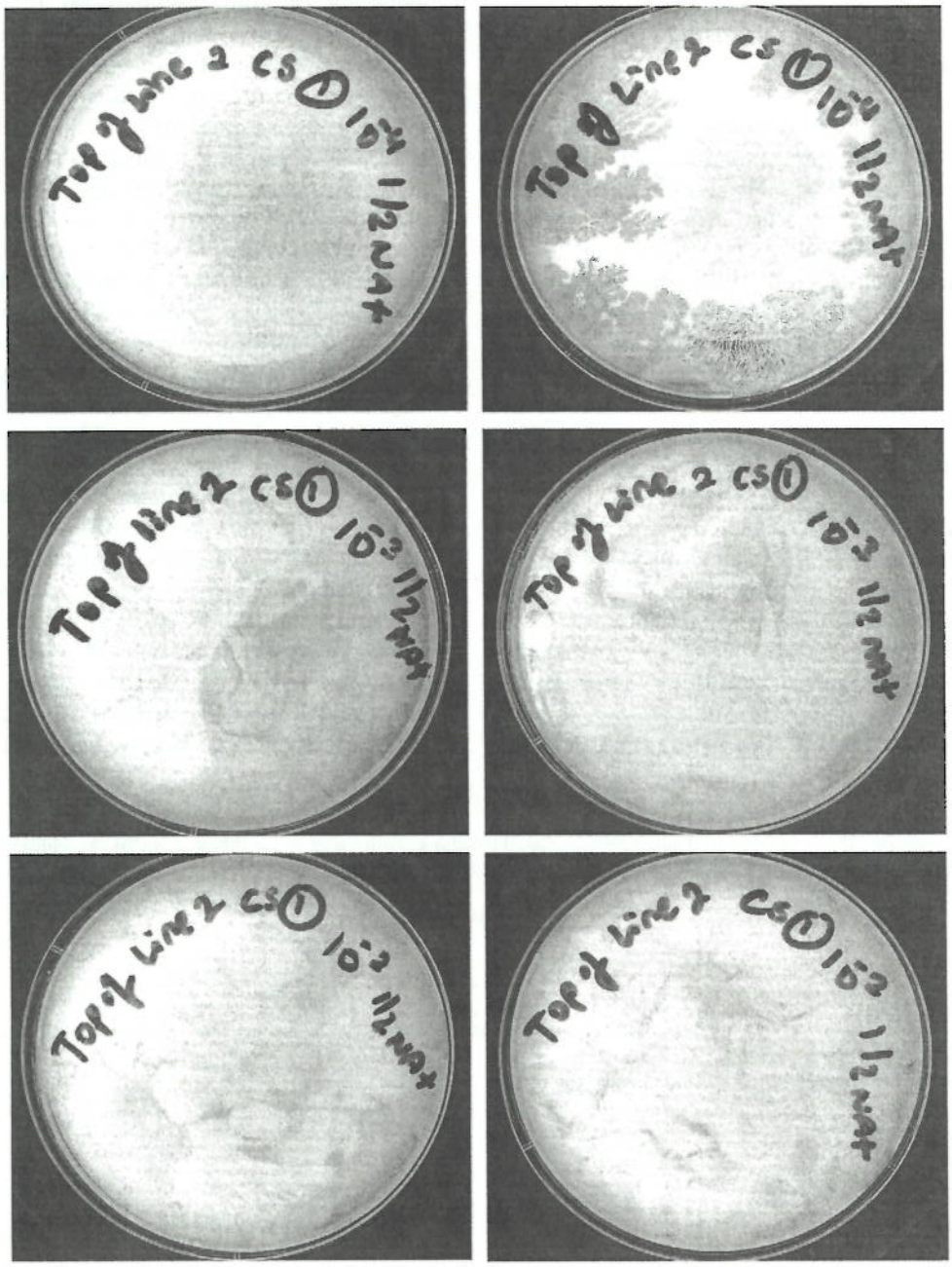


Fig. 1. Actinomycetes growth using half strength nutrient media (NA). Plates show clear evidence of masking effect, as individual colonies of actinomycetes are difficult to distinguish.

antifungal cycloheximide, dissolved in 2 ml of HPLC grade ethanol. In each case, the agar medium (12 ml) was poured into Petri dishes to a depth of ca. 2 mm and allowed to cool on a horizontal surface before being inoculated with the sample solution as described above. Colonies grown at an incubation temperature of 44 °C on both media were enumerated visually after 7 days, employing the BS 5763 standard (British Standards Institution, 1996).

3. Results and discussion

Actinomycetes were enumerated by estimated count from 76 air samples inoculated on NA plates. However, 60 of these samples showed either full or partial overgrowth of other bacteria ('masking') that obscured actinomycetes growth and it was therefore difficult to count the colonies of actinomycetes (Fig. 1). This resulted in these plates being rejected. From the 24 compost samples inoculated on NA plates, all showed 'masking' by overgrowth of other bacteria (Table 1). Serial dilution of the samples was not able to address this masking effect that we attribute to a very high bacterial burden in samples taken very close to source.

In contrast, the SCA plates, incubated at a temperature of 44 °C, showed no masking by eubacteria or fungi (Table 1), after allowing 7 days for the actinomycetes to grow and sporulate. In each case, the enumeration of actinomycetes colonies was proportionate to the dilution factor applied in constructing the plates, improving the confidence interval limit of the study. The actinomycetes grown on SCA were easily identified by the white powdery colour of their spores and spider web-like formation appearing on the colonies (Fig. 2). Of the 13 samples where no actinomycetes were found on the SCA plates, one of the NA plates showed bacteria growth with no actinomycetes, seven of the NA plates showed no actinomycetes and five NA plates showed masking by other bacteria.

Several media have previously been used for the identification and enumeration of actinomycetes (Table 2). The Composting Association (1999) suggests the use of half-strength NA. Most significantly, Crawford et al. (1993), during their experiments on plant roots in British soils, secured optimum enumeration using a low nutrient organic media and compost extract agar and using this, the overgrowth of media by eubacteria and fungi was dramatically reduced. Curtis and Beuchat (1998) argue that a common problem related to quality control of culture media is the non-inhibition and growth of unwanted microorganisms on selective media. High colony counts of unwanted microorganisms may lead to significant colony overlap on the growth media plate, 'masking' the growth of the species of interest.

The enumeration methodology described here offers substantive methodological improvements over existing approaches (Composting Association, 1999) and allows a reliable estimation of the actinomycetes load, especially where concentrations are expected to be high, such as at source. This method has proved useful in achieving consistent results. In addition, it has proven to be cost effective and simple, as well as reducing

Table 1
Enumeration outcome for air and compost samples with actinomycetes growth using soil compost agar (SCA) and half strength nutrient agar (NA) (samples taken on nine occasions between 26/10/2003 and 10/03/2005)

Enumeration outcome	Air samples				Compost samples			
	SCA		NA		SCA		NA	
	Samples[a]	%[b]	Samples[a]	%[b]	Samples[a]	%[b]	Samples[a]	%[b]
Actinomycetes enumeration achieved	28	37	0	0	23	96	0	0
Actinomycetes enumeration achieved by estimated count	33	44	6	8	1	4	0	0
Full masking	0	0	48	63	0	0	22	92
Partial masking	0	0	12	16	0	0	2	8
No actinomycetes	13	17	8	11	0	0	0	0
Bacteria, no actinomycetes	1	1	2	3	0	0	0	0
Total samples	75	100	76	100	24	100	24	100

[a]The number of samples that achieved each enumeration outcome.
[b]The percentage of samples for each media that achieved each enumeration outcome.

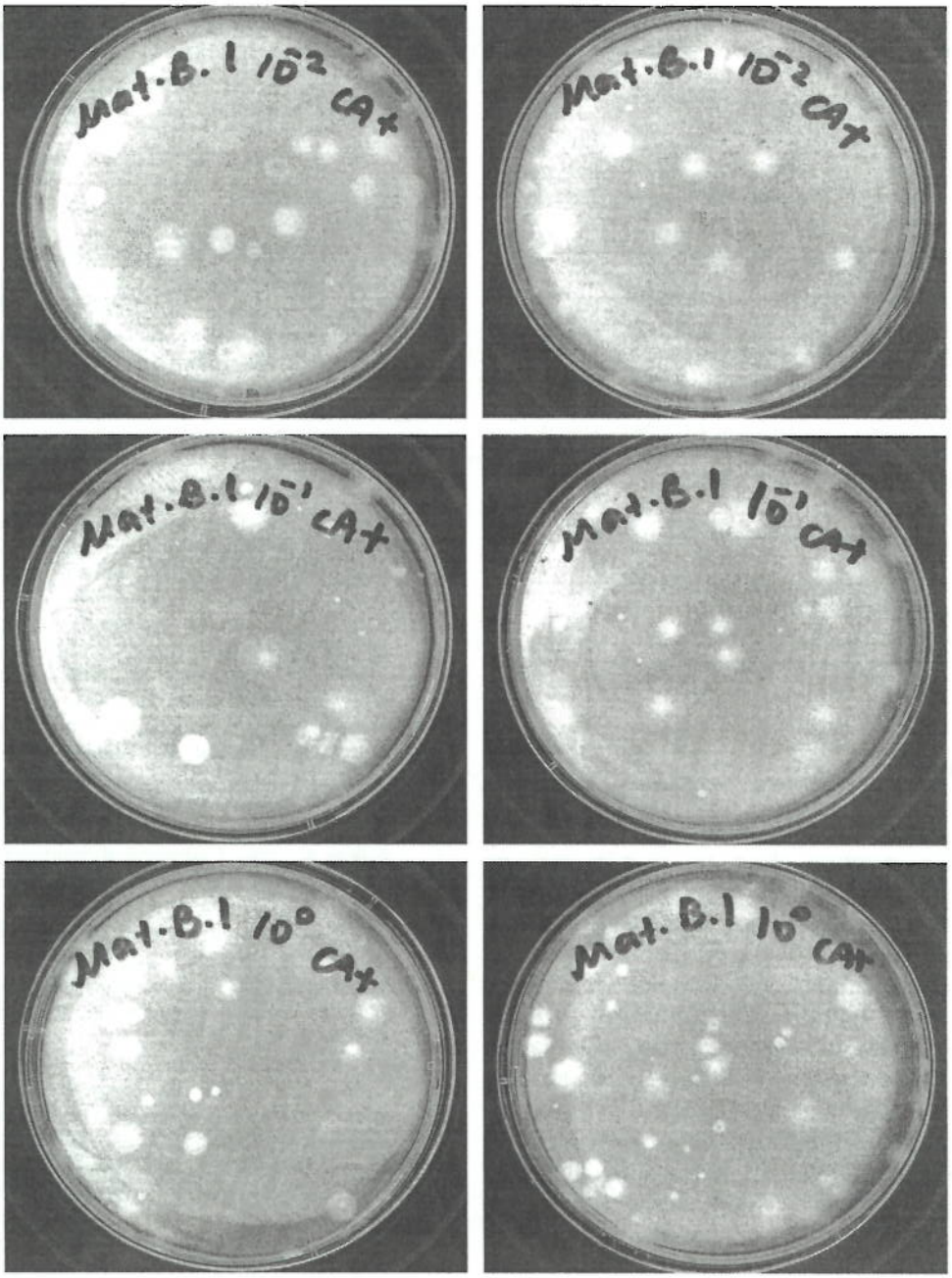


Fig. 2. Actinomycetes growth using soil compost agar (SCA). Plates show clear evidence of improved visual inspection using SCA, as individual colonies of actinomycetes are clearly visible.

analysis time. This method is also inline with the findings of Griffiths and Stewart (1999), who suggest the tailoring of microorganism analysis for the application of interest, as it focuses on composting. This is because no one single assay is suitable for the study of microorganisms.

The results presented here are encouraging for the further development of this method. Future work will include the analysis of the consistency of the extracted compost supernatant, as well as testing batch-to-batch variation and the use of different types of compost.

Table 2
Media used for the identification and enumeration of actinomycetes

Medium	Reference
Nutrient oxoid agar	Nielsen et al. (1997), Würtz and Breum (1997) and Breum et al. (1997)
Half strength nutrient agar	Composting Association (1999)
10% w/v nutrient agar	Nielsen et al. (1997), Würtz and Breum (1997) and Breum et al. (1997)
Starch–casein (CS) agar	Folmsbee and Strevett (1999)
Czapek's solution agar (CZ)	Asan et al. (2004)
Starch-ammonia medium	Andreeva et al. (2001)
Half-strength (50% w/v) nutrient	Lacey and Dutkiewicz (1976), Recer et al. (2001)
Tryptone soya with casein hydrolysate agar	Lacey and Dutkiewicz (1976), Recer et al. (2001)
Half-strength tryptic soya agar	Dutkiewicz et al. (2001)
Trypticase soya agar	Lavoie and Alie (1997)
Low nutrient organic media and compost extract agar	Crawford et al. (1993)

4. Conclusions

A novel method for the enumeration of compost-derived actinomycetes close to source and in bioaerosol samples has been supported by evidence from over 70 air and compost samples taken over 9 separate sampling days. The method is suited to the enumeration of actinomycetes sampled from green waste compost facilities and significantly reduces the masking of actinomycetes by other bacteria. It provides substantive improvements over the NA media (e.g. Nielsen et al., 1997; Würtz and Breum, 1997; Breum et al., 1997) for source term samples. The method is cost effective, reduces analysis time and produces replicable results. Its application is particularly significant for practitioners enumerating bioaerosols in support of regulatory risk assessments for the waste management sector.

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Coupling Hidden Flows And Waste Generation For Enhanced Materials Flow Accounting

Thomas Raffield[12], Martin Herben[2], Stephen Billington[2], Phil Longhurst[1] and Simon Pollard[1] *

[1]*Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Bedfordshire, MK43 0AL, UK*
[2]*Enviros Consulting Ltd, Culham Science Centre, Oxfordshire, OX14 3DB, UK*
**Corresponding author: email: s.pollard@cranfield.ac.uk, phone: +44 (0)1234 754101, fax: +44 (0)1234 751671*

ABSTRACT

We present an adaptation of an existing materials flow model to account for waste flows in the domestic environment. The revised approach offers added functionality for economic parameters that influence waste production and disposal. Hypothetical waste and resource management futures illustrate the utility of model. A sensitivity analysis confirms that imports, domestic extraction and their associated hidden flows impact mostly on wastes generation. The model offers enhanced utility for policy and decision makers with regard to economic mass balance and strategic waste flows.

KEY WORDS

Resource management, material flow, modelling, accounting, waste

1. INTRODUCTION

An essential contribution to informed policy decisions on waste and resource management is the analysis of the materials flow within an economy. Several authors (Matthews *et al*, 2000; Hendricks *et al*, 2000; Bringezu and Schütz, 2001a, b; EUROSTAT 2001; 2002; Bringezu *et al*, 2003; 2004; Longhurst *et al*, 2005; Mutha at al, 2006; Dahlström and Ekins 2006a, b) have developed mass balance models based on the principles of industrial ecology, and present important insights into resource efficiency and productivity in industrialised economies.

One objective of these studies has been to evaluate the decoupling of economic growth from waste production (Defra, 2002). Though reasonably resource efficient, the UK economy makes a considerable demand on materials use (Bringezu and Schütz, 2002). Officer (2007) reports the real gross domestic product (GDP) of the UK in 2005 as £1.17 x 106m and, with a growth rate of ca. 3% per annum (Asif and Muneer, 2007), this is one of the fastest in Europe. Sheerin (2002) reports a UK materials input (total materials requirement for the economy) of 35.1 tonne (t) per capita. The Royal Society for Wildlife Trusts (2006) estimate a UK ecological footprint of 5.4gha (global hectares – an area of productive land or sea required to produce the resources consumed and absorb the wastes generated in an economy) per capita, compared to a global average of 2.2gha per capita, exceeding the available global biocapacity of 1.8gha per capita.

Several studies have quantified resource flows and their associated impacts in the context of waste management (Matthews *et al.*, 2000; Hicks *et al.*, 2004; Zhao *et al.*, 2005; Jose *et al.*, 2005; Longhurst *et al.*, 2005). In an influential study, Matthews *et al.*, (2000) present a comprehensive account of materials flow modelling and detail a number of critical materials flows to which the reader is referred. Adapting their approach, we present a materials flow model for the UK that couples hidden and waste flows. We introduce and test a strategic waste flow element to the model (Raffield, 2006; Figure 1), that can be used to explore hypothetical scenarios on waste and resource futures.

2. METHODOLOGY

Key model variables are presented in Table 1. The direct material input (DMI; Figure 1) is the principal variable representing material tonnage into the economy. The relationships between DMI and other variables enable the model to express the onward fate of the DMI in million tonnes (Mt) per unit time as material

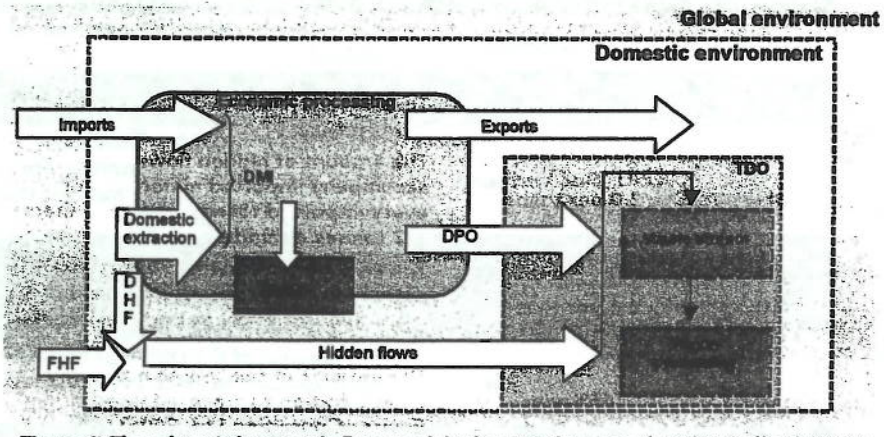


Figure 1: The advanced materials flow model (after Matthews *et al.*, 2000; Raffield, 2006)

is used for economic processing, in manufacturing, for example.

Flows in the model were constructed in consecutive Excel™ spreadsheet layers where variables can be altered. To model the constituent components of the DMI and the onward fate of materials as output flows, a number of additional variables were incorporated, adapting Bringezu and Schütz, (2002) and Enviros Consulting Ltd, (2006) (Table 2). For quality control, sheets with underpinning assumptions were "locked" and preconditions set (Table 2) to ensure input data was consistent. For example, the precondition of securing a mass balance throughout.

A fundamental assumption of this approach is described by Matthews *et al.*, (2000). Hidden flows enter the domestic environment from foreign imports and domestically extracted materials (Figure 1). They include domestic material such as mining overburden, eroded soil and ancillary substances extracted coincidently with the desired resource (coal, sand and gravel, clay etc) and accumulating residues that can become waste. Once hidden flows enter the domestic environment they remain largely unaltered and are represented by a simultaneous input and output (Figure 1). Here, we utilise an adapted model (Matthews *et al.*, 2000) to explore innovative scenarios and secure detailed DPO and TDO outputs including those for specific waste streams. Data were selected from Environment Agency (2006a; Table 3). Sewage sludge was estimated as contributing <1% w/w of the UK waste production and, for the illustrative purposes of simplifying the modelling calculations, assumed to be zero. To expand the utility of the model, it was necessary also to represent wastes disposal routes (Environment Agency, 2006b; Table 4). Input data were used to evaluate a proof of concept and examine a number of hypothetical scenarios. The consistency of model outputs were verified by reference to an independent parallel analysis (Enviros Consulting Ltd., 2006) and found to be consistent.

Input or output flow	Flow name	Symbol	Flow description
I	**Imports**	**Qi**	**Imported materials from abroad**
I	**Domestic extraction**	**Qdex**	**Domestically extracted materials**
I and O	**Foreign hidden flows (FHF)**	**Qfhf**	**Foreign hidden flows entering the domestic environment with the imports, e.g. loose soil and foliage attached to timber**
I and O	**Domestic hidden flows (DHF)**	**Qdhf**	**Domestic hidden flows, e.g. mining overburden or the dust like material from aggregate crushing that has no utility**
I and O	**Hidden flows**	**Qhf**	**Total of both foreign and domestic hidden flows**
I	**Net additions to stock**	**Qnas**	**Additions to stock that occur within the economy and domestic environment**
O	**Domestic processed output (DPO)**	**Qdpo**	**Materials used in the economy and then flow to the domestic environment. Include wastes and emissions. Materials recycled would be deducted from this output**
O	**Exports**	**Qe**	**Materials exported from the economy**
I	**Direct material input (DMI)**	**DMI**	**Total material input into the economy from both domestic and foreign sources**
I	**Total material input**	**TMI**	**The total input of materials from all sources including imports (= DMI + Qi)**
-	**Initial stock**	**Initial S**	**The initial level of stock in the economy and domestic environment**
-	**Total stock**	**Total S**	**The total level of stock in the economy and environment after any net additions (Total S = Qnas)**
O	**Total domestic output**	**TDO**	**The total output to the domestic environment including waste, emissions and hidden flows (= Qdpo + Qhf)**
O	**Total material output**	**TMO**	**The total output of materials from all sources including exports (= TDO + Qe)**

Table 1: Key model variables (adapted from Matthews *et al*, 2000)

3. RESULTS AND DISCUSSION

3.1 Scenario analysis

The utility of the model was illustrated using three scenarios: (i) a UK reference base case; (ii) a UK depleted of domestic resources; (iii) a dramatically reduced UK reliance on landfill. We also discuss a sensitivity analysis, commenting on critical model features. The base scenario input variables are presented in Table 5 and model outputs in Table 6.

The resulting mass output derived from the base calculation is presented in Table 6, acting as a reference for the subsequent scenarios. When a scenario did not require variables to be changed they remained as presented in the base case.

The UK is increasingly reliant on imported resources. We sought to understand the impact of future changes on materials and waste flows over successive time intervals, T1, T2 and T3. Table 7 identifies variables modified from the base case (Table 5).

Model results (Table 8) illustrate the principal change is associated with the FHF as a result of growing imports. Imports increased by 461Mt over the time period with a consequent impact on FHF of +940Mt. FHF make up 62.3% of the original DMI and could surpass this figure if the trends continued. Domestic extraction fell by 467Mt, equating to a drop of 281Mt for the DHF, reflecting current UK trends (Sheerin, 2002). As a result of these combined effects, TDO increased by 659Mt with a total over time of 8346Mt, > 39% greater than that produced for the base case.

A growth in imports increases foreign hidden flows (FHF) that must be treated and disposed of within the UK (Table 8). The UK environment, already strained due to the extraction of the remaining resources, has added pressure from the escalating

Symbol	Value	Description
Qi	33%w/w	The amount of the DMI imported for abroad
Qfhf	2.0 per tonne	The amount of hidden flows that accompany imported materials. For every imported tonne of material there is 2 tonnes of hidden flow
Qnas	65%w/w	The amount of the DMI that becomes a net addition to stock (adapted Enviros Consulting Ltd, 2006)
Qdpo	27%w/w	The amount of DMI that passes out of economic processing as wastes and emissions (adapted Enviros Consulting Ltd, 2006)

Table 2: Values for the base model variables (adapted from Bringezu and Schütz, 2002; and Enviros Consulting Ltd., 2006)

Waste stream	%w/w contribution
Agriculture	20
Sewage sludge	0 (assumed)
Municipal	8
Commercial	6
Total	434 Mt per annum

Table 3: Waste streams incorporated into the base models (after Environment Agency, 2006a)

Waste / route %w/w	Landfill	Energy recovery	Recycled	Other recovery	Other disposal	Reference
Agriculture	2.0	0.0	0.0	0.0	98.0	Environment Agency, 2006b
Sewage sludge	2.9	21.6	0.0	71.0	4.5	Defra, 2006a
Municipal	75.0	9.0	16.0	0.0	0.0	Environment Agency, 2006b
Commercial	47.9	3.9	30.9	6.7	10.6	Defra, 2006b

Table 4: Waste streams and disposal routes for the base model (Environment Agency, 2006b, Defra 2006a, b and Morris, 2006)

TDO as a result of FHF attributed to imports. Unless trading partners increase their extraction efficiency or ensure their resources are of a higher quality prior to export, then the UK continues to see an increase in FHF and the associated environmental pressures. The impacts of this scenario will not only be felt in the UK because by becoming increasingly dependant on imports, we place increased environmental burdens on our trading partners.

The statutory instruments introduced in response to the requirements of the EU Landfill Directive and, specifically, the diversion targets for biodegradable municipal waste (BMW) introduced under the Landfill Allowance Trading Scheme allow construction of scenario representing a reduced reliance on landfill (Table 9). The economic variables remained as for the base case. According to Europa (2004), BMW accounts for between 60%w/w and 70% w/w of municipal solid waste and, as such, the change in the landfill variable was based on assumption over three successive time intervals and the targets identified above.

Table 10 highlights the changes in model output. With the exaggerated targets in place, the amount of municipal waste going to landfill decreased by 68.2Mt while other disposals increased commensurately. The overall tonnage of waste in other disposal and therefore diverted from landfill was 234Mt, without discussion (here) of other treatment or disposal options.

Strictly hypothetical, the output provides rudimentary insight however into the challenges the UK faces with respect to waste and resource management infrastructure. Simplistically, if energy-from-waste was adopted for 234Mt of diverted waste (Table 10), assuming incineration facilities were large with an average capacity of 0.7Mt/annum, then 334 such facilities would be required, with a significant density of plant likely to be required in central city areas (Longhurst *et al.*, 2005). More usefully however, with the option to incorporate and modify a range of waste and resource management options in response to landfill diversion targets, the revised approach now has improved utility as a strategic planning tool.

Variable	Value	Reference
Qi / I	33%	Bringezu and Schütz (2002)
Qnas / Split_NAS	65.0%	Adapted from Enviros Consulting Ltd. (2006)
Qdpo / Split_DPO	27.0%	
Qdhf / DHF_ton	0.6 tonnes / tonne	Bringezu and Schütz (2002)

Table 5: Variables for the base case (after Enviros Consulting Ltd., 2006; Bringezu and Schütz, 2002)

Variable	Total (Mt) over three time periods
Imports	14923
FHF	2986
Exports	362
TDO	6026
Landfill	1647
Recycled	1819
Other disposal	2333

Table 6: Model output for the base UK scenario

3.2 Sensitivity analysis

A comprehensive sensitivity analysis is presented in Raffield (2006). This analysis processed the base case parameters with the waste streams and disposal pathways excluded as they are not main drivers of the model and fluctuate in response to the DPO. For ease, parameters on the economic side of the model were altered, in turn, applying a 10% increase on the base case parameter value (Table 11) and the knock-on influences on other parameters examined.

The direct material input (DMI) has most influence on the other parameters (Table 11). A 10% increase in DMI (a total material variance of 642 Mt) resulted in increases to domestic extraction (+100Mt) and TDO (+200Mt). Similar increases to imports and domestic extraction (Table 11) have a direct impact on hidden flows (DHF and FHF). The domestic economy parameters (NAS, DPO and exports) are influenced by the DMI, irrespective of the percentage share of DMI they account for. The only other parameter these variables impact upon was the TDO.

The sensitivity analysis supports the trends that emerge from the scenario modelling. Hidden flows (DHF and FHF) are sensitive to changes in key materials flow (Matthews *et al.*, 2000; Sheerin, 2002). TDO rises are important and increase if DMI grows in parallel. DMI is the most influencing parameter, but when accompanied by changes in other parameters the results are often dramatic. Overall, the model parameters are interdependent and while one parameter change will not see a significant shift in results, a change in a combination of sensitive parameters can lead to the most significant variances.

Variable	Time			Reference
	T1	T2	T3	
Imports	55.0%	68.8%	86.0%	adapted from DTI (2003)

Table 7: Variable for the UK running out of domestic resources scenario

Variable	Time Period Totals (Mt) T1	T2	T3	Total (Mt)	Change (Mt)
Imports	**829**	**1030**	**1290**	**3149**	**+ 461**
FHF	**1650**	**2070**	**2590**	**6310**	**+ 940**
TDO	**2464**	**2759**	**3123**	**8346**	**+ 659**

Table 8: Results for UK running out of domestic resources scenario

Variable	Time T1	T2	T3	Reference
Municipal – landfill	**48.7%**	**24.4%**	**6.1%**	**Adapted from Europa (2004) the BMW in the MSW was reduced by 50% w/w and then 75% w/w to exaggerate the reduction required**

Table 9: Variables for a reduced reliance on landfill

Variable	Time Period Totals (Mt) T1	T2	T3	Total (Mt)	Change (Mt)
Municipal – landfill	**78.2**	**38.8**	**10.0**	**127.0**	**- 68.2**

Table 10: Model output for the change in legislation for the UK

3.3 Model limitations and developments

Although the model was constructed as closely as possible to the materials flow process, there were features excluded due to their complexity. Matthews *et al.* (2002) included air and water as part of the material flows that were excluded here. Furthermore NAS should take into account a certain degree of outflow due to end-of-life products and buildings lost from the chain of utility as wastes. Both these factors were considered too complex to model at the proof of concept stage and their representation therefore needs to be accounted for in future developments. Additional improvements could include accounting for dynamic decay in stock, so that an inward and outward flow could be attributed, providing a more representative account. With additional sophistication, waste treatment capacity, emissions and carbon and energy flows (Uihlein *et al.*, 2006; Biffaward, 2002) could all be incorporated.

4. CONCLUSIONS

The ability to link economic trends, hidden flows and waste generation provides additional utility to the work of Matthews *et al.* (2000). We offer a proof of concept for these modest amendments and an initial demonstration of utility by references to three hypothetical scenarios. The amendments have utility across a range of scales. Future advancements could include implementing a decay function to the materials stock and the incorporation of flows for air and water. Specific waste streams could be further evaluated and reuse/disposal routes modelled, allowing the model to explore a range of scenarios for the new waste technologies.

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Parameter	Model Parameters	Base case (Mt)	With 10% change (Mt)	Variance (Mt)
Imports from 33.0 to 36.5%	Imports	497	547	+ 50
	FHF	995	1090	+ 95
	NAS	980	980	0
	DPO	407	407	0
Total Variance (Mt) (positive and negative)				295
	Dom. extraction	1010	1110	+ 100
	DHF	606	666	+ 60
	Exp	120	120	0
	TDO	2000	1867	- 133
Total Variance (Mt) (positive and negative)				596
DHF from – 0.6 to 0.66 tonne/ tonne	Imports	497	497	0
	FHF	995	995	0
	NAS	980	980	0
	DPO	407	407	0
Total Variance (Mt) (positive and negative)				120
	Dom. extraction	1010	960	0
	DHF	606	606	0
	Exp	120	120	0
	TDO	2000	2100	+ 100
Total Variance (mt) (positive and negative)				195
Exports from 8.0 to 8.8%	Imports	497	497	0
	FHF	995	995	0
	NAS	980	980	0
	DPO	407	395	- 12
Total Variance (Mt) (positive and negative)				34
	Dom. extraction	1010	1010	0
	DHF	606	606	0
	Exp	120	120	0
	TDO	2000	1010	- 90
Total Variance (Mt) (positive and negative)				278
DPO from 27.0 to 29.7%	Imports	497	497	0
	FHF	995	995	0
	NAS	980	939	- 41
	DPO	407	447	+ 40
Total Variance (Mt) (positive and negative)				121
	Dom. extraction	1010	1110	+ 100
	DHF	606	666	+ 60
	Exp	120	132	+ 12
	TDO	2000	2200	+ 200
Total Variance (Mt) (positive and negative)				642

Table 11: Summary of sensitivity analysis

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Hydrocarbon Wastes at Petroleum- and Creosote-Contaminated Sites: Rapid Characterization of Component Classes by Thin-Layer Chromatography with Flame Ionization Detection

Simon J. Pollard[†] and Steve E. Hrudey*

Environmental Health Program, Faculty of Medicine, University of Alberta, Edmonton, Alberta, T6G 2G3, Canada

Bryan J. Fuhr, Randy F. Alex, Larry R. Holloway, and Frank Tosto

Oil Sands and Hydrocarbon Recovery Analytical Laboratory, Alberta Research Council, P.O. Box 8330, Station F, Edmonton, Alberta, T6H 5X2, Canada

■ Adaptation of thin-layer chromatography with flame ionization detection for the semiquantitative characterization of residual hydrocarbon contamination at petroleum and wood-preserving hazardous waste sites is described. Soils collected from an abandoned oilfield battery site and a former creosote wood treatment facility in Alberta were solvent extracted and the residues characterized using two mobile-phase systems, one capable of separating polar waste components and the other of separating constituent aromatics according to ring number. The method provides a rapid component class fingerprint of the saturate, aromatic, and polar components of heavy hydrocarbon wastes, is analogous to column chromatography, and is useful for estimating the extent of weathering experienced by aged hydrocarbon wastes in the soil environment. As such, it can be useful for preliminary screening of the potential biotreatability or inherent recalcitrance of hydrocarbon waste mixtures.

Introduction

Site assessments at petroleum and wood-preserving hazardous waste sites invariably face the problems posed by a complex matrix of contaminants having a diverse range of environmental and toxicological properties (*1–3*). Elaborate analytical techniques such as conventional gas chromatography–mass spectrometry (GC–MS) are essential for indicator compound quantitation but are often unable to estimate the full extent of hydrocarbon contamination at these sites because quantitative recovery of nonvolatile components (isopropenoid alkanes, naphthenic acids, asphaltenes) from the column is rarely achieved. Furthermore, GC–MS usually requires extensive sample cleanup and analytical costs may be prohibitive for adequate site evaluation (*4*). As a result, many remedial investigations have relied on the "oil and grease" content of contaminated soils for determining the presence and extent of hydrocarbon contamination (*1, 4, 5*) and for the performance monitoring of contaminated soil treatment technologies, particularly enhanced land treatment (solid-phase bioremediation) (*6–8*).

A measure of the free and residual oil phases at contaminated sites has merit because these phases represent the primary sink for hydrophobic organic contaminants. The oil and grease parameter, however, represents a simple gravimetric determination of "solvent-extractable organics", irrespective of origin or character (*1*). This parameter provides no information on waste composition or on the distribution of problem contaminants such as the higher molecular weight polynuclear aromatic hydrocarbons (PAHs).

Informative and cost-effective techniques are required which can address the complexity of waste mixtures at contaminated sites, improve site evaluation efforts, and aid in the selection and assessment of remedial technologies (*4, 5*). Thin-layer chromatography with flame ionization detection (TLC-FID) offers some advantages for these purposes. TLC-FID involves separation of solvent-extractable organics on silica-coated quartz rods into saturate, aromatic, and polar chemical component classes combined with semiquantitative detection by automated FID (*9*). This procedure has been employed widely in the petroleum industry for the component class characterization of heavy oils, bitumens, and coal-tar liquids (*9–15*). Fuhr et al. (*9, 12, 13*) described application of the technique for the characterization of bitumens from oil sand deposits and for process monitoring during the upgrading of heavy oil residues. Poirier et al. (*15*) used TLC-FID for the class analysis of residues obtained from the coprocessing of bitumen and sub-bituminous coal in order to establish the degree of coal conversion in the liquefaction process.

In this paper, we present an extension of the TLC-FID methodology for the rapid analysis of soil extracts obtained from contaminated petroleum and creosote wood-preserving sites and compare the separation achieved with that obtained by the more time-consuming preparative column fractionation technique.

Experimental Section

Site Descriptions. Soils from two abandoned hydrocarbon-contaminated sites in Alberta were selected for the evaluation of the TLC-FID methodology (Tables I and II). An abandoned oilfield battery site in east-central Alberta was selected as representative of similar plants operating in the 1940s–1950s. At these sites, crude oil was dewatered and desalted, the light fractions were removed for further processing off-site, and the residual heavy crude process wastes were disposed of on-site, typically in unlined pits. Wastes currently identified at this site include spilled crude, flowing heavy oil seepage, and consolidated asphaltic material.

Creosote-contaminated soils were obtained from the process area of a former wood-treatment facility in central Alberta which, over a period of 60 years, used pentachlorophenol (PCP), coal-tar creosote, and chromated copper arsenate (CCA) treatment solutions for the preservation of railway ties, utility poles, and foundation piling. Surficial soils comprising the drip pad of the central process area were highly contaminated with wood treatment solutions, most visibly in front of the creosote pressure treatment retorts.

Soil Sampling and Sample Preparation. Surficial (0–0.25-m depth), grab samples (3.0 kg) representing a range of visible hydrocarbon contamination were collected

[†] Current address: Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, United Kingdom.

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Table I. Sample Identification and Solvent-Extractable Organics

sample	sampling location	% extractable organics	% moisture (freeze-dried)	% soil solids (wet basis)
		Oilfield Battery Site		
A	crude loadout area	0.59 ± 0.15	24.8	74.7 ± 0.3
C	cultivated area	0.81 ± 0.13	17.6	81.1 ± 0.2
E	former process area	0.13 ± 0.01	19.2	80.7 ± 0.0
G	drainage channel	1.70 ± 0.56	31.2	67.1 ± 1.7
Y	residuum pit	0.79 ± 0.02	19.1	79.7 ± 0.1
bckgrd	site boundary	0.012 ± 0.0001	6.8	93.3 ± 0.1
		Creosote Site		
1	central process area	1.68 ± 0.01	7.2	90.8 ± 0.1
4	central process area	6.18 ± 0.15	10.3	83.5 ± 0.2
9	central process area	6.02 ± 0.21	8.2	85.6 ± 0.1
10	central process area	7.23 ± 0.27	7.0	86.1 ± 0.2
13	central process area	1.83 ± 0.08	9.6	88.4 ± 0.1
bckgrd	site boundary	0.017 ± 0.0001	17.1	85.0 ± 0.1

Table II. General Site Characteristics at Former Refinery and Wood-Preserving Facilities

	oilfield battery site	wood-preserving site
	Background Soil Characteristics	
sand (% w/w)	61	14
silt (% w/w)	33	45
clay (% w/w)	7	41
organic C (% w/w)	2.30	1.04
pH	5.4	7.7
elec conduc, dS/m	0.47	0.97
	Site Conditions	
site stratigraphy	fine-grained brown sands to 1.2 m; fractured silty clay till to 4.25 m; unfractured till to >10 m	clay, silt, and minor sands to 10 m; till to 25 m; sands and gravel to 36 m
solvent-extractable organics (% w/w)	disposal pits, 0.07–28.2; drainage channel, 32.6–71.2; north site, 2.3–19.7	product storage area 1–15.0; former process area, to 7.2; south ditch to 44.0
elec conduc (dS/m)	disposal pits; 14–67.7; drainage channel <14; north site; 2.9–25.2	no site data available
Na adsorptn ratio	typically 20–40; extremes 1–130	no site data available
pH	6–9	7–8

using a handheld, continuous-flight power auger. Representative background soils (Table II) were collected from beyond the site boundaries. At each sampling position, the spoil from the auger was collected in sealed polythene bags and transferred to acid-washed 3-L borosilicate glass jars (BDH) on arrival at the laboratory. Soil samples were shaken thoroughly, sieved (20 min, ASTM No. 8) to <2.38 mm and stored at 4 °C prior to analysis (Figure 1). Freeze-dried (24 h) subsamples (0.5–1.0 kg) were further homogenized by mortar and pestle and divided into four equal portions using a riffler. Percent moisture removed was recorded.

Solvent Extraction. For each sample, three of the four portions were Soxhlet extracted using HPLC grade dichloromethane (DCM). A 30–100-mL aliquot of DCM was used to extract 50–150 g of sample for 3 h (Figure 1). DCM extracts were reduced on a rotary evaporator, transferred using DCM to 50-mL centrifuge tubes, and spun at 2000 rpm for 15 min to remove fine particles that passed

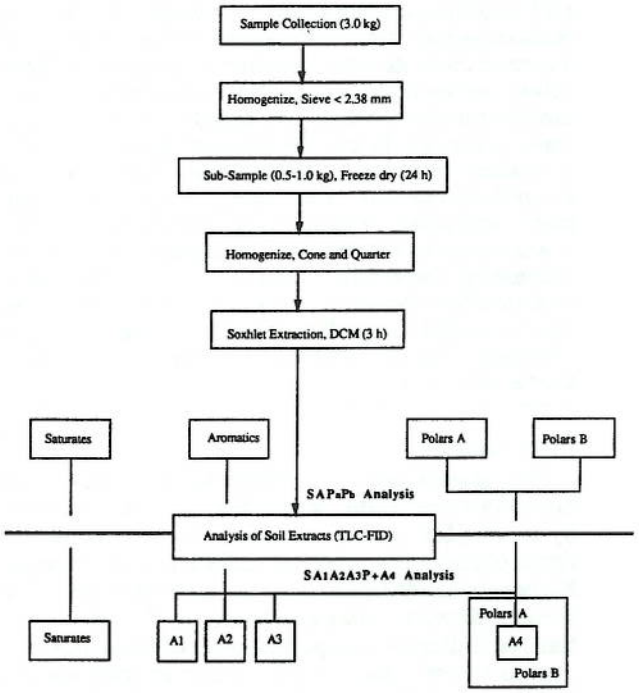


Figure 1. Sample preparation and analytical scheme for the TLC-FID analysis of contaminated soil extracts.

through the thimble during extraction. Supernatants were transferred to 50-mL round-bottom flasks, and the solvent was removed by rotary evaporation. The solvent-free weight of residue recovered (solvent-extractable organics) was recorded before the contents were transferred to a suitable volumetric flask to achieve the desired concentration of extracted oil in DCM (~50 μg/μL).

Separation on TLC Rods. Two chromatographic schemes, which separate polar and aromatic components respectively by group type, were employed, each scheme requiring an individual mobile-phase system (Figures 1 and 2; Table III). Three reference materials were run as standards; Athabasca bitumen (No. 82-02; Alberta Research Council Sample Bank), NIST crude petroleum standard 1582, and neat creosote-based treating solution obtained from a sister wood treatment plant to the one sampled.

(i) SAP_aP_b Analysis. Extracts of known concentration from each of the three subsamples were spotted onto triplicate silica-coated quartz Iatron S-III Chromarods (SPE Limited, Concord, ON) using 1-μL spotting tubes. Separation into saturate (S), aromatic (A), polar "A" (P_a, associated with resins) and polar "B" (P_b, associated with

Table III. Representative Model Compounds Separated by TLC-FID

SAP_aP_b	model compounds	$SA_1A_2A_3P+A_4$	model compounds
saturates	triacontane *n*-hexadecane *n*-dodecane squalene tetratriacontane	saturates	triacontane
aromatics	decylbenzene biphenyl naphthalene	aromatics 1	decylbenzene biphenyl naphthalene
	phenanthrene fluoranthene pyrene	aromatics 2	phenanthrene pyrene benz[*a*]anthracene
	benz[*a*]anthracene benzo[*a*]pyrene dibenzo[*a*,*h*]anthracene benzo[*ghi*]perylene coronene dibenzothiophene	aromatics 3	benzo[*a*]pyrene dibenz[*a*,*h*]anthracene
		aromatics 4 + polars	coronene
polars A	carbazole		
polars B	decanedioic acid 2-hydroxyphenyl acetic acid		

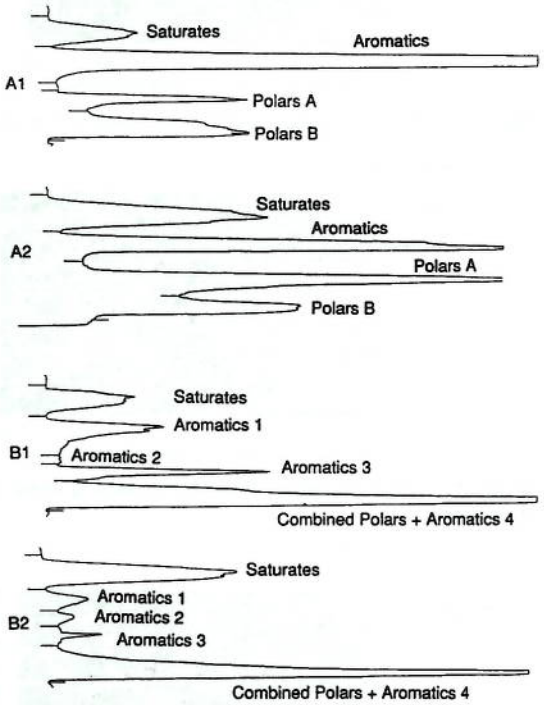


Figure 2. Representative chromatograms from hydrocarbon-contaminated soil extracts: (A) SAP_aP_b analysis of (1) Athabasca bitumen and (2) creosote soil sample 1; (B) $SA_1A_2A_3P+A_4$ analysis of (1) Athabasca bitumen and (2) creosote soil sample 1.

asphaltenes) class components was achieved by timed, stepwise development with 200 mL each of *n*-hexane (34 min), DCM (15 min), and DCM–methanol 98:2 (5 min) solvents in individual paper-lined (Whatman No. 1) TLC developing tanks.

(ii) $SA_1A_2A_3P+A_4$ Analysis. Estimating the content and distribution of aromatics in hydrocarbon wastes is important because this fraction is anticipated to contain the PAH compounds of greatest toxicological concern. Retention time ranges for aromatic components of increasing ring number were determined using reference compounds (Table III): decylbenzene, naphthalene, biphenyl, phenanthrene, pyrene, benz[*a*]anthracene, dibenz[*a*,*h*]anthracene, benzo[*a*]pyrene, and coronene and a representative saturate, *n*-triacontane (C_{30}). Development of S-III chromarods using *n*-hexane (33 min), *n*-hexane–DCM 90:10 (20 min), and DCM (5 min), 200 mL of mobile phase in each case, provided separation of a standard mixture of the above compounds into the saturates (S), one- and two-ring (group 1; A_1) aromatics, three- and four-ring (group 2; A_2) aromatics, five-ring (group 3; A_3) aromatics, and combined polars + greater than five-ring aromatic compounds ($P+A_4$), confirmed on the basis of single-compound retention times.

Flame Ionization Detection and Calculations. Sets of rods were dried of solvent at 20 ± 2 °C and placed in the Iatroscan TH-10 Mk III (Iatron Laboratories, Tokyo, Japan) automated FID for analysis using a H_2–air flame (H_2 flow 160 mL/min; air flow 2 L/min) interfaced with a Spectra Physics SP4290 integrator. Quantitation of SAP_aP_b component classes as a function of area response was performed (*9*) using the following power law equations derived from Athabasca bitumen column chromatographic fractions:

$$\text{saturates } (\mu g) = (\text{peak area})^{0.6084}/108 \quad (1)$$

$$\text{aromatics } (\mu g) = (\text{peak area})^{0.6608}/298 \quad (2)$$

$$\text{polars A } (\mu g) = (\text{peak area})^{0.6332}/184 \quad (3)$$

$$\text{polars B } (\mu g) = (\text{peak area})^{0.7301}/711 \quad (4)$$

Quantitation of aromatic component classes was performed relative to peak areas provided by the mixed standard above. Representative chromatograms are given in Figure 2 indicating the resolution of individual component classes on the chromarods. Percent contributions of individual classes to the total solvent-extractable residue (normalized to 100% recovery) were calculated (*9*, *13*). Development of the chromarods (10 of which can be developed in parallel), FID, and subsequent data analysis takes ~2 h per solvent system. The chromarods are cleaned for subsequent reuse by passage through the H_2–air flame, and experience has shown that they can be reused ~100 times prior to deterioration of the silica coating. Fuhr et al. (*9*) observed relative standard deviations in the range 7–9% for repeated measurements made on an identical bitumen sample over a 6-month period, indicating satisfactory repeatability.

Column Fractionation. The SAP_aP_b separation obtained by the TLC-FID analysis was compared with that achieved using a preparative column technique (*13*) for selected soil extracts designated 10, Y, and C. Similar

column fractionation methods have been employed for the characterization of hydrocarbon wastes prior to bioremediation (*6*) but, in contrast to the TLC-FID procedure, are time consuming to perform and embody reproducibility problems associated with packing and development of the column.

Briefly, a stainless steel chromatography column (137 cm × 0.94 cm) was prepacked in its lower length with 42 g of Davison grade 12 silica (28–200 BS mesh) activated at 250 °C for 20 h. The top half was then packed with 47 g of Alcoa F-20 alumina (80–200 BS mesh) activated at 400 °C for 20 h. A medium-pressure Milton-Roy pump connected to the column was adjusted to a pumping rate of 200 mL/h (40% capacity) and the column prewetted with 100 mL of *n*-pentane. A known amount of soil extract in each case was then injected onto the upflow column using a 2-mL injection loop. Eluting solvents were placed in a pressure-equalizing filling funnel in the following order: 150 mL of *n*-pentane [for elution of saturates (S)], 250 mL of 30% (v/v) toluene–*n*-pentane [for aromatics (A)], and 300 mL of 50% (v/v) methanol–DCM [for combined polars (P)]. Preweighed Pyrex collection beakers were used to isolate component class eluates, beakers being changed one column volume past the point of solvent changeover. Asphaltenes (A) were precipitated from soil extracts using *n*-pentane prior to column fractionation. Solvent was removed from each component class by air-drying under a fume hood (16 h), and gravimetric recoveries were calculated accordingly.

Results and Discussion

Class Composition of Fossil Fuel Products. Fossil fuel components have historically been grouped into four generic classes according to their differential solubilities in *n*-pentane, benzene, pyridine, or carbon disulfide (*11*, *16*): the *saturates* (*n*- and branched-chain alkanes, refractory waxes, and cycloparaffins), the *aromatics* (mono-, di-, and polynuclear), the *resins* (e.g., pyridines, quinolines, carbazoles, thiophenes, sulfoxides, and amides), and the *asphaltenes* (e.g., extended polyaromatics, naphthenic acids, sulfides, polyhydric phenols, fatty acids, and metalloporphyrins). The relative distribution of component classes in a natural or synthetic oil determines its classification as a heavy, intermediate, or paraffinic (waxy) crude (*11*). Distillation, cracking, and reforming operations result in the progressive enrichment or elimination of various component classes to yield lighter or heavier distillate cuts, which have a shifted composition relative to the parent oil (*1*).

Coal-tar creosote (*3*, *17*, *18*) represents a distillation product of gasified coal in which the main chemical classes are the homocyclic polynuclear aromatics (~85% w/w), phenolics of various degrees of substitution (~12% w/w), and heterocyclic polyaromatics (~3% w/w). A widely documented practice in the Canadian wood preservation industry has been to deliver creosote to the untreated timber in combination with a petroleum-based carrier oil, frequently No. 2 or No. 6 fuel oil (Bunker C) (*19*). The extreme chemical complexity of even refined fossil fuel products cannot be overstated, with high-temperature distillation products such as coal-tar creosote, pitch, and still bottom residues estimated to contain more than 10000 individual compounds (*17*, *18*).

The composition of waste-derived oil and grease at hydrocarbon-contaminated sites can therefore vary significantly depending on the *nature* [natural or synthetic crude, coal-tar creosote, and carrier oil(s)], the *composition* (paraffinic, naphthenic, aromatic, or intermediate crude oil), and the *degree of processing* (crude, blended, or refined)

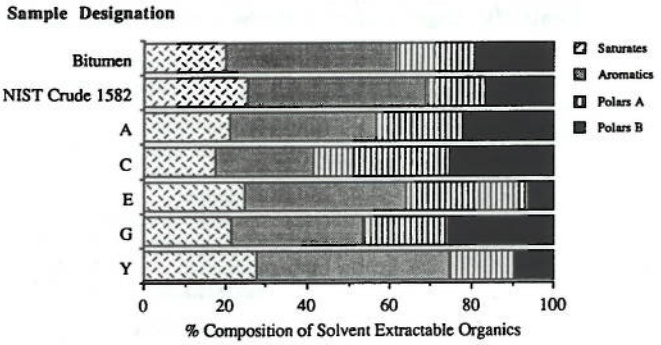


Figure 3. SAP_aP_b analysis by TLC-FID of petroleum waste-soil extracts.

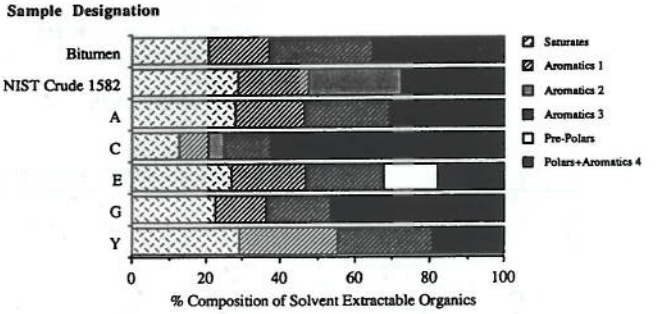


Figure 4. $SA_1A_2A_3P+A_4$ analysis of petroleum waste-soil extracts.

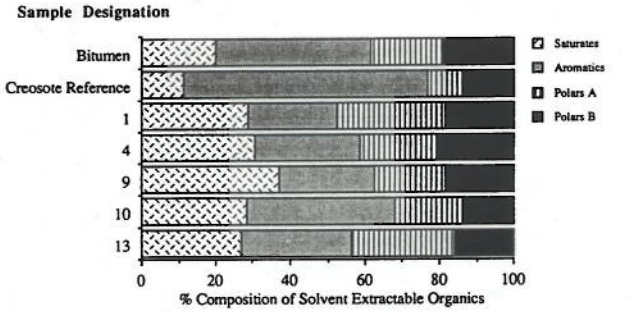


Figure 5. SAP_aP_b analysis by TLC-FID of creosote waste contaminated soil extracts.

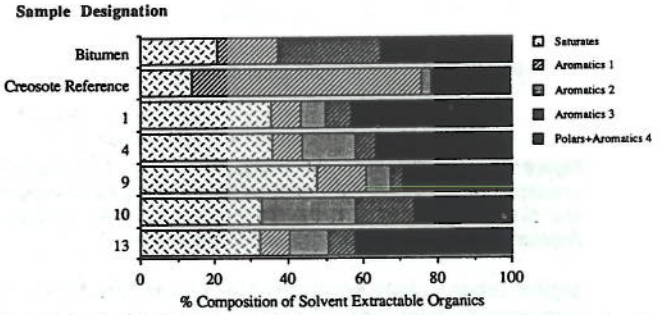


Figure 6. $SA_1A_2A_3P+A_4$ analysis of creosote waste contaminated soil extracts.

of the waste source and the *extent of weathering* experienced by the exposed product.

TLC-FID Analysis of Contaminated Soil Extracts. The normalized class compositions of petroleum and creosote-contaminated soil extracts (Table I) by SAP_aP_b and $SA_1A_2A_3P+A_4$ analysis are shown in Figures 3–6. Background concentrations of solvent-extractable organic material were insignificant (Table I) and did not interfere with the class compositions of contaminated soil extracts. Each bar represents the component class "fingerprint" (derived from the overall mean) of soil extracts at each sampling location. Triplicate subsamples were analyzed

Table IV. Analysis of Variance (ANOVA) and Method Repeatability for Sample 10

component class	subsample results			ANOVA				
	10-1[a]	10-2[a]	10-3[a]	overall mean	between subsample variance	within subsample variance	SD[b]	R[c]
SAP_aP_b								
saturates	26.1, 27.6, 27.4	27.8, 29.5, 29.0	26.2, 29.5, 30.8	28.2 ± 1.6	5.2	1.7	1.7	4.8
aromatics	40.4, 40.6, 41.1	39.3, 38.8, 38.5	42.9, 40.0, 41.8	40.4 ± 1.4	0.9	2.4	1.6	4.4
polars A	18.6, 17.6, 17.1	19.0, 17.6, 19.2	17.3, 17.6, 19.6	18.2 ± 0.9	0.8	0.9	0.9	2.6
polars B	14.9, 14.2, 14.3	13.9, 14.2, 13.3	13.6, 13.0, 12.5	13.8 ± 0.7	0.4	0.6	0.8	2.2
$SA_1A_2A_3P+A_4$[d]								
saturates	32.9, 33.1, 34.3	32.1, 30.0, 33.5	33.1, 33.1, 34.1	32.9 ± 1.3	2.8	1.2	1.3	3.8
aromatics 2	24.3, 24.9, 22.6	24.9, 27.5, 25.4	24.7, 24.7, 25.1	24.9 ± 1.3	1.5	1.6	1.3	3.6
aromatics 3	15.5, 16.9, 17.0	16.5, 15.1, 15.5	16.5, 16.1, 15.3	16.0 ± 0.7	0.0	0.7	0.8	2.3
polars + arom 4	27.4, 25.1, 26.0	26.5, 27.6, 25.6	25.7, 26.1, 25.6	26.2 ± 0.8	0.5	0.7	0.9	2.4

[a] Three chromarods spotted per subsample. [b] SD, standard deviation. [c] R, repeatability. [d] No detectable response for aromatics 1.

individually by triplicate TLC-FID. Each class represents a *combination* of components exhibiting similar polarity and retention on the chromarod.

An analysis of variance (ANOVA) for sample 10 is presented in Table IV (*20*). With the exception of the saturates component, the variance between subsamples is slightly less than that within triplicate chromarod analysis of individual subsamples, indicating separation on the chromarod to be the determining factor in reproducibility. Relative standard deviations (RSDs) of individual component classes between subsamples in both chromatographic schemes are typically 2–6% of the overall mean in agreement with Fuhr et al. (*9*). Repeatability (*21*) was calculated according to

$$R = 2\sqrt{2}\mathrm{SD} \qquad (5)$$

The ANOVA analysis illustrates the semiquantitative nature of the method.

(i) Petroleum Waste Components. Soil extracts isolated from the oilfield battery site (Figures 3 and 4) display component characteristics similar to the bitumen reference (No. 82-02) with a generally larger proportion of polars (A and B) and the aromatic fraction divided equally between group 1 and 3 aromatic components. The "prepolars", identified for sample E (Figure 4) present a shoulder in the sample chromatogram eluting immediately prior to "combined polars". For interpretive purposes, we have considered this fraction to be more closely associated with the $P+A_4$ components rather than the group 3 aromatics.

The distribution of aromatics in sample C (Figure 4) is noticeably the most complex of the oilfield battery site samples. Furthermore, >60% of residual organics isolated from this soil sample are polar in nature. The heavier composition of this sample is believed to result from repeated tilling and crop growing in the cultivated area from which it originated. These factors may have enhanced biotransformation of the residual oil contamination. This hypothesis is supported by a significant reduction (~40% of the class) in the more degradable saturate and group 1 aromatic (~60%) fractions combined with a proportional increase in combined polars (~70%) compared with the other samples from this site.

While numerous reports continue to demonstrate the biotransformation of *n*-alkanes (*22*), aromatic hydrocarbons (*23*), and certain heterocyclic components (*24*) in petroleum, several authors have noted the refractory nature of the asphaltenes (*25–27*). Westlake et al. (*26*) observed changes in the chemical composition of four crude oils toward more recalcitrant class components following microbial utilization by a mixed culture over a 10-day period. Increases in the asphaltene content of weathered oils suggest that, during biotransformation, other hydrocarbon fractions are transformed into polymeric asphaltenes. Such changes apparently occur via free-radical-initiated polymerizations to yield cross-linked, high molecular weight, refractory residues (*27*). Huddleston and Cresswell (*28*) noted for an oil initially containing 22% (w/w) paraffins, 28% (w/w) aromatics, and 50% (w/w) resin–asphaltenes that 82% (w/w) of the paraffin, 60% (w/w) of the aromatic, and only 1% (w/w) of the resin–asphaltene fractions of petroleum refinery wastes were lost over a 22-month period during land treatment. Recent investigations (*29*, *30*) into the persistence of heavy oil constituents in soil microcosms, including N-, S-, and methyl-substituted PAHs, have also indicated that certain heterocyclic components (acridine, carbazole, dibenzothiophene) are sufficiently recalcitrant to be proposed as residual indicators of soil contamination by heavy oil wastes. The enrichment of refractory petroleum residues other than asphaltenes such as the pentacyclic hopanes, the steranes and diasteranes, and the high molecular weight *n*-alkanes has also been reported (*31*, *32*). Elucidation of refractory compounds in contaminated soil extracts will require extended characterization and biotreatability studies of individual class components isolated by preparative column chromatography.

One proposed application of the TLC-FID method, therefore, is the estimation of refractory components in *weathered* waste-soil matrices. Such information related to residual soil contamination would clearly be of use to remediation specialists prescreening hydrocarbon wastes for biotreatability but is not provided by oil and grease measurements. Aged wastes at the oilfield battery site exhibited a class composition heavily weighted toward the more refractory hydrocarbon components, suggesting limited potential biotreatability of in-situ residual contamination. Confirmation of component class biotransformation potential, however, will still require waste-specific treatability studies in soil microcosms.

(ii) Creosote Waste Components. Soil extracts isolated from the wood-preserving site exhibit substantial deviations in class composition from the reference creosote treating solution (Figures 5 and 6). The most striking differences are in the proportion of saturates (~130% higher than reference), polars A (~120% higher), and group 1 (one and two ring, ~85% lower) aromatics. The reduction in group 1 aromatics for the weathered soil extracts is attributed to biotic (biotransformation) and abiotic (leaching, photolysis, volatilization) losses of benzene, toluene, ethylbenzene, and xylene (BTEX), naphthalene, and alkyl-substituted naphthalene constituents from surficial soil.

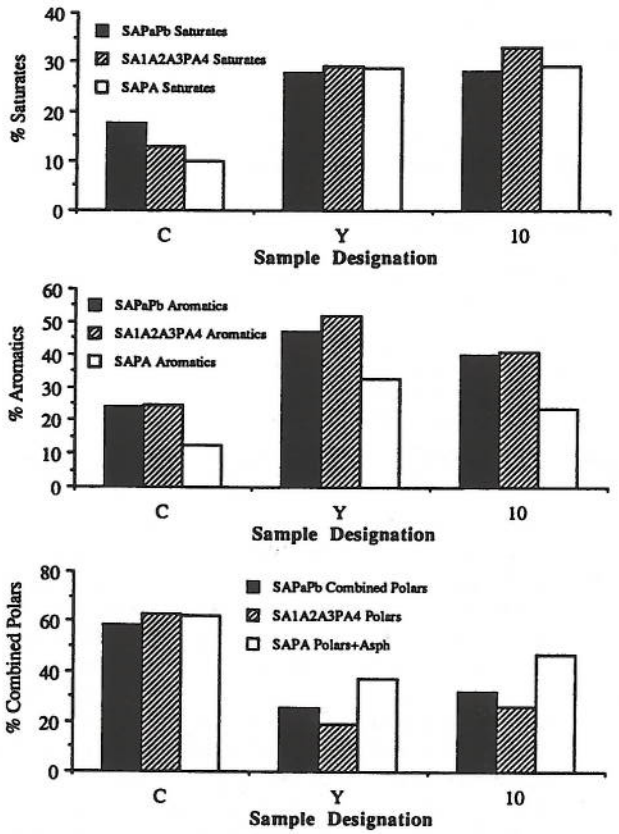


Figure 7. Component class analysis of samples 10, Y, and C by SAP_aP_b and $SA_1A_2A_3P+A_4$ and SAPA column fractionation.

The higher proportion of saturate and polar A classes in creosote site soils may be attributed to the documented use of No. 2 fuel oil and Bunker C as carrier oils for coal-tar creosote during wood treatment at this abandoned site. The residual contamination at this site differs from that at the oilfield battery site most notably in the contribution from group 2 (three and four ring) aromatics (phenanthrene, fluoranthene, pyrene) which are often the most dominant PAHs in weathered/degraded creosote wastes (*33*, *34*).

Comparisons with Column Fractionation. Approximate agreement between TLC-FID and the preparative column chromatography (Figure 7) is desirable for the preparation and characterization of useable amounts of representative class components for toxicity testing and fate and transport studies. The most notable discrepancy between the chromarod and column separations is a 35–50% lower fraction of aromatics reported by the column method. GC–MS investigations confirmed this effect to be largely caused by the elution of high molecular weight PAHs in the polar cut during column separation (data not shown) as indicated by the higher proportion of "combined polars" for samples Y and 10 (Figure 7). A more detailed column chromatographic elution sequence will allow separate collection of the higher molecular weight PAH fraction and reduce discrepancies in observed class compositions between methods.

Comparisons of the destructive TLC-FID method with preparative column chromatography have also been made by other workers (*10*, *13*). Selucky (*10*) characterized component classes of anthracene oil obtained by gravity column fractionation on activated fuller's earth using TLC-FID analysis. Using 80:20 benzene–*n*-hexane solvent for development of the chromarods, resins supplied approximately 15% of the material to the hydrocarbon (saturates + aromatics) fraction collected by preparative column chromatography. Fuhr et al. (*13*) have partially overcome discrepancies between the two techniques by using the medium-pressure column method (SAPA) reported in the present study.

Limitations of the TLC-FID Method. The speed, convenience, and reliability of the TLC-FID technique are considerable advantages over the use of conventional gravity column separation for the class analysis of heavy hydrocarbon samples. However, the class compositions obtained must be regarded as semiquantitative because individual class components respond slightly differently in the FID. Calibration with bitumen fractions appears to be appropriate for heavy hydrocarbon extracts containing different distributions of components, although the method should not be used for hydrocarbon wastes with highly volatile hydrocarbons as their principal constituents because they may be lost from the chromarod before FID quantitation. The equating of polars A with resins and polars B with asphaltenes is recognized to be approximate and most applicable to refinery residues (*9*, *12*). Furthermore, the sulfur heterocyclic components are not sufficiently polar to fall within the polar A class and commonly report with the aromatics as noted by Fuhr et al. for dibenzothiophene (*12*).

Caution should be also exercised when separations achieved by the TLC-FID are compared with column methods because they employ different stationary and mobile phases. Furthermore, the conventional description of component classes in fossil fuel products is based on solubility alone without reference to the adsorption mechanisms which also contribute during chromatographic separation.

Extension of the methodology to a wider range of soil textures and hydrocarbon waste type is currently underway in our laboratory, as is the identification of specific class components likely to present the greatest challenge to bioremediation strategies. This information will complete our initial evaluation of the methodology and place the TLC-FID technique within a tiered analytical protocol for the characterization of hydrocarbon wastes in the soil environment.

Conclusions

Thin-layer chromatography with flame ionization detection provides a rapid, semiquantitative characterization of heavy hydrocarbon residue extracts according to component type. Selection of the mobile-phase system allows separation of the polar or aromatic components, the latter providing a relative distribution of aromatic components according to ring size. The method is particularly useful for revealing the extent of weathering experienced by petroleum and creosote-derived wastes in soil. As such, the method offers potential for screening the biotreatability or inherent recalcitrance of hydrocarbon waste mixtures and for monitoring the progress of biotreatment technologies for petroleum- and creosote-contaminated soils.

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Simon J.T. Pollard[1,2] Sandra L. Kenefick[1], Steve E. Hrudey[1], Bryan J. Fuhr[3], Larry R. Holloway[3] and Marv Rawluk[4]

A TIERED ANALYTICAL PROTOCOL FOR THE CHARACTERIZATION OF HEAVY OIL RESIDUES AT PETROLEUM-CONTAMINATED HAZARDOUS WASTE SITES

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ABSTRACT: The analysis of hydrocarbon-contaminated soils from abandoned refinery sites in Alberta, Canada is used to illustrate a tiered analytical approach to the characterization of complex hydrocarbon wastes. Soil extracts isolated from heavy oil- and creosote-contaminated sites were characterized by thin layer chromatography with flame ionization detection (TLC-FID), ultraviolet fluorescence, simulated distillation (GC-SIMDIS) and chemical ionization GC-MS analysis. The combined screening and detailed analytical methods provided information essential to remedial technology selection including the extent of contamination, the class composition of soil extracts, the distillation profile of component classes and the distribution of individual class components within various waste fractions. Residual contamination was characteristic of heavy, degraded oils, consistent with documented site operations and length of hydrocarbon exposure at the soil surface.

KEYWORDS: petroleum-contaminated soils, heavy oils, weathered oils, tiered analysis, screening methods, site investigations, risk management

The recent discovery of contaminated land in many industrialized countries is a major environmental concern with substantial social and financial implications. At several sites in Alberta, Canada, the uncontrolled disposal of complex hydrocarbon wastes to the soil environment has resulted in the accumulation of oil constituents beyond the assimilative capacity of receiving soils (Hrudey and Pollard 1993). The evaluation of potential risks to human health and the environment that result from these releases, and the allocation of resources for site remediation decisions, relies increasingly on the application of

[1] Postdoctoral Research Fellow, Research Associate and Professor, respectively, Environmental Health Program, Faculty of Medicine, University of Alberta, Edmonton, Alberta, CANADA, T6G 2G3

[2] currently: Lecturer, Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, EH9 3JJ, UK

[3] Manager and Senior Research Technologist, respectively, Oil Sands and Hydrocarbon Recovery, Alberta Research Council, PO Box 8330, Edmonton, Alberta, CANADA, T6H 5X2

[4] Manager, Mass Spectrometry Facility, Manufacturing Technologies Dept., Alberta Research Council, PO Box 8330, Edmonton, Alberta, CANADA, T6H 5X2

quantitative risk assessment (Paustenbach 1989). Within this process, waste characterization represents the essential first stage towards the ultimate management of risk.

An underlying problem in site assessment is the extensive multiplicity of the waste-soil matrix. Ongoing studies of hydrocarbon-contaminated soils in the province have highlighted the following problems for the chemical characterization of residual contamination at these and similar petroleum-contaminated sites: (a) the existence of a complex matrix of chemical contaminants with a diverse range of physiochemical and toxicological properties; (b) the occurrence of multimedia contamination; (c) the expensive and time-consuming analytical procedures necessary for a detailed account of the extent of contamination; and (d) the inadequacy of many existing procedures for the characterization of highly weathered wastes in the soil environment. Use of the non-specific "oil and grease" parameter in isolation for quantifying the extent of contamination has proven inadequate for meaningful site assessment purposes because it provides no information on the overall waste composition and is incapable of quantifying the oil phase distribution of problem contaminants. Conventional gas chromatography-mass spectrometry (GC-MS), though essential for specific compound quantitation, has limited application for characterizing entire soil extracts containing heavy or weathered oil constituents (Pollard and Hrudey 1992b).

Remediation specialists are now developing tiered analytical approaches to characterization of petroleum products (Miller and Stainken 1990). Other tiered analytical approaches that can be applied to more complex or more weathered wastes have yet to be fully developed. Tiered approaches must present a range of techniques, increasing in analytical sophistication, and their application facilitates the *proper* use of site assessment funds by allowing *appropriate* analytical methods to be matched to *specific site assessment needs* and by assisting the realistic selection of remedial technologies. Only by a continual re-evaluation of analytical requirements and careful control over the analytical program can genuine cost savings be realized in this regard.

In this paper, the analysis of residual contamination at five hydrocarbon-contaminated sites in Alberta is used to illustrate a tiered approach to weathered waste characterization. Rather than undertake an exhaustive analysis of each individual site, we focus on the utility of the tiered approach for site evaluation purposes.

EXPERIMENTAL

Site Unit Processes

Five priority hydrocarbon waste sites in Alberta reflecting range of unit operations were selected for investigation. Site I, an abandoned oilfield battery site, operated in the 1940s-1950s for de-watering and de-salting of crude oil. Site II operated from 1924-1937 as a crude oil refinery with auxiliary cracking and desulphurization units. Site III unit processes (1956-63) included hydro-treating, catalytic reforming, de-salting and Bunker C storage. Site IV operated between 1939 and 1961 as an integrated oil refinery with distillation, cracking, reforming and sweetening processes. At Site V, hydrocarbon-contaminated soils were sampled from the process area of a former wood-treatment facility. Treatment of railway ties, utility poles and foundation piling (1924-87) had been achieved using Bunker C and No. 2 fuel oil as diluents for the delivery of coal-tar creosote and pentachlorophenol, respectively.

Soil samples isolated from the above sites were subjected to the tiered analytical protocol, outlined in Figure 1.

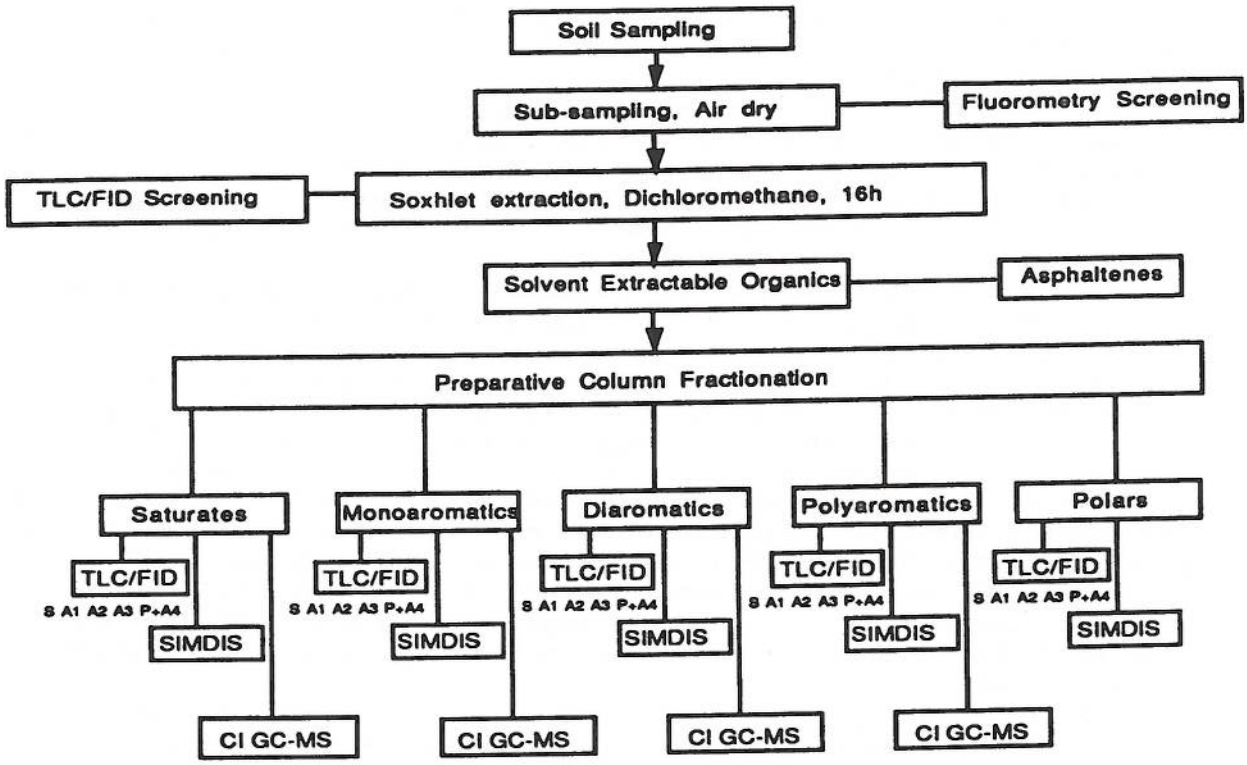


FIG. 1--Schematic of tiered analytical protocol

Soil Sampling and Sample Preparation

Soils containing representative levels of residual hydrocarbon contamination were collected from the five selected petroleum-contaminated sites. Rather than analyzing extreme levels of free oil contamination typical of residuum or burn pits at the above sites, sampling locations with soils ~1-5%^{W}/w in solvent extractable organics were identified from previous site investigation reports. These levels are fairly typical of residual contamination present in significant volumes across many refinery sites in Alberta and represent levels of contamination often considered for treatment by bioremediation. Surficial (0-0.25m depth), grab samples (5.0kg) were collected using a clean, dry shovel or hand-held, continuous flight power auger. At each sampling location, surficial soil or spoil from the auger was collected and sieved (ASTM No. 8, <2.38mm) into acid-washed 3L borosilicate glass jars (BDH) to remove rock fragments. Samples were shaken thoroughly within the jars and stored at 4°C prior to analysis.

Fluorometric Screening of Waste-Soil Extracts

Fluorometric readings on soil extracts were obtained using a portable Turner Designs series 10 Fluorometer equipped with a UV lamp and filters to provide excitation at 350nm and allowing measurement of fluorescent emission in the 410-550nm waveband. Initial investigations demonstrated hexane to be a preferable extractant to dichloromethane (DCM), which appeared to induce fluorescence quenching and interference effects. Standard solutions containing equal concentrations of 16 USEPA priority polynuclear aromatic hydrocarbons (PAH) in hexane were used to calibrate the fluorometer. Two standard reference sediment samples (HS-3 and HS-6; National Research Council Marine Analytical Laboratory), and two well-characterized creosote-contaminated soils (CRD and CRL) were

used to assess the hexane extraction efficiencies of the rapid extraction method.

Using a method adapted from Theis et al. (1991), contaminated soil samples were accurately weighed and transferred to flasks on a wrist action shaker. Known volumes of hexane were added to each and the flasks shaken for 70 min. Soil-solvent mixtures were filtered through a Whatman No. 2 filter paper and diluted $x10^4$ with HPLC grade hexane, then analyzed. Extractions were carried out in triplicate on dry samples and on samples that had been re-wetted with 5 mL distilled water. A standard addition method was also used in an attempt to more accurately quantify the PAH levels in hexane extracts. Five aliquots of known concentrations of a NIST standard PAH mixture were added and the fluorometric reading taken after each addition. Total extractable PAH concentrations in the extracts were then calculated from the linear regression analysis of the standard addition curve.

Solvent Extraction

For the preparation of soil extracts for column fractionation, a sub-sample of each contaminated soil was air dried at 20±2°C overnight in a fume hood. Portions of the dried contaminated soils (~30g) were then Soxhlet extracted using 150mL HPLC grade DCM. The DCM extracts were reduced on a rotary evaporator, the solvent removed by rotary evaporation and the solvent-free weight of residue recovered (solvent extractable organics) recorded.

Preparative Chromatographic Separation

Soil extracts were fractionated into component classes (saturates, mono-, di- and polyaromatics, polars and asphaltenes) using an established preparative chromatographic procedure (Fuhr et al. 1988) (here, termed $SA_mA_dA_pPA$ analysis). Asphaltenes (A) were precipitated from soil extracts using *n*-pentane prior to column fractionation. A stainless steel chromatography column (137cm x 0.94cm) was prepacked in its lower length with 42g Davidson Grade 12 silica (28-200 BS mesh) activated at 250°C for 20h. The top half was then packed with 47g Alcoa F-20 alumina (80-200 BS mesh) activated at 400°C for 20h. After asphaltene precipitation, preparative fractions of component classes were obtained and quantified using the following series of eluents (with nominal component class abbreviations in parentheses): 150mL *n*-pentane for the elution of saturates (S), 250mL 5%^{v}/v toluene-*n*-pentane for monoaromatics (A_m), 300 mL 30%^{v}/v toluene-*n*-pentane for diaromatics (A_d), 300mL 70%^{v}/v toluene-*n*-pentane (for polyaromatics (A_p) and 300mL 50%^{v}/v methanol-DCM for combined polars (P). Pre-weighed borosilicate collection beakers were used to isolate component class eluates. Solvent was removed from each component class by air drying in a fume hood (16h) and gravimetric recoveries calculated. A well characterized Athabasca bitumen reference material (#82-02; Alberta Research Council) was also fractionated for comparative purposes.

Thin-Layer Chromatography with Flame Ionization Detection

Class component distributions of initial DCM soil extracts and of fractions prepared above were determined using the method of Pollard et al. (1992). A single chromatographic scheme, $SA_1A_2A_3P+A_4$ analysis, which separates aromatic components by group type was employed. Extracts and extract fractions were spotted onto triplicate silica S-III chromarods using 1µL spotting tubes. Stepwise development of chromarods in paper-

lined (Whatman No.1) TLC tanks was performed using 200mL each of *n*-hexane (33min), *n*-hexane-DCM 90:10 (20min) and DCM (7min) and provided separation of samples into the saturates (S), 1-2 ring (A_1) aromatics, 3-4 ring (A_2) aromatics, 5 ring (A_3) aromatics and combined polars + >5 ring aromatic compounds ($P+A_4$). Rods were dried of solvent at 20±2°C and analyzed by automated FID using a H_2/air flame (H_2 flow 160mL/min; air flow 2000mL/min) interfaced with a Spectra Physics SP4290 integrator. Quantitation of component classes was performed relative to peak areas using calibration factors obtained from the standard Athabasca bitumen #82-02 (Pollard et al. 1992). Calculated values were normalized to 100% and reported as a percentage of the total fraction.

GC Simulated Distillation

Simulated distillation (SIMDIS) GC analysis of each of the saturate, mono-, di- and polyaromatic and polar fractions was performed by gas chromatography according to procedures and calculation methods adapted from ASTM method D2887-89. The boiling point distribution profiles of the extract fractions were obtained using a calibration curve that was extended to an atmospheric boiling point of 720°C. This was done using a Hewlett-Packard GC equipped with an on-column temperature-controlled injector and an aluminum clad Quadrex column (8m x 0.53mm ID) coated with 5% phenyl silicone of 0.15µm thickness. This column allowed for an oven temperature program from 55-420°C at a linear rate of 10°C/min.

Chemical Ionization GC-MS

Saturate, mono-, di- and polyaromatic fractions of individual soil extracts were analyzed by initial separation on a 25m x 0.25mm ID DB-5 column of 0.32µm film thickness. Gas chromatographic separation (Carlo Erba HRGC 5160; 2µL injection volume; 50-320°C at 10°C/min) was followed by mass spectrometric determination of the eluates using nitrous oxide (N_2O) chemical ionization (CI) on a Finnigan Mat 4500 instrument. CI spectra were obtained using a Townsend discharge ionization source (0.6 Torr N_2O at 120°C). Identification of open chain and alicyclic saturates, alkyl benzenes, benzo-, naphtho- and phenanthro- alicyclics and homocyclic polyaromatics was performed from reconstructed ion chromatograms by analysis of raw molecular ion data and carbon number and ring number of the component structure. Ring type and carbon number distributions were then constructed for S, A_m, A_d, and A_p fractions obtained from each soil extract. Results are only semi-quantitative since they assume that the total ion count for each fraction equals the sum of intensities of all identified components. Furthermore, equal response factors were assumed for all individual components.

RESULTS AND DISCUSSION

Screening Methodologies

Screening methods allow the rapid assessment of soils, groundwater and vapors and then can be used to direct further sampling and analysis, so saving time and resources (Chudyk 1989). The handful of existing methods available for the routine, on-site monitoring of organic pollutants in hydrocarbon-contaminated soils currently rely on the use of headspace analysis, and require the collection and analysis of vadose zone soil vapors (Miller and Stainken 1990). These techniques commonly utilize field gas chromatographs, flame or photoionization detectors and

are restricted at present to the more volatile organics, a serious limitation for weathered hydrocarbon wastes. Screening methods for semi-volatiles are also being developed , but are not yet in routine field use (Pollard and Hrudey 1992a; USEPA 1991). In our tiered approach, the utility of solvent extractable organics, TLC-FID and UV-fluorescence was assessed for contaminant screening purposes. Immunoassay screening tests were also carried out, but because this paper focuses on chemical characterization, these results will be reported elsewhere (Zemanek 1993)

Solvent extractable organics--Quantified solvent extractable organics at each of the sites (sample identification numbers in parentheses) were: Site I (NRP6) 4.10%^{W}/w; Site II (NRSS21) 5.81%^{W}/w; Site III (NR1) 2.39%^{W}/w; Site IV (NR22C) 5.37%^{W}/w; and Site V (NRSS1) 3.34%^{W}/w. These values are consistent with values obtained during initial site investigations and are representative of residual contamination at each site. The measurement of "oil and grease" is widely used as an indicator of total contaminant load and for monitoring the performance of treatment technologies, particularly bioremediation. A substantial limitation is that it provides no compositional information or oil phase distribution of problem contaminants such as the polynuclear aromatic compounds which are being used increasingly as indicator compounds during exposure assessments at petroleum and coal tar-contaminated sites. The continued use of the "oil and grease" parameter in isolation, though inexpensive, is clearly inadequate for meaningful site assessment purposes, hence application of TLC/FID for providing a class composition of the entire extract offers a significant improvement on the quantitation of solvent extractable organics alone.

Screening soil extracts by thin-layer chromatography--Class compositions for DCM-extractable organic fractions of soils at selected sites I-V, obtained using TLC-FID are shown in Table 1. Athabasca bitumen and creosote-based wood treating solution are provided as reference materials for illustrative comparison. Hydrocarbon contamination at the selected sites is dominated by the refractory polar compounds (P+A_4). Class compositions similar to Athabasca bitumen are indicative of crude oils which have been extensively degraded to a refractory heavy oil product (Tisset and Welte 1978). Previous site observations and the documented disposal of heavy oil residues at these sites lend additional support to the proposed high molecular weight composition of these residues: (a) hydrocarbon contamination at Site I sampled alongside the former rail loadout area and from the disposal pits showed a simulated distillation profile indicative of heavy oil or bitumen; (b) oily wastes at Site II, characterized by simulated distillation were ~75%^{W}/w in C_{21} compounds and above; (c) tarry sludge isolated from the oil storage lagoon at Site III exhibited a flash point in excess of 100°C consistent with properties of Bunker C; (d) simulated distillation profiles of wastes at Site IV include those representative of heavy oil residues and mid-distillates (C_{10}-C_{16}) blended with heavier oils; (e) contamination at the former wood-preserving site (Site V) included highly elevated levels of high molecular weight PAH in wastes isolated from the south ditch (benzo[a]pyrene 110 µg/g; benzo[*b*+*k*]fluoranthene 280 µg/g) and process area.

Polar and asphaltenic constituents are well recognized refractory components of heavy and weathered oils. Westlake et al. (1974) observed changes in the chemical composition of four crude oils towards class components resistant to degradation following microbial utilization by a mixed culture over a 10 day period. These increases in the asphaltene content of weathered oils suggest that other hydrocarbon fractions are

TABLE 1--$SA_1A_2A_3P+A_4$ Analysis of DCM extractable organic material (triplicate analyses)

Sample	Saturates	Aromatics (%w/w)			Polars
	(%w/w)	A1	A2	A3	+A4 (%w/w)
Bitumen (82-02)	21 ±1	16 ±4	-	28 ±5*	35 ±2
Creosote Soln.	14 ±2	62 ±6	3 ±1	-	22 ±3
Site I (NRP6)	11 ±1	5 ±1	2 ±1	5 ±4*	78 ±5
Site II (NRSS21)	15 ±4	8 ±3	3 ±3	11 ±3*	63 ±8
Site III (NR1)	23 ±1	19 ±2	30 ±1	-	28 ±3
Site IV (NR22C)	32 ±1	16 ±2	3 ±3	7 ±8*	42 ±12
Site V (NRSS1)	36 ±2	9 ±1	8 ±1	3 ±2*	44 ±2

* some polar material may also report in Aromatics 3 class

transformed into polymeric asphaltenes during biotransformation. Huddleston and Cresswell (1976) noted that for an oil initially 50%^{w}/w in resin-asphaltenes, only 1% ^{w}/w of this fraction was lost over a 22-month period during land treatment. The observed persistence of polar constituents in soil microcosms suggests that some heterocyclic components (e.g., acridine, carbazole and dibenzothiophene) are also sufficiently resistant to biodegradation to be indicators of residual heavy oil contamination (Bulman et al. 1990). Within the saturate class, enrichment of the pentacyclic hopanes, steranes and the *n*-alkane waxes in petroleum residues has also been reported (Atlas 1981).

TLC-FID $SA_1A_2A_3P+A_4$ analysis of extract fractions (Figure 1) was also used to assess the resolution of the preparative column fractionation for sites I-V and for the Athabasca bitumen (Table 2). The TLC-FID results for the bitumen standard showed general agreement with the overall component class separation achieved preparatively. The saturates fraction was relatively "clean", the aromatics fractions contained predominantly aromatic components (although not comparatively resolved) and the "polars fraction" contained approximately 25% aromatic components. This trend is approximated for each of the respective site fractions, although the resolution is largely site specific.

Screening of extracts using ultraviolet fluorometry--Correlations between total extractable PAH measured by fluorometry and those measured by GC-MS for standard sediments (HS-3, HS-6) and characterized creosote-contaminated soils (CRD, CRL) demonstrate the potential utility of the UV-fluorescence technique (Table 3). Total extractable PAH concentrations were obtained using both a standard calibration curve and standard addition linear regression curves. The total extractable PAH concentration in a sample extract using the standard addition method is estimated from the extrapolated value at the x-axis intercept in a plot of fluorometer units versus total standard PAH added. Hexane extraction of dry samples, coupled with the standard calibration method of quantitation, yielded the most favorable results for the standards.

Ultraviolet fluorescence spectroscopy has been proposed as a field screening technique for estimating the total PAH content of hydrocarbon-contaminated soil extracts (Theis et al. 1991). The technique has advantages for weathered hydrocarbon sites, where the low volatilities of residual organics invalidate the use of organic vapor analytical techniques (Pollard and Hrudey 1992b). For typically contaminated

TABLE 2-- TLC-FID $SA_1A_2A_3P+A_4$ for preparative column fractions (triplicate analyses)

Sample		Saturates (S) (%w/w)	Aromatics (%w/w) A1	A2	A3	Polars (P+A4) (%w/w)
Site I	(S)	60 ±2	20 ±1	10 ±2	1 ±2	9 ±0
	(Am)	20 ±1	48 ±3	13 ±1	4 ±3	15 ±2
	(Ad)	5 ±0	33 ±1	0 ±0	3 ±0	19 ±0
	(Ap)	1 ±1	0 ±0	49 ±1	5 ±0	46 ±2
	(P)	1 ±1	1 ±0	13 ±2	18 ±5	67 ±4
Site II	(S)	67 ±2	21 ±1	7 ±1	1 ±1	5 ±1
	(Am)	20 ±1	49 ±2	16 ±3	5 ±3	10 ±2
	(Ad)	1 ±2	0 ±0	80 ±4	5 ±7	0 ±0
	(Ap)	1 ±1	0 ±0	70 ±1	0 ±0	30 ±0
	(P)	0 ±0	1 ±0	9 ±1	30 ±0	60 ±1
Site III	(S)	59 ±2	21 ±1	16 ±1	1 ±1	4 ±1
	(Am)	32 ±3	52 ±5	7 ±0	0 ±0	9 ±2
	(Ad)	2 ±3	2 ±0	75 ±4	1 ±1	20 ±5
	(Ap)	0 ±0	1 ±1	70 ±5	0 ±0	29 ±5
	(P)	4 ±4	0 ±0	22 ±0	36 ±2	39 ±2
Site IV	(S)	88 ±1	8 ±0	0 ±0	0 ±0	4 ±1
	(Am)	19 ±3	64 ±3	10 ±1	1 ±1	5 ±1
	(Ad)	0 ±0	48 ±4	39 ±4	6 ±4	8 ±3
	(Ap)	1 ±2	1 ±0	82 ±1	0 ±0	17 ±1
	(P)	1 ±1	1 ±0	14 ±1	34 ±1	50 ±0
Site V	(S)	97 ±2	1 ±2	0 ±0	0 ±0	2 ±1
	(Am)	96 ±0	0 ±0	2 ±0	0 ±0	2 ±0
	(Ad)	5 ±4	0 ±0	86 ±7	1 ±1	9 ±3
	(Ap)	2 ±0	0 ±0	90 ±1	0 ±0	9 ±1
	(P)	0 ±0	0 ±0	7 ±1	51 ±1	42 ±2
82-02	(S)	95 ±1	0 ±0	1 ±0	1 ±1	3 ±1
	(Am)	3 ±0	79 ±1	8 ±0	0 ±0	11 ±1
	(Ad)	3 ±1	40 ±4	41 ±5	5 ±6	10 ±5
	(Ap)	2 ±2	0 ±0	60 ±1	0 ±0	37 ±1
	(P)	1 ±1	0 ±0	12 ±1	13 ±4	74 ±3

samples at gas plant sites, the error at 100µg/g total PAH was approximately 25% and at 1000µg/g decreased to 3% (Theis et al. 1991). A reliable detection limit of 100µg/g total PAH was reported for contaminated samples. Total target PAH concentrations measured by GC/MS on DCM extracts obtained from sites I-V soils were near this limit or below it. Fluorometric results obtained for 16h DCM extracts and "field" hexane extracts of site I-V soils did not compare favorably at these levels (Table 4). Neither standards data nor site data provided good correlations. Experimental problems relating to site specific interference effects, fluorescence quenching and concentration effects must be quantified before this technique can receive routine use.

Extended Characterization of Waste-Soil Extracts

Preparative chromatographic separation--Quantitative recoveries of individual component classes following column fractionation of DCM extracts isolated from Sites I-V are presented in Table 5. The

significant contribution of asphaltene components precipitated from these samples to the overall extract composition is evident and confirms the refractory nature of residual contamination at these sites. Results show general agreement with the component type analyses performed by TLC/FID on the entire soil extracts (Table 1). Comparisons must be undertaken with caution, however, because the two methods employ different stationary and mobile phases. Furthermore, some sulphur heterocyclic components are not sufficiently polar for the polars class and commonly report with the group 3 aromatics (Fuhr et al. 1986).

TABLE 3-- Fluorometric quantitation of "field" extracts of standard soils and sediments after 10000 fold dilution with hexane (based on dry soil weights and triplicate extractions)

Sample	Total PAH* by Fluorometry	Total PAH‡ by Fluorometry	Total PAH** by GC/MS
HS-6 (wetted)	165 ±184	80 ±55	30 ±7**
HS-3 (wetted)	133 ±79	197 ±89	283 ±59**
CRD (wetted)	3112 ±2110	1220 ±399	4729 ±1262
CRL (wetted)	1939 ±1062	809 ±90	3812 ±1841
HS-6 (dry)	207 ±214	254 ±141	30 ±7**
HS-3 (dry)	455 ±144	304 ±157	283 ±59**
CRD (dry)	4101 ±1197	1639 ±77	4729 ±1262
CRL (dry)	3533 ±1233	1442 ±591	3812 ±1841

*using standard calibration.(in µg/g)
‡using standard addition linear regression (in µg/g)
**reported by supplier (in µg/g)

TABLE 4-- Fluorometric quantitation of DCM and "field" hexane extracts of site specific soils (10000 fold dilution with hexane; single analyses)

Sample	DCM Extract PAH total (µg/g) by Fluorometry*	"Field" Extract PAH total (µg/g) by Fluorometry*	PAH total by GC/MS (µg/g)
Site I(NRP6)	1410	1465	2
Site II(NRSS21)	1150	902	20
Site III(NR1)	1288	1364	22
Site IV(NR22C)	2314	1391	236
Site V(NRSS1)	1708	1719	230

*using standard calibration

TABLE 5--Preparative $SA_mA_dA_pPA$ fractionation of DCM extractable organic material at selected sites I-V (triplicate analyses for Site I and V extracts and duplicate analyses for all other extracts)

Sample	Saturates (%w/w)	Aromatics(%w/w)			Polars (%w/w)	Asphaltenes (w/w)
		Am	Ad	Ap		
Bitumen(82-02)	21	17	14	9	20	19
Site I(NRP6)	18 ±5	5 ±1	4 ±3	6 ±3	30 ±0	38
Site II(NRSS21)	15	5	8	10	21	41
Site III(NR1)	28	5	14	9	27	17
Site IV(NR22C)	33	11	16	6	19	15
Site V(NRSS1)	31 ±5	8 ±3	12 1	6 ±2	14 ±1	30

The main purpose of the fractionation procedure was to prepare cuts for extended characterization and ultimately for toxicity evaluation purposes. Considering the significant saturate contribution to the overall composition of the extract, a primary objective of the extended characterization was the elucidation of class components within this fraction. Such information has particular significance when assessing the potential biotreatability of these waste-soil mixtures.

GC simulated distillation--SIMDIS profiles for extract fractions are given in Figures 2 and 3, with the plot of boiling point versus carbon number for *n*-alkanes C_4-C_{100} included for interpretive purposes. The relative steepness of these curves indicates the boiling point range over which a defined portion of the fraction is distilled, hence giving information on the relative molecular weight distribution between fractions. The position of individual curves relative to the y-axis provides a description of the distillation range of the fraction (light, mid-distillate, heavy residue). The point at which the intercept at the SIMDIS profile (obtained from interpolating horizontally from 25% cumulative weight distilled) crosses the carbon number plot during vertical interpolation to the x-axis provides a relative description of the molecular weight of >75%^{w}/w of the sample, in terms of *n*-saturate carbon number. As an example of this interpretation for the refinery sites, the saturate fraction at Site I was observed to be >75%^{w}/w in C_{25} compounds (402°C) and above and the polar fraction >75%^{w}/w in C_{42} (534°C) compounds and above. Similar results obtained from the remaining SIMDIS plots for the refinery samples enabled them to be ranked in terms of their boiling distribution of the extract: Site I > (heavier than) Site II _ Site III > Site IV>Site V). These are in direct agreement with the polars contributions obtained by $SA_mA_dA_pPA$ analysis on the preparative column, as expected, demonstrating that the polar fraction of these extracts dominate their distillation behavior on the column. Site V, the creosote soil extract, exhibited quite different behavior with narrower boiling point distributions and lower atmospheric equivalent boiling points for extract fractions. This suggests the extract is composed of a lower and more defined distillate, possibly associated with documented use of No. 2 fuel oil at the site. This contrasts quite markedly with the heavy oil residues present at each of the petroleum sites, now confirmed in their molecular weight distribution by GC-SIMDIS analysis.

The atmospheric equivalent boiling point (molecular weight) distribution of waste components in individual classes is important in providing information relating to the relative resistance to degradation of the saturate and aromatic fractions in these wastes. In general, high molecular weight compounds are less easily transformed than their low molecular weight counterparts. However, boiling point and the resistance to microbial degradation of heavy oil constituents is also a function of component structure in addition to molecular weight distribution. Among the saturate class components found in petroleum residues, the isopropenoid alkanes (pristane, phytane) and the polycyclic alkanes (hopanes, steranes) are recognized as refractory compounds (Gough and Rowland 1990; Volkman et al. 1992). Analysis of these fractions in these complex waste matrices can be achieved by chemical ionization GC-MS with progression to a further tier of the analytical protocol.

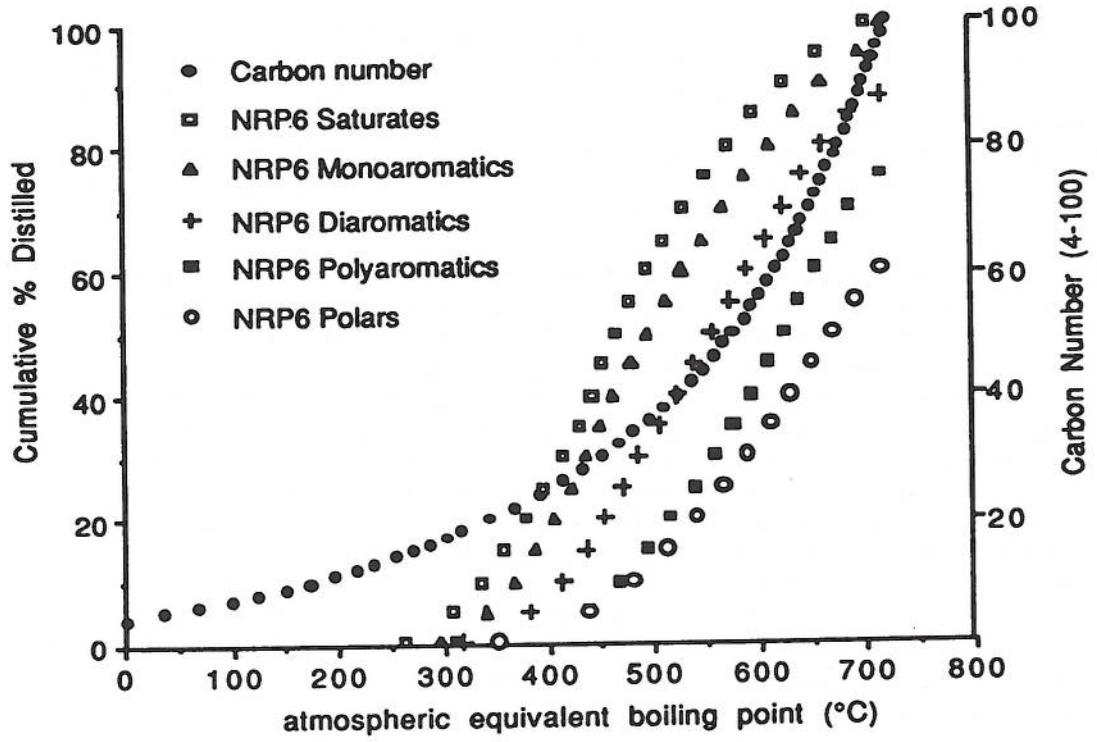


FIG. 2--Simulated distillation profile for sample NRP6 (Site I)

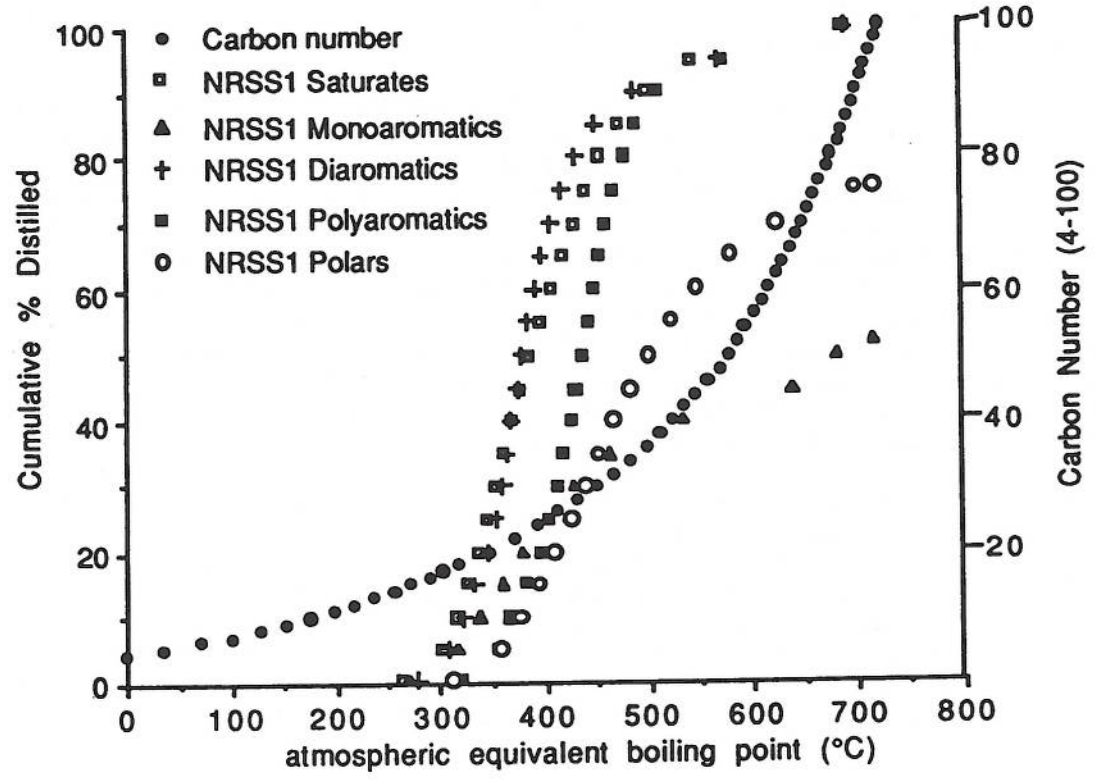


FIG. 3--Simulated distillation profile for sample NRSS1 (Site V)

Chemical ionization GC-MS--For brevity, only the relevant hydrocarbon component distributions for the saturate and polyaromatic fractions of Site V are provided (Figure 4). These condensed diagrams indicate the class component distribution by component type and carbon number. Extract fractions identifiable by CI GC-MS show hydrocarbon distributions typical of mid- to high distillate residues (C_{13}-C_{27}). In general, the saturate fractions are dominated by the 2-4 ring alicyclic saturates which are recognized as being resistant to biodegradation (Overcash and Pal 1979).

A relative assessment of the extent of weathering experienced by these samples can be obtained from the C_{17} open chain/pristane and C_{18} open chain/phytane ratios (Senn and Johnson 1985), pristane and phytane being more resistant to microbial degradation than the equivalent *n*-alkanes. From the raw molecular ion data, these were calculated, respectively as: Site I (0.3, 0.3); Site II (0.5, 0.5); Site III (0.5, 0.7); Site IV (1.2, 1.1); and Site V (6.9, 4.9). Hence, residual contamination can be ranked according to its relative weathered state: Site I > Site II ≈ Site III > Site IV >Site V. This sequence shows direct agreement with the SIMDIS profile data. These ratios may be used, cautiously, to distinguish between contaminant source terms at contaminated sites. Clearly, hydrocarbon contamination at the creosote site is markedly different from that encountered at petroleum sites and is significantly less weathered in composition. Sites I-III are characteristic of significantly weathered oils (Senn and Johnson 1985) and Site IV characteristic of a mid-distillate residue. Significant contributions also come from alkyl benzenes, which may report in the saturate class in cases where extensive alkyl- substitution overcomes ring aromaticity. Likewise, some of the benzocycloparaffins (also resistant to biotransformation) report in this class. The PAH distribution for fractions isolated from Site V indicate compositions dominated by the pyrenes/benzofluorenes, the fluorenes, and the phenanthrenes/anthracenes (+ chrysenes/benzanthracenes), respectively (Figure 4). The apparent absence of polyaromatic components in the A_p fractions from the highly weathered sites (I and II) may lend support to the argument that PAH may undergo co-oxidation over extended periods of time (Gauger et al. 1990). Co-oxidation of higher molecular weight PAHs is recognized as involving a complex chain of oxidative transformations and gradual metabolite assimilations. Petroleum and creosote waste-soil matrices provide suitable environments in which co-oxidation can occur. Weathering, in which microbial degradation plays a dominant role, results in the selective utilization of easily degradable compounds and the concomitant accumulation of heavy PAH and their partially oxidized product (Herbes and Schwall 1978). However, the absence of high molecular weight PAH from A_p fractions at Sites I and II may also be attributed to their tendency to report in the polar fraction.

CONCLUSIONS

Analytical costs demand that site assessments are well-focused and sufficiently streamlined so as to maximize the utility of site data for risk management purposes. A tiered analytical protocol has been demonstrated that employs a variety of screening methods and detailed analytical techniques, and that provides essential information to remediation specialists pre-screening hydrocarbon wastes for their potential biotreatability. Such information is not currently provided by simple "oil and grease" measurements.

Weathered wastes at the sites investigated exhibited class compositions heavily weighted towards refractory hydrocarbon components, suggesting limited potential biotreatability of residual contamination.

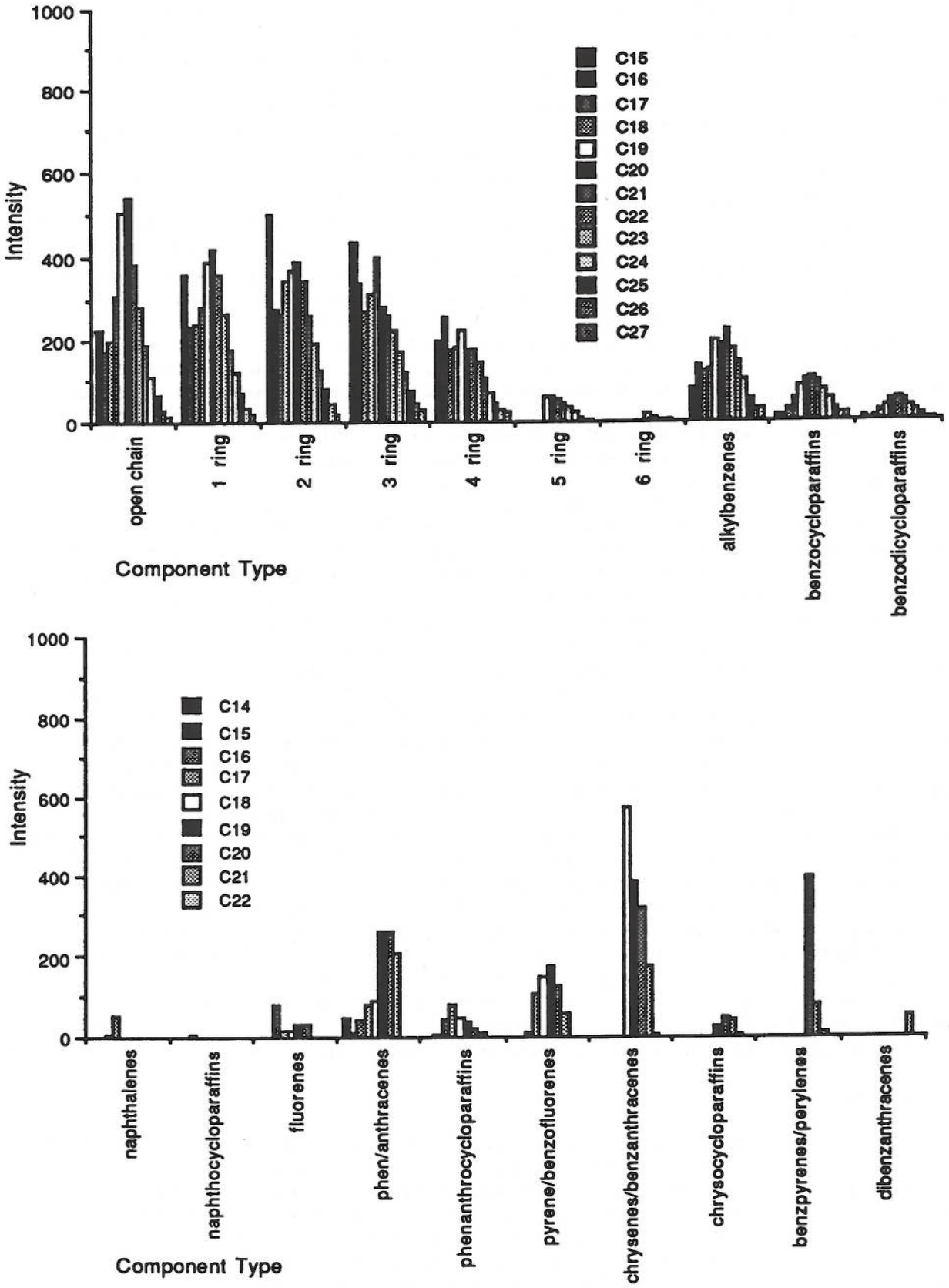


FIG. 4--Hydrocarbon distribution for saturate and polyaromatic fractions of NRSS1 (Site V)

Biotreatability studies can be performed to demonstrate the utility of this method as a predictive tool. Future development of the tiered approach will focus on its integration with a toxicity testing protocol for the combined bioassay-directed analysis of hydrocarbon-contaminated soils.

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PAPER



Characterisation of weathered hydrocarbon wastes at contaminated sites by GC-simulated distillation and nitrous oxide chemical ionisation GC-MS, with implications for bioremediation

Simon J. T. Pollard,*[a] Steve E. Hrudey,[b] Marv Rawluk[c] and Bryan J. Fuhr[c]

[a]*Integrated Waste Management Centre, Cranfield University, Cranfield, Bedfordshire, UK K43 0AL. E-mail: s.pollard@cranfield.ac.uk; Fax: +44 (0)1234 751671; Tel: +44 (0)1234 754101*

[b]*Environmental Health Sciences, Department of Public Health Sciences, 10–102 Clinical Sciences Building, University of Alberta, Edmonton, Alberta, Canada T6G 2G3*

[c]*Fuels and Lubricants Group, Alberta Research Council, 250 Karl Clark Road, Edmonton, Alberta, Canada T6N 1E4*

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An extended analytical characterisation of weathered hydrocarbons isolated from historically contaminated sites in Alberta is presented. The characterisation of soil extracts, chromatographically separated into component classes, by GC-simulated distillation and nitrous oxide (N_2O) chemical ionisation (CI) GC-MS provides new insights into the composition of the residual oil at these sites, the principal partition medium for risk critical components. The combined polar and asphaltene content of representative soil extracts ranged from 40% w/w to 70% w/w of the oils encountered. An abundance of C_{14}–C_{22} 2–4 ring alicyclics, alkylbenzenes and benzocycloparaffins is prevalent within the saturate fractions of site soils. Implications for the partitioning of risk critical compounds at sites with weathered hydrocarbons and the practical application of bioremediation technologies are discussed.

Introduction

The identification of soils that have become contaminated with hydrocarbons through accidental spillage and gradual inventory loss often occurs when industrial facilities are identified for decommissioning, sale or redevelopment.[1,2] The more toxic components of hydrocarbon residues drive the health and environmental risk assessments that inform decisions on site remediation.[1,3,4] Historic hydrocarbon contamination long in the ground will have often weathered through a range of physical, chemical and microbiological processes. The complexity of weathered mid-distillate and heavy oil residues is widely acknowledged[5–8] and is evidenced at sites where they are encountered by (i) the heterogeneity of the oil–soil matrix; (ii) the extensive analytical cleanup procedures required for the quantification of contaminants in these matrices and (iii) the unresolved gas and ion chromatograms that analytical chemists invariably elicit from soil extracts.[7]

Research into heavy oils at contaminated sites has been sparse. Research efforts need to extend beyond simply quantifying the concentrations of risk critical compounds (*e.g.* the polynuclear aromatic hydrocarbons (PAH)) for risk assessment purposes to a broader analysis of the oil matrix. This is because the partitioning behaviour that drives the environmental fate of individual compounds is largely determined by the affinity of the residual weathered oil for priority compounds; a property that changes with the type of oil (the 'source term') and degree of weathering it experiences. In our attempts to better understand the characteristics and environmental behaviour of these weathered hydrocarbon wastes in soils, we have reported on the composition[9] and relative toxicities[10] of a range of chemical classes isolated from soil extracts at petroleum and creosote-contaminated sites, the development of tiered strategies for the analysis of weathered oils[11] and the performance of a suite of biomarker indices as indicators of the source and progressive biotransformation of oily wastes.[12] We have demonstrated (i) that the analysis of the class composition (*e.g.* saturates, aromatics, polars, asphaltenes) of solvent extracts at hydrocarbon-contaminated sites provides valuable insights into the potential biotreatability of oily wastes;[9] (ii) that the residual oil phase is the principal partition medium for PAH in hydrocarbon-contaminated soils[13] and (iii) that biomarker indices comprising hopane pairs (*e.g.* the ratio of 17α(H)21β(H)-norhopane to 17α(H)21β(H)-hopane) within the saturate class can be used (a) to track biotransformation or (b) as source identification indices for weathered oils.[12]

Aim of investigation

Despite these and other insights and the frequent occurrence of weathered oils at contaminated sites, our understanding of how weathered mid-distillate and heavy oils behave in the environment remains incomplete. In part, this is a consequence of standardised analytical procedures used for the analysis of priority substances in soils sampled during site investigation, which tends not to require in-depth characterisation of the oil matrix in which these substances reside. The unresolved complex mixtures (UCM) characteristic of weathered mid-distillate and heavy oils[14–16] mask a complexity of composition rarely elucidated using conventional electron impact (EI) gas chromatography-mass spectrometry (GC-MS).

In this study, we apply preparative chromatography and specialist GC and GC-MS techniques to an extended characterisation of weathered oily wastes (Fig. 1). We present a qualitative analysis, using simulated distillation GC[17] (GC-SIMDIS) and nitrous oxide (N_2O) chemical ionisation GC-MS[18] (CI GC-MS) of the chemical classes that comprise chromatographically separated fractions of soil extracts at five historically contaminated sites in Alberta, Canada. Simulated distillation GC allows the elucidation of the effective carbon

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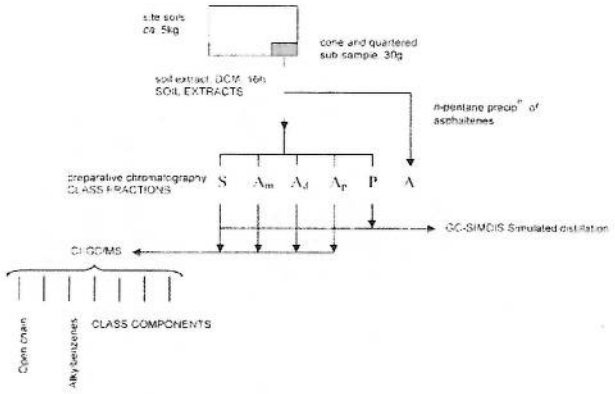


Fig. 1 Analytical strategy and terminology employed in this study.

number (EC_n) distribution of the component classes of contaminated soil extracts by using a non-polar GC column as a surrogate distillation column from which analytes are 'distilled' using a linear temperature profile. Chemical ionisation GC-MS, in which gaseous atoms of the analyte are bombarded in a mass spectrometer with ions produced from the electron bombardment of a reagent gas (here, N_2O), allows construction of parent (molecular) ion chromatograms and, with reference to our previous work,[9,11] the analysis of the 'fine' composition of individual chemical classes separated by preparative chromatography.

The results presented are relevant in the context of the recent interest in establishing soil assessment criteria for the heavier hydrocarbons and, more broadly, in setting realistic remediation objectives for hydrocarbon-contaminated sites.[1,2] Our analysis further informs the source characterisation of these difficult wastes and our understanding of their candidacy for bioremediation.

Materials and experimental procedures

Sample preparation and analysis were performed according to the schedule set out in Fig. 1.

Soil sampling and preparative soil extract fractionation

We have previously described the sampling of residual hydrocarbon contamination from soils at five historically contaminated hydrocarbon waste sites in Alberta.[9] Briefly, surficial (0–0.25 m depth) soils (*ca.* 5 kg) from the process areas of four former petroleum refineries (sites I–IV) and a former coal-tar creosote wood treatment facility (site V) were sampled using a hand held soil auger, sieved to below 2.38 mm (< ASTM No. 8) and stored at 4 °C prior to analysis. Air-dried (20 ± 2 °C, overnight), cone and quartered sub-samples (*ca.* 30 g) of grab sampled soils contained between 2.4% w/w (typically ± 0.2 w/w% RSD) and 5.4% w/w dichloromethane (HPLC grade DCM; 16 h) extractable organic matter as gravimetrically determined by Soxhlet extraction to exhaustion (Fig. 2).

DCM extracts were chromatographically separated (Fig. 2) into six component class fractions (saturates, mono-, di- and polyaromatics, polars and asphaltenes) using an established technique;[1] the fractions being designated S, A_m, A_d, A_p, P and A, respectively (Fig. 2). Asphaltenes (A) were gravimetrically recovered from separate portions of DCM extracts using *n*-pentane[9,12] precipitation. A stainless steel chromatography column (137 cm × 0.94 cm) was then pre-packed in its lower length with 42 g Davidson grade 12 silica (28–200 BS mesh) activated at 250 °C for 20 h. The top half was packed with 47 g Alcoa F-20 alumina (80–200 BS mesh) activated at 400 °C for 20 h. Preparative class fractions were obtained and quantified using the following series of eluents:

(1) For saturates (S): 150 mL *n*-pentane.

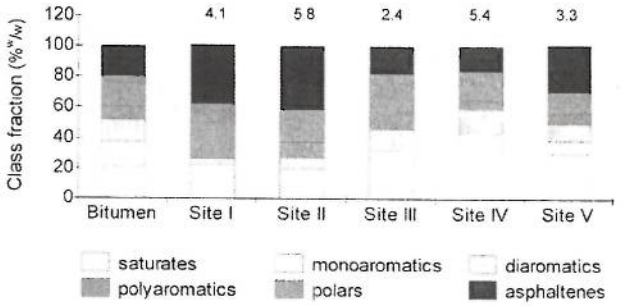


Fig. 2 Normalised composition of soil extracts from sites I–V by class fraction (bar labels showing % w/w DCM-extractable matter in sample, ± 0.2 w/w% RSD).

(2) For monoaromtics (A_m): 250 mL 5% v/v toluene in *n*-pentane.

(3) For diaromatics (A_d): 300 mL 30% v/v toluene in *n*-pentane.

(4) For polyaromatics (A_p): 300 mL 70% v/v toluene in *n*-pentane.

(5) For polars (P): 300 mL 50% v/v methanol in DCM.

Pre-weighed glass beakers were used to collect eluates. The solvent was then removed by air-drying in a fume hood (16 h) and the gravimetric recoveries (typically ± 5% RSD[9]) for each class fraction estimated (Fig. 2). A well characterized Athabasca bitumen reference material (#82-02; Alberta Research Council, Edmonton, Canada) was fractionated for comparative purposes.

Simulated distillation

Simulated distillation (GC-SIMDIS) of the S, A_m, A_d, A_p and P class fractions of each soil extract was undertaken using a modified ASTM method D2887-89.[19] Boiling point distribution profiles for each class fraction, illustrated in Fig. 3 for soil extracts from sites I, III and V, were obtained using a *n*-carbon number calibration curve extended to an atmospheric equivalent boiling point of 720 °C (nC_{100}). GC-SIMDIS was performed on a Hewlett-Packard 5890 GC equipped with an on-column temperature-controlled injector and an aluminium clad Quadrex column (8 m × 0.53 mm ID) coated with 5% phenyl silicone of 0.15 μm thickness. An oven temperature programme of 55–420 °C was employed at a linear rate of 10 °C min^{-1}.

Chemical ionisation GC-MS

S, A_m, A_d and A_p class fractions from individual soil extracts were analyzed by GC separation (Carlo Erba HRGC 5160) on a DB-5 column (25 m × 0.25 mm ID × 0.32 μm film thickness) using a 2 μL injection volume and linear temperature profile between 50–320 °C at 10 °C min^{-1}. Subsequent mass spectrometric determination (*m/z* range 44–500) of the eluates employed nitrous oxide (N_2O) chemical ionisation (CI) on a Finnigan Mat 4500 mass spectrometer calibrated using standard reference oils (Alberta Research Council) used routinely for the analysis of homologous hydrocarbon series in tar sands and heavy oils. CI spectra were obtained using a Townsend discharge ionisation source (0.6 Torr N_2O at 120 °C). For each class fraction the identification of the following class components: open chain and alicyclic saturates, alkyl benzenes, benzo-, naphtho- and phenanthro-alicyclics and the homocyclic polyaromatics was performed from reconstructed ion chromatograms by analysis of the raw molecular ion data and by reference to the nominal masses of these hydrocarbons[20] and their alkyl-substituted analogues (Fig. 1). Relative ring type and carbon number distributions for these

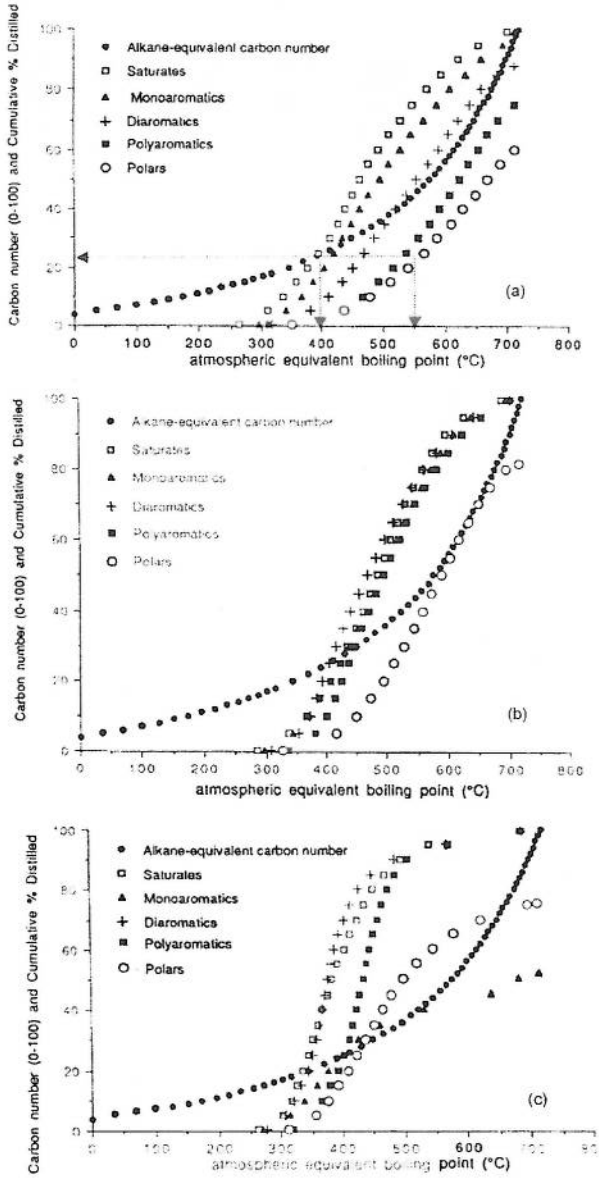


Fig. 3 SIMDIS GC profiles for DCM extracts from sites (a) I; (b) III and (c) V.

class components were constructed for each of the S, A_m, A_d and A_p class fractions, illustrated in Fig. 4 for site III class fractions and Fig. 5 for the saturate fractions of sites I, II and V. Our results are necessarily qualitative since the CI GC-MS of the polar and asphaltene class fractions was not possible and, for the remaining fractions, the interpretations of the relative distributions of chemical components in each class assumes (i) that the total ion count for each fraction equals the sum of intensities of all identified components and (ii) equal response factors for all individual components. The resulting distributions (Fig. 4(a)–(c) and Fig. 5(a)–(c)) provide a relative abundance of homologous classes (*e.g.* the benzocycloalkanes) reporting in each of the S, A_m, A_d and A_p class fractions for selected site soils.

Results and discussion

Distillation profiles

The boiling point distribution of class fractions can be broadly related to their relative resistance to microbial degradation. In

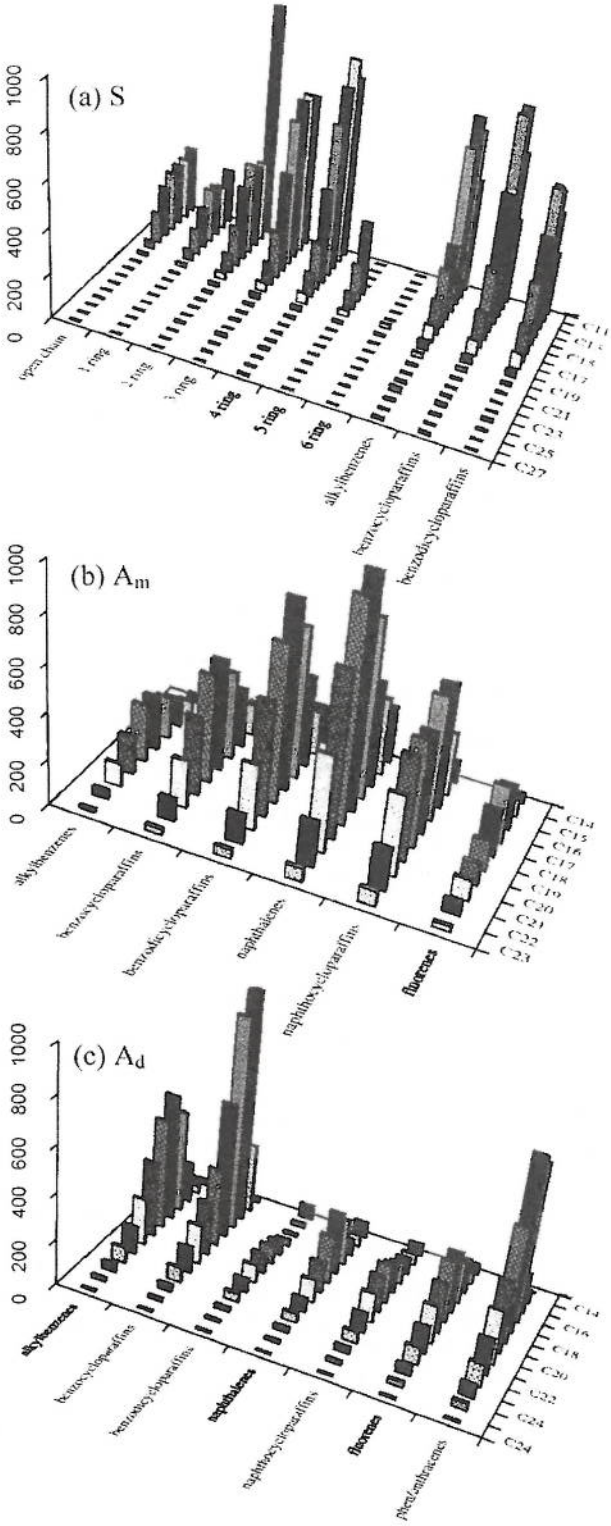


Fig. 4 Relative composition of site III soil extract fractions by class component, carbon number and relative ion count (unitless).

general, high molecular weight compounds are less easily biotransformed. GC-SIMDIS profiles for extract fractions from sites I, III and V are illustrated in Fig. 3(a)–(c) with the reference plot of boiling point *versus* carbon number for *n*-alkanes C_4–C_{100} included for interpretive purposes. Differences in character between class fractions can be inferred by interrogating three aspects of these profiles: (i) the relative gradient of the boiling point curve indicates the boiling point

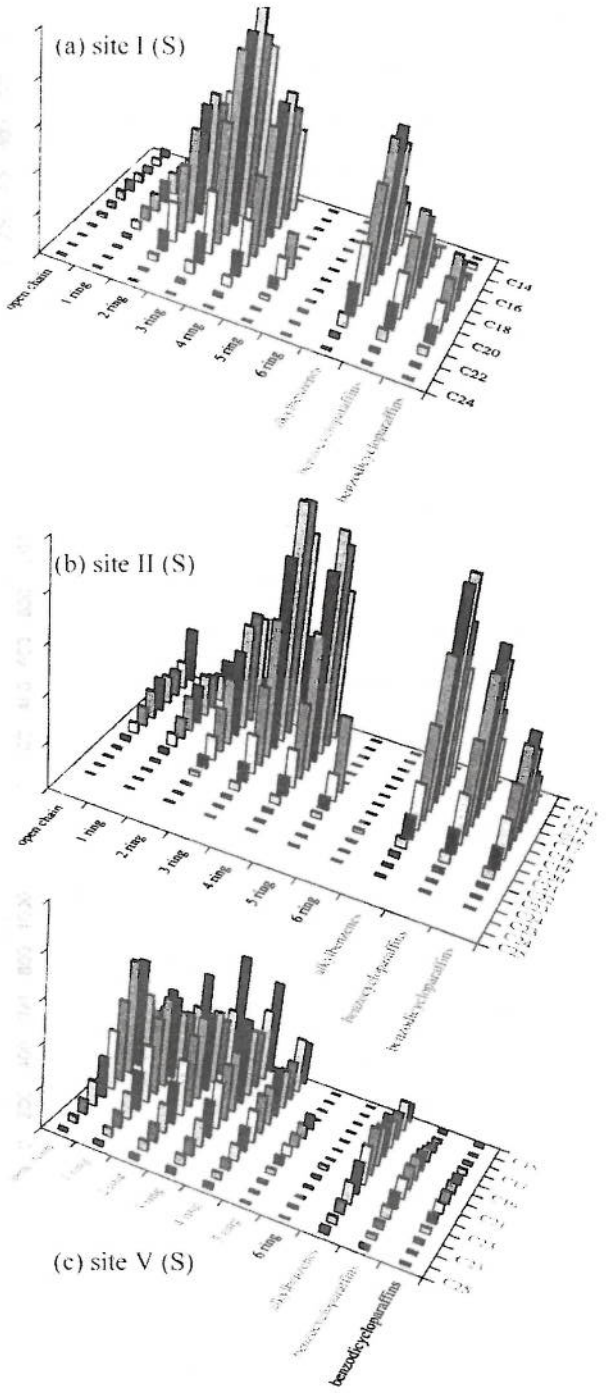


Fig. 5 Relative composition of site extract saturate (S) fractions by class component, carbon number and relative ion count (unitless).

range over which a class fraction is 'distilled' from the column, and by inference, the relative molecular weight distribution of that fraction. Steep curves have tight distributions; lower gradient curves have broader distributions; (ii) the relative position of individual curves away from the *y*-axis allows a qualitative description of the distillation range of the class fraction (*e.g.* light, mid-distillate, heavy) and (iii) the point above the temperature on the *x*-axis obtained from interpolating 25% cumulative weight distilled from the profile of an individual class fraction represents the boiling point of the remaining 75% w/w of the sample, and can be expressed in terms of an equivalent *n*-saturate carbon number. For example, the saturate fraction at site I (Fig. 3(a)) was >75% w/w in C_{25} equivalent compounds (402 °C) and above, and the polar fraction was >75% w/w in C_{42} equivalent compounds (534 °C) and above. Similar results obtained from the polar fraction of the remaining GC-SIMDIS plots for the samples enables them to be ranked in terms of their boiling distribution: site I > (heavier than) site III ≈ site II > site IV > site V. This sequence is in agreement with the decreasing percentage contributions of the polar fraction to site soil extracts obtained by preparative column fractionation (Fig. 2), inferring that the polar fraction of these extracts dominates their distillation behaviour on the GC column.

Site V (Fig. 3(c)), the creosote soil extract, exhibited a distinct distillation profile with narrower boiling point distributions and lower atmospheric equivalent boiling points for all extract fractions except the polars and an anomalous portion of the monoaromatics fraction. This indicates the extract is composed of a lower and narrower distillate, consistent with the documented use of N° 2 fuel oil as a diluent for coal tar creosote at this site. This contrasts with the heavy oil residues observed at each of the petroleum sites (I, III), now confirmed by their apparent molecular weight distribution by GC-SIMDIS analysis.

Class components in individual class fractions at weathered hydrocarbon sites

The boiling point and the general resistance of heavy oils to microbial degradation is a function of their chemical structure and molecular weight distribution.[5,6] Among the saturate class components found in petroleum residues, the isoprenoid alkanes (pristane, phytane) and the polycyclic alkanes (hopanes, steranes) are recognized as refractory compounds.[21–23]

Detailed analysis of the total ion data by examining the nominal molecular masses[20] for homologous aliphatic, alicyclic and aromatic groups provides useful information on the relative composition of each component class by equivalent carbon number. In Fig. 4(a)–(c), the progressive representation of linear, alicyclic, alkyl benzene, benzocycloparaffin, naphthalene and phenanthrene class components is illustrated in successive class fractions of the soil extract. In each case the carbon number range suggests the extent of alkyl substitution of the parent structure. Significant 'carry over' is observed, with identical class components reporting in more than one class fraction. The class composition of individual fractions from different soils can be compared using this approach. The saturate class composition from sites I, II and V, for example (Fig. 5(a)–(c)), is presented as distribution of component type and carbon number. Extract fractions identifiable by CI GC-MS show hydrocarbon distributions typical of mid to high distillate residues (C_{13}–C_{27}). In general, the saturate fractions are dominated by the 2–4 ring alicyclics, recognised as resistant to biotransformation.

A tentative assessment of the extent of weathering experienced by these samples may also be obtained from the C_{17} open chain : pristane and C_{18} open chain : phytane ratios;[24] pristane and phytane being regarded generally as more resistant to microbial degradation than the equivalent *n*-alkanes, though this indicator has recognised limitations.[12,25] From the raw molecular ion data, these ratios were calculated, respectively as: site I (0.3 : 0.3), site II (0.5 : 0.5), site III (0.5 : 0.7), site IV (1.2 : 1.1) and site V (6.9 : 4.9). Hence, residual contamination can be ranked according to its apparent relative weathered state: site I > (more weathered than) site II ≈ site III > site IV > site V. This sequence is in close agreement with the GC-SIMDIS profile and % w/w polar contribution data (Fig. 2), lending additional support to these indicators as potential surrogates for distinguishing between the extent of weathering of the hydrocarbons at these sites. Hydrocarbon contamination at the creosote site (site V) was markedly different in its

characteristics from that encountered at petroleum sites (Fig. 3(c)) and was significantly less weathered in composition. Sites I–III were characteristic of significantly weathered oils and site IV (not shown) was characteristic of a mid-distillate residue. Significant contributions come from alkyl benzenes, which report in the saturate class in cases where extensive alkyl-substitution overrides ring aromaticity as a determinant of polarity. Likewise, some of the benzocycloparaffins (also resistant to biotransformation) report in this class.

Implications for bioremediation

Many hydrocarbon-contaminated sites (former refineries, coal carbonisation plants and integrated steelworks) contain (i) oils that are weathered because the source term has aged significantly since release; (ii) heavy fuel oil residues such as Nos. 4, 5 and 6 fuel oil used in commercial boilers or heavy diesel engines and/or (iii) viscous tars and solid bituminous process residues that are difficult to treat biologically. In contrast to lighter gasoline (petrol), diesel and aviation fuels, the literature on heavy oil wastes is not extensive and the risks to human health are not well characterised. Understanding the physico-chemical and toxicological characteristics of contaminants in these wastes is critical because these factors drive the design of analytical strategies, our understanding of exposure and the selection and operation of remediation technologies.

Our previous studies[13] have shown that compositional changes during weathering affect the partitioning behaviour of risk critical components (*e.g.* the PAHs) prior to, during and following biological soil treatment. The data presented in this study provide additional insight into the composition of weathered hydrocarbon wastes and the residual oil that form the principal partition medium for risk critical components. We have shown that taken together, the recalcitrant polar and asphaltene content of soil extracts from these sites contributes between 40% w/w and 70% w/w of the oils encountered (Fig. 1), with the polars determining the distribution profile of the soil extracts. With respect to the class composition of chromatographically-separated fractions, the abundance of C_{14}–C_{22} 2–4 ring alicyclics (Fig. 5), alkylbenzenes and the benzocycloparaffins is prevalent within the saturate (S) class fractions of site soil extracts. These hydrophobic, recalcitrant compounds, together with the polar and extended hetero-polyaromatic asphaltene structures in these oils[26] comprise the partitioning medium for PAHs in weathered oil wastes into which between 71–96% w/w of PAH in the creosote-contaminated soils is partitioned (84% w/w for benzo[*a*]pyrene).[13] Under these conditions, the availability of PAHs to pose human health risk may be substantially reduced.

Bioremediation is used internationally for sites contaminated with fossil fuel hydrocarbons, organic wood-preserving wastes and high volume industrial organics (*e.g.* polychlorinated biphenyls, tetrachloroethylene). Its application to hydrocarbon wastes, principally as *ex-situ* engineered biopiling, has been assisted in the US by a shift to risk-based, remedial objective-led remediation which has forced a scientific rigour on site investigation, remedial design and technology verification. The move towards risk-based corrective action has been slow in the UK and, whilst some progress has been made in integrating aspects of analysis, exposure assessment and technology verification,[3] there tends to be a lack of synthesis between these aspects of risk management. Indeed, bioremediation performance tends to be evaluated by reductions in hydrocarbon load[27,28] rather than combined reductions in toxicity, chemical mass and risk. Studies that integrate these aspects are essential if risk-based decision-making is to become the basis for the management of contaminated land.

Conclusions

The data in this study increase our understanding of the nature of oily wastes at weathered hydrocarbon sites and the extent to which bioremediation might practically progress for these wastes. Bioremediation technologies express operational limits beyond which, because of the composition and recalcitrance of the partition medium for risk critical compounds and the strength of association between, say, PAH and the weathered source term, prolonged bioremediation is futile in terms of progressive risk reduction. A key factor is to recognise the partitioning behaviour of contaminants like PAHs into recalcitrant heavy oil residues. One research challenge is to now demonstrate the optimisation of bioremediation (*e.g.* biopiling) processes by reference to risk reduction and to identify the practical limits of this technology using knowledge gained on the composition of weathered hydrocarbons.

Acknowledgements

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Toxicity and Mutagenicity of Component Classes of Oils Isolated from Soils at Petroleum- and Creosote-Contaminated Sites

Michael G. Zemanek
Contaminated Sites Decommissioning Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, Edmonton, Alberta, Canada

Simon J. Pollard
Environmental Strategy Directorate, Scottish Environment Protection Agency, Stirling, Scotland, United Kingdom

Sandra L. Kenefick
Department of Chemistry, Okanagan University College, Kelowna, British Columbia, Canada

Steve E. Hrudey
Environmental Health Sciences Program, Department of Public Health Sciences, Faculty of Medicine and Oral Health Sciences, University of Alberta, Edmonton, Alberta, Canada

ABSTRACT

Microtox and Ames bioassays were employed to assess acute toxicity and mutagenicity of water soluble components of class-fractionated oils extracted from one creosote- and four petroleum-contaminated soils. Microtox results revealed that potential acute toxicity resides mainly in the polar class fractions at three sites and indicated potential synergistic and antagonistic effects between compounds in the total extracts at two sites. Ames *Salmonella*/microsome testing indicated that the polyaromatic fractions at two sites exhibit weak mutagenicity with enzymatic activation, while the polar fractions at two sites are weakly mutagenic without enzyme activation. Further chemical characterization of the polar and polyaromatic fractions is required to fully assess the potential of health and ecological risks at the creosote-and petroleum-contaminated sites exhibiting these toxic responses.

IMPLICATIONS

The combined results from two bioassay techniques are used to explore relationships between the chemical composition of major class fractions and their potential acute and mutagenic toxicities in oil extracts isolated from samples of petroleum- and creosote-contaminated soils. Water-soluble fractions of extracts derived from the contaminated sites represent mobile contaminants that present a potential toxic hazard to biota. Evaluation of the relative toxicity of the six chromatographically-defined component classes illustrates the distribution of hazardous components in the complex oil/soil matrix in relation to total extractable oil concentration. An approach for focusing an evaluation of the (human) health (and ecological) risks associated with petroleum- and creosote-contaminated sites is illustrated.

INTRODUCTION

Interpretations of toxicity during site investigation and risk assessment at hazardous waste sites are often impaired by a lack of information on the integrated toxic effects of complex mixtures and the distribution of chemical toxicity among component classes of chemical mixtures. Acknowledgment of these limitations has led to the development and implementation of toxicity reduction, identification and evaluation (TRE/TIE) programs.[1-4] These programs seek demonstrable reductions in toxicity alongside the disappearance of specific contaminants as evidence of effective remediation and risk management. In addition to their established use in aqueous effluent monitoring, TRE/TIE protocols have been developed for contaminated soils and groundwaters by several research groups and are often used in conjunction with detailed environmental analysis. The combined efforts of such approaches are referred to as bioassay-directed chemical analyses[5-7] because the principal toxic response is used to focus detailed analytical effort in characterizing the waste matrix.

Hydrocarbon contamination at waste sites can be described with reference to the accepted component classes of carbon-based fuels: the saturates, aromatics, polars, and asphaltenes.[8] Though somewhat arbitrary, this

Table 1. Five petroleum- and creosote-contaminated sites under investigation for toxicity.

Site Reference	Site 1 (Petroleum)	Site 2 (Creosote)		Site 3 (Petroleum)	Site 4 (Petroleum)	Site 5 (Petroleum)
Operations	Skimming; cracking; Bunker C storage; hydrotreating; reforming; desalting	Treatment of lumber; 100% creosote; 50% creosote with Bunker C and No. 2 fuel oil carriers, PCP, CCA, and ACA		Oil/water separation; desalting; dewatering and crude transfer	Refining; cracking; desulphurisation; oil terminal	Crude distillation; cracking; reforming; sweetening
Years of Operation	1956-1963	1924-1987		1942-1958	1924-1937	1939-1961
		Medium contamination	High contamination			
Oil Content (w/w% of soil)	2.39	3.34	5.69	4.1	5.81	5.37
Natural Water Content (w/w% of soil)	2.57	1.27	14.19	4.75	1.97	4.17
Field Capacity (w/w% of soil)	Not determined	Not determined	40.08	Not determined	Not determined	Not determined

classification provides a suitable framework in which to study the toxicity of individual and combined classes of chemicals because separation can be readily performed using conventional preparative chromatographic methods that rely on differences in chemical class polarity to distinguish between groups or classes of compounds.[9] Furthermore, individual classes appear to exhibit toxic responses associated with the collective members of the class. Therefore, there is merit in examining both individual classes as well as the combined classes as a whole. Using this approach, a toxicity-based approach can be used to evaluate synergistic, antagonistic, and matrix effects in complex waste mixtures, while aiding analysis by identifying and separating the fractions of greatest toxicological concern. For example, chemical class fractions from polynuclear aromatic compound (PAC)-contaminated soils can be evaluated using relevant bioassays to determine the contribution of various waste fractions to the acute toxicity or genotoxicity of the total soil extract. This has been successfully achieved in the determination of toxic components in diesel exhaust emissions, synfuels,[2] and suspended particulate matter,[6] and for quantifying the performance of treatment technologies for the remediation of contaminated soils and aquifers.[10] A combined approach of bioassay testing and GC-MS compound identification has been used successfully to identify the problematic PAC fractions of contaminated river and coastal sediments.[5,6]

The *Photobacterium phosphoreum* (Microtox) bioassay[11] has been widely used for estimating the acute toxicity of the water-soluble fractions from hydrocarbon wastes isolated from refinery and wood-preserving operations.[10,12,13] The bioassay employs a strain of bioluminescent bacteria to measure acute toxic effects in a water extract containing soluble compounds. Toxicity values are typically reported as Effective Concentration$_{50}$ (EC_{50}), the concentration of the contaminant causing a 50% reduction in bacterial light production. Microtox testing of water extracts of saturate, aromatic, and polar fractions of a heavy oil waste sampled from an enhanced oil recovery plant indicated that the aromatic fraction was most acutely toxic. Chemical identification of this fraction demonstrated that it included both alkyl-substituted polynuclear aromatic hydrocarbon (PAH) and sulphur-containing polynuclear aromatic hydrocarbon (PASH) components.[14]

In addition to the Microtox acute toxicity bioassay, the *Salmonella typhimurium* mammalian microsome assay (Ames test) has been widely used for the mutagenicity testing of multicomponent pollutant mixtures from a variety of sources.[15,16] The Ames assay uses a mutant strain of the bacteria *Salmonella typhimurium* that cannot synthesize histidine, and consequently cannot reproduce into colonies. This strain is exposed to a pollutant mixture in a growth medium, and if components within the mixture are mutagenic, they can cause the histidine-synthesis-deficient bacteria to mutate and revert back to their original growth capability so that they can multiply and produce a colony on histidine-deficient agar plates. Two commonly used *Salmonella typhimurium* bacterial strains, TA98 and TA100, detect different mutational events. The TA98 detects frameshift DNA mutagens and TA100 detects base-pair DNA substitution mutagens.

METHODS

Soil Sampling and Sample Preparation

Surficial (0–0.25 m depth) grab samples (3.0 kg) representing a range of visible hydrocarbon contamination[8]

(Table 1) were collected using a hand-held, continuous-flight power auger. Soil from the auger was collected in sealed polyethylene bags and transferred to acid-washed 3L borosilicate glass jars (BDH) on arrival at the laboratory. Soil samples were shaken thoroughly, sieved (20 min, ASTM No. 8) to <2.38 mm, and stored at 4 °C prior to analysis. Air-dried (24 h) sub-samples (0.5–1.0 kg) were further homogenized by mortar and pestle and divided into four equal portions using a riffler.

Solvent Extraction and Gravimetric Oil Determination

Solvent-extractable organic compounds residing in the oil-contaminated soil were separated from the soil using Soxhlet extraction. Approximately 10 to 20 g of soil were Soxhlet-extracted with 150 mL of double distilled dichloromethane (DCM) solvent (16 h). Extracts were dried through a Na_2SO_4 column and concentrated to <50 mL on a rotary evaporator at 30 °C. Extracts were washed into 50 mL volumetric flasks, brought up to volume, then stored in Teflon lined screwcap vials at 4 °C until required. Then 10 mL aliquots of concentrate were placed in shallow, preweighed aluminum dishes and allowed to dry in a fumehood for approximately one hour for complete evaporation of the DCM. Mass percentage of solvent-extractable organic matter was calculated.

Chromatographic Separation and Preparation of Oil Extracts

Soxhlet extracts from the creosote-and four petroleum-contaminated soils were subjected to class component chromatographic separation. Extracts were separated into six components—saturates [S]; mono-[A_m]; di-[A_d] and polyaromatics [A_p]; polars [P]; and asphaltenes [A]—using an established liquid chromatographic method that employed a mixed silica gel and alumina column.[22] Asphaltenes (A) were precipitated from the oil using *n*-pentane prior to column fractionation. Following asphaltene precipitation, fractions of the various component classes were obtained using the following series of eluting solvents: 150 mL *n*-pentane for the saturates (S), 250 mL 5% $^{V}/_{v}$ toluene-*n*-pentane for the monoaromatics (A_m), 300 mL 30% $^{V}/_{v}$ toluene-*n*-pentane for the diaromatics (A_d), 300 mL 70% $^{V}/_{v}$ toluene-*n*-pentane for the polyaromatics (A_p), and 300 mL 50% $^{V}/_{v}$ methanol-DCM for the combined polars (P). A well-characterized Athabasca bitumen reference material (Reference 82-02; Alberta Research Council) was used as an external reference to ensure reproducibility of the fractionation procedure.[8,9] Pre-weighed borosilicate collection beakers were used to isolate the eluates. Solvents were removed from each eluate by air drying in a fume hood for 16 hours. Gravimetric distributions for each of the fractions in the total extract were calculated and are summarized in Table 2. The preparative fractions were placed in glass vials and stored at 4 °C until required for analysis.

Table 2. Mass distribution of class fractions in petroleum- and creosote-contaminated soil extracts (% of total weight).

Class Fraction	Site[1]					
	1	2	3	4	5	82-02[2]
Saturates	27.9	30.5	17.6	15.5	32.6	20.9
Monoaromatics	5.2	8.0	4.7	5.4	11.3	16.6
Diaromatics	13.8	12.4	4.4	7.6	15.6	14.4
Polyaromatics[3]	9.3	5.9	6.1	10.3	6.1	8.9
Polars	27.3	13.5	29.7	20.6	19.2	20.3
Asphaltenes	16.7	29.8	37.5	40.7	15.3	18.9

[1] Site descriptions are provided in Table 1.

[2] Alberta Research Council reference bitumen.

[3] Recovery efficiencies determined for triplicate soxhlet extraction of 15 PAH from two reference sediments (NRC H5-3 and NRC H5-6, National Research Council of Canada) averaged 107% (±47%) and 117% (±44%) for individual PAH compounds.

Each component fraction ($SA_mA_dA_pPA$) and its respective total raw oil extract was resolubilized in 10 mL DCM. A 2 mL aliquot of each fraction was transferred to a 35 mL glass centrifuge tube and dried under a fume hood for 16 h. Following complete removal of the DCM, 25 mL of a 1% $^{V}/_{v}$ solution of dimethylsulfoxide (DMSO; HPLC grade) in distilled/deionized water (DDW) was added to the centrifuge tube. Centrifuge tubes were sealed with Teflon-lined caps and brought to equilibrium in a rotary tumbler over a seven-day period at 20 °C. Incomplete dissolution of all the class fractions was observed, and the 1% $^{V}/_{v}$ DMSO/DDW phase was assumed to contain water-soluble components from the class fractions. The glass tubes were centrifuged at 2,000 rpm for 1 h and the supernatant drawn off and passed through a 0.45 µm filter to ensure no solid particles or oil droplets were present to interfere with the toxicity analysis. Each solution was subjected to Microtox evaluation for acute toxicity within four hours of the filtration step.

For the preparation of a direct water extract of a soil highly contaminated with creosote from Site 2, distilled or deionized water was added to a glass jar containing 500 g of the high-level creosote contaminated soil, to the point of field capacity. The jar was tumbled at 20 °C and brought to equilibrium over seven days. The resulting slurry was centrifuged at 10,000 rpm, leaving an aqueous supernatant that was drawn off and passed through a 0.45 µm filter. The water extract was subjected to Microtox evaluation for acute toxicity within four hours of the filtration step.

A water extract of a fresh, raw creosote oil used for wood preservation was prepared for comparison of its acute toxicity with that of the direct water extract from the creosote-contaminated soil and the 1% $^{V}/_{v}$ DMSO/DDW soluble fraction of the oil extracted from the creosote-contaminated soil (Site 2). A 20 mL aliquot of creosote- oil was combined

with distilled or deionized water in a 35 mL glass centrifuge tube with no headspace. The centrifuge tube was sealed with a Teflon-lined cap and brought to equilibrium in a rotary tumbler over seven days at 20 °C. The glass tube was centrifuged at 20,000 rpm for 1 h and the supernatant drawn off and passed through a 0.45 μm filter to ensure that no oil droplets were present to interfere with the toxicity analysis. The solution was subjected to Microtox evaluation for acute toxicity within four hours of the filtration step.

Microtox Assay for Acute Toxicity

The 1% $^{v}/_{v}$ DMSO/DDW extracts of the $SA_mA_dA_pPA$ class fractions, the water extract from the creosote-contaminated soil at field capacity, and the water extract from the raw creosote oil were analyzed for acute toxicity according to the 100% test procedure.[17] Three serial 2:1 dilutions, using Microtox diluent, were transferred to separate glass testing cuvettes. The dilution procedure resulted in 4 test concentrations of 89.9, 45.0, 22.5, and 11.2% $^{v}/_{v}$ of the original sample, while a fifth control cuvette contained only diluent. For the $SA_mA_dA_pPA$ water extracts, the Microtox diluent was adjusted to 1% $^{v}/_{v}$ DMSO to maintain a consistent organic solvent concentration in all cuvettes. Duplicate 100% tests were run on each sample at the same time. Freeze-dried luminescent bacteria were reconstituted and co-mingled with temperature-equilibrated samples (15 °C) in the cuvettes over a total of 15 minutes. Light readings in the control and sample cuvettes were read and automatically stored by computer at 5-and 15-minute intervals and the EC_{20} and EC_{50} values of bacterial luminescence inhibition was calculated by the Microbics data reduction program. A 15-minute EC_{50} toxicity value lower than the minimum dilution value of 11.2% $^{v}/_{v}$ signified that the inhibition of 50% of the bacteria would be caused by a concentration less than the lowest sample concentration tested. In this instance, the test was repeated at lower dilution values to ensure the estimated 15-minute EC_{50} value fell within the range of dilutions in the cuvettes to avoid unreliable extrapolation beyond the dilution range. A 100 mg/L phenol standard was used to confirm the reproducibility of the Microtox testing protocol,[17] the activity of the luminescent bacteria upon reconstitution, and the continuing bacterial activity throughout the test.

Ames *Salmonella*/Microsome Assay for Mutagenicity

The plate-incorporation *Salmonella* microsome assay using bacteria strains TA100 and TA98 was performed on portions of the $SA_mA_dA_pPA$ class fractions to evaluate their potential mutagenicity. Procedures for the test followed those outlined by Maron and Ames.[18] Two mL of each

Table 3. Qualitative summary of Microtox and Ames *Salmonella*/Microsome assay responses on $SA_mA_dA_pPA$ class fractions.

Site or Sample	$SA_mA_dA_pPA$	Microtox	Ames *Salmonella*/Microsome Assay	
			TA98 (+S9)	TA98 (-S9)
82-02 reference bitumen	Polyaromatics	na	-	-
	Diaromatics	na	-	-
	Monoaromatics	na	-	-
	Saturates	na	-	-
	Polars	na	-	-
	Asphaltenes	na	na	na
	Combined	na	na	na
1	Polyaromatics	-	"+"	-
	Diaromatics	-	-	-
	Monoaromatics	-	-	-
	Saturates	-	-	-
	Polars	-	-	-
	Asphaltenes	-	na	na
	Combined	-	na	na
2	Polyaromatics	-	"+"	-
	Diaromatics	-	-	-
	Monoaromatics	-	-	-
	Saturates	-	-	-
	Polars	-	-	-
	Asphaltenes	+	na	na
	Combined	+	na	na
3	Polyaromatics	-	-	-
	Diaromatics	-	-	-
	Monoaromatics	-	-	-
	Saturates	-	-	-
	Polars	+	-	"+"
	Asphaltenes	-	na	na
	Combined	-	na	na
4	Polyaromatics	-	-	-
	Diaromatics	-	-	-
	Monoaromatics	-	-	-
	Saturates	-	-	-
	Polars	-	-	-
	Asphaltenes	-	na	na
	Combined	-	na	na
5	Polyaromatics	-	-	-
	Diaromatics	-	-	-
	Monoaromatics	-	-	-
	Saturates	-	-	-
	Polars	-	-	"+"
	Asphaltenes	-	na	na
	Combined	+	na	na

na signifies sample was not analyzed in the indicated assay.
+ in the Microtox column indicates a 15 minute $EC_{50} \leq 25\%$ by volume (see Figure 1).
"+" in the Ames assay columns indicates an increase in revertants double those for the reference control in either the pilot study or the subsequent study (see Figures 2 to 5).
- indicates that a test was performed but a toxic response which would satisfy the above criteria for + or "+" was not observed.

$SA_mA_dA_pPA$ class fraction solubilized in DCM (excluding the asphaltenes) was placed in a 10-mL vial and dried in a fume hood for 16 hours. Each dried extract was suspended in 4 mL sterile DMSO and allowed to solubilize at 4 °C for seven days prior to the analysis. All $SA_mA_dA_pPA$ class fractions did not completely dissolve in the DMSO, therefore only the DMSO soluble fraction was assayed. Approximately 1×10^8 stationary-phase, strain TA98, or TA100 *Salmonella typhimurium* bacterial cells were exposed to 0.1 mL of full-strength sample. A negative control of 0.1 mL DMSO and a positive control of 5 mg 2-aminoanthracene per 0.1 mL DMSO were used to evaluate the quality of the analysis and microbial activity. Each sample and both controls were assayed with and without simulated metabolic activation (+/-S9) using rat liver enzymes (MolTox, Annapolis, MD). Revertant colonies were counted in each of the positive and negative control plates as well as the sample plates. Mutagenic ratios were calculated and assessed using the ratio of the number of sample-revertant colonies to the number of revertant colonies in the negative control plate. Single samples of the $SA_mA_dA_pPA$ fractions were assayed in a pilot study and triplicate samples were reanalyzed in a subsequent study after two months.

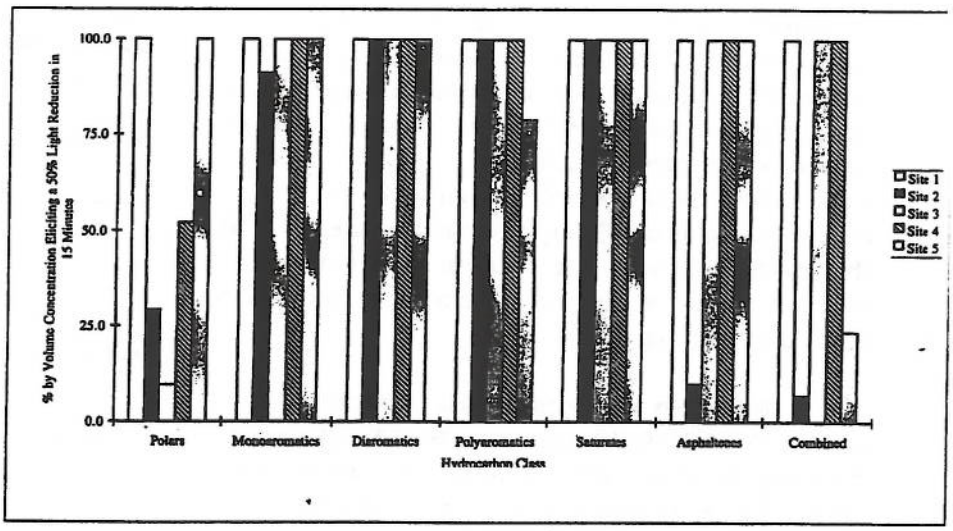


Figure 1. 15-min EC_{50} Microtox assay on petroleum and creosote $SA_mA_dA_pPA$ class fractions.

RESULTS

Microtox Acute Toxicity of $SA_mA_dA_pPA$ Classes

Table 3 shows the results of the EC_{50} Microtox analysis of the 1% $^{V}/_{V}$ DMSO/water soluble component of the total and fractionated creosote and oil extracts as a percent of the full-strength sample. The 15-minute EC_{50} responses in the test are illustrated in Figure 1. A lower EC value indicates greater toxicity. The standard measure of effect recognized by regulatory authorities is the EC_{50}.[19] Dombroski et al.[20] suggest that semi-quantitative scales could be used with 15-minute EC_{50} values to relate the degree of toxicity between samples. A categorization of the concentration ($^{V}/_{V}$) scales suggested by Dombroski et al.[20] for EC_{50} was: <25% = very toxic; 25 to 50% = toxic; 51 to 75% = moderately toxic; 76 to 100% = slightly toxic; and >100% = non-toxic (no toxic response).

Examination of the 15-minute EC_{50} values in Figure 1 reveals a relatively non-toxic response for the saturates and the mono-, di-, and polyaromatic fractions, with levels greater than 100% by volume in most cases. The response of the *Photobacterium phosphoreum* to organic compounds in the water soluble fraction will always be, in part, a function of the concentration of the toxicant in solution, determined by the aqueous solubility of the species. The sparingly soluble nature of the saturate and the mono-, di-, and polyaromatic components is likely a factor in their apparent lack of toxicity on the microorganisms. Failures of the Microtox system to detect toxicity in contaminated samples have been attributed to the hydrophobicity (low water solubility) of the toxic components. Pratt et al.[4] and Kamlet et al.[21] showed that many toxic responses of individual organic compounds in the Microtox test can be correlated and predicted by means of a single generalized linear solvation energy relationship. Because acute toxicity depends

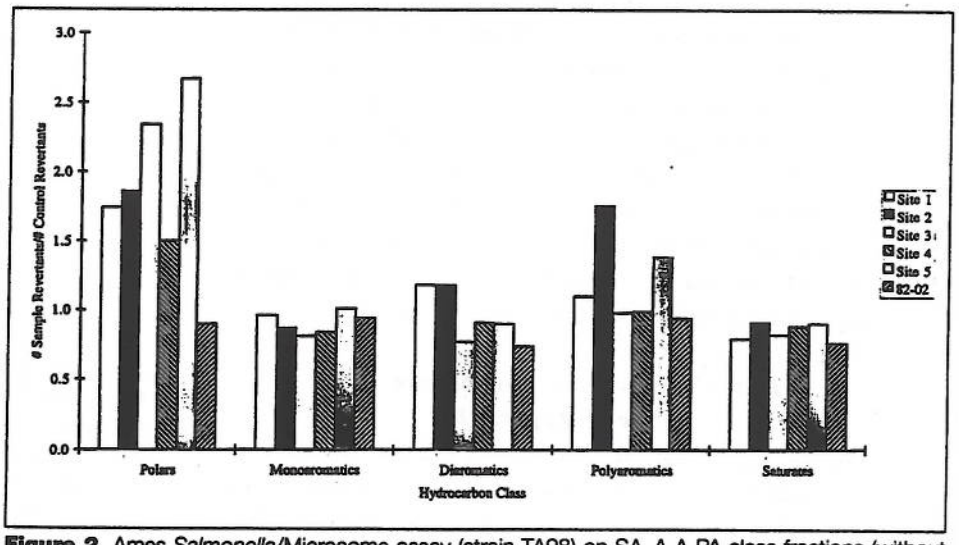


Figure 2. Ames *Salmonella*/Microsome assay (strain TA98) on $SA_mA_dA_pPA$ class fractions (without S9 activation).

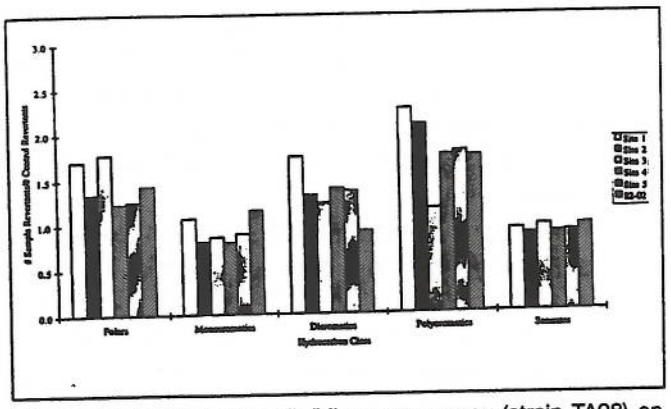


Figure 3. Ames *Salmonella*/Microsome assay (strain TA98) on $SA_mA_dA_pPA$ class fractions (with S9 activation).

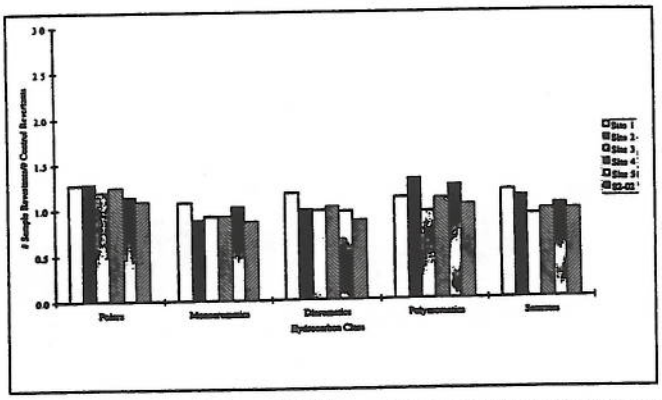


Figure 4. Ames *Salmonella*/Microsome assay (strain TA100) on $SA_mA_dA_pPA$ class fractions (without S9 activation).

upon dose of active agents, more polar—hence, more water-soluble—compounds will have a greater concentration in a bulk aqueous extract, and therefore, may show more contribution to acute toxicity. The polar component from three sites show greater acute toxicity in Figure 1. The polar fraction at sites 2, 3, and 4 shows EC_{50} values of 29.2, 9.6, and 51.9%, respectively, and in the case of the latter two, caused toxic responses greater than the combined extract.

The non-toxic response of the total extract from sites 3 and 4, while their polar components exhibit a substantial effect, could be due to either a chemically interactive antagonistic action on the polars by other compounds in the total complex mixture, or a competitive solubility/adsorption phenomenon between the total oil extract and the DMSO and water mixture that acts to limit solubility of the polar compounds in the aqueous phase. Organic compounds have a significant affinity for the oil phase[22,23] and, as such, the total extract may hamper partitioning or dissolution of the polar fraction into the aqueous phase during the aqueous extraction procedure. This would also imply that dissolution of these potentially toxic agents and subsequent subsurface percolation into the groundwater under field conditions would be impeded by their preferential partitioning into an immobilized bulk oil phase.

Another form of toxicity interaction appears evident in the total extract from Site 5. While the water-soluble fraction of the individual class fractions from this site exhibit relatively nontoxic actions, the total extract produces a tangible toxic response (EC_{50} = 23.4%) (Figure 1). The $SA_mA_dA_pPA$ fractions derived from this extract were recombined in proportionate amounts and extracted in water under the same conditions as the total extract to verify the action of the compound class combinations. The response with the combined $SA_mA_dA_pPA$ fractions from Site 5 (EC_{50} = 18.4%) was comparable to the response of the total unfractionated extract (EC_{50} = 23.4%).

Microtox Evaluation of Creosote Contaminated Soil Extracts

The oil extract from the creosote-contaminated soil (Site 2) had a slightly greater toxicity (EC_{50} = 2.9%) than a direct soil-water extract at field capacity (EC_{50} = 4.8%). However, the values were not substantially different and were comparable to the response from the water extract of the fresh, raw creosote oil (EC_{50} = 2.3%). These findings indicate that comparable acute toxicity values for petroleum- and creosote-contaminated soils can most likely be obtained directly from water extracts of the contaminated soil rather than performing an extra step of transferring the contaminants in an organic solvent extract. Importantly, the Microtox evaluation performed at the field capacity condition defines the soil water toxicity at an important physical transition point related to movement of water soluble chemicals away from the contaminant source.

Acute toxicity of equilibrated soil water at field capacity represents the soil condition of the total maximum mass of dissolved contaminants per unit volume of soil and any additional water content could mobilize these contaminants into the subsurface. Dombroski et al.[20] note that typical soil-water extracts for Microtox analysis have been performed by a number of researchers at a 1:4 mass soil:mass water ratio. While this excess water condition might mimic sediment conditions in aqueous environments such as lakes and streams, the soil-water content in surficial contaminated soils will rarely exceed field capacity, let alone a 1:4 (soil:water) mass ratio. Therefore, determination of the toxicity at field capacity gives a value that is more representative of extreme environmental conditions that occur periodically with rainfall (i.e., soil saturation for extended periods, at petroleum and creosote contaminated sites). This is the condition where the potential for contaminant migration to the groundwater is the greatest.

Ames Mutagenicity Assay of $SA_mA_dA_pPA$ Class Fractions

Salmonella typhimurium mutagenicity test results are illustrated in Figures 2-5 for the different classes of compounds derived from the $SA_mA_dA_pPA$ extraction procedure from the creosote-and four petroleum-contaminated sites, as well as a petroleum reference material (ARC Bitumen 82-02).

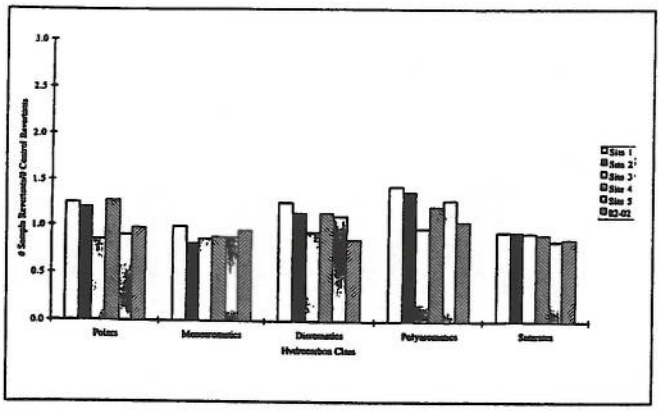


Figure 5. Ames *Salmonella*/Microsome assay (strain TA100) on $SA_mA_dA_pPA$ class fractions (with S9 activation).

A potential mutagenic response is presumed whenever a twofold increase in the number of revertants in the sample plate occurs in relation to the number of revertants in the control. The *Salmonella typhimurium* mutagenicity assay normally requires a demonstrable linear dose-response relationship to confirm mutagenic activity, in addition to a minimum twofold increase in the number of revertants.[18] The assay was applied in this study for screening purposes only at what could be considered the maximum soluble dose level because, in all cases, the $SA_mA_dA_pPA$ fractions only partially dissolved in the DMSO solvent. Therefore, a twofold increase in the number of revertants at this dose level was considered only to indicate, but not confirm, possible mutagenic activity at a maximum DMSO-soluble dose concentration. Mutagenic activity could be verified if a linear dose-response relationship was demonstrated over a lower dose range by performing the test on serial dilutions of the soluble fraction in the DMSO extract.

Results suggest that none of the compound classes induce base-pair substitution mutations, as evident in the low revertant responses in the TA100 strain (Figures 4 and 5). Weakly mutagenic responses are, however, evident in the TA98 strain with (Figure 3) and without (Figure 2) metabolic activation (+/-S9), indicating induction of frameshift mutations in some component classes.

The assays with the TA98 bacterial strain revealed a weak mutagenic response of the polyaromatic and polar $SA_mA_dA_pPA$ class fractions from some sites (Figures 2 and 3). The remaining fractions, mono-and diaromatics, and saturates induced either a marginal increase in the number of revertants or no revertants with the TA98 strain.

Comparing across the class fractions, the polars fractions tend to invoke a higher number of histidine revertants without metabolic activation in the TA98 strain. Several researchers have shown mutagenic activity in the strongly polar, higher molecular weight constituents of oil. However, these responses were observed with metabolic activation.[24-26] The results of this study suggest that the polar constituents at sites 3 and 5 are direct-acting mutagens because they do not require S9 enzyme activation to induce a genotoxic effect (Figure 2). The polars fraction also represents a substantial probability of exposure to biota because the fraction tends to be the most water-soluble of all the classes.

The polyaromatics fraction at sites 1 and 2 exhibit a weakly mutagenic response with metabolic activation in the TA98 strain (Figure 3). These findings are consistent with the results of other researchers who have found the primary mutagenic activity of petroleum to be contained in the polycyclic aromatic hydrocarbon fraction.[27-29] Simulated metabolic activation of PAH with the S9 enzyme fraction was required before a mutagenic response was observed. Therefore, reactive intermediate metabolites of PAH are likely causing the mutagenesis in the *Salmonella typhimurium*. Ames et al.[30] demonstrated that epoxides formed from mammalian metabolism of PAH function as frameshift mutagens. Because epoxides are not intermediates in metabolism of PAH by bacteria, bacterial degradation of PAH may provide a suitable technique for detoxification and assimilation of PAH at petroleum-and creosote-contaminated sites.[31]

Other studies exist to suggest that polycyclic aromatic hydrocarbons are not necessarily the principal mutagenic components of oil and that there is a distinction between the mutagenic and carcinogenic components of fuel-derived oils.[32-34] Such differences in experimental observations may be a result of differing oil-processing histories and wide variabilities in corresponding chemical compositions, differential sensitivities between individual class components for the Ames test itself, or the effects of interfering solvents.

DISCUSSION

Application of the Microtox and Ames Assays at Creosote-and Petroleum-Contaminated Sites

It must be emphasized that while some of the water-soluble compounds in the total and fractionated water extracts from the creosote-and petroleum-contaminated sites exhibit a "positive" response in the Microtox and Ames bioassays, no reliable quantitative relationship can be implied to predict health effects in humans and animals from complex petroleum-and creosote-contaminated soil matrices from these data. Only suggestive evidence of biological impact on higher organisms and clues as to which portion of the contamination should be investigated further by chemical analysis are provided for ultimate remedial option decision-making.

Donnelly et al.[2,35] have suggested that toxicity results from the Ames and Microtox assays can be used to rank contaminated sites from a health and environmental risk perspective, as well as identify areas within a particular site that may require further analytical attention and

remediation. The Microtox test can also be applied to determine biological treatability potential for contaminated soil, as toxic organics in the water phase may inhibit growth of beneficial soil microbial populations, allowing for the greatest potential of leaching and subsequent contamination of the groundwater.[11] Good correlations have been found between residue decline, microbial activity, and toxicity reduction in fuel-contaminated soil.[36] Thus, bioassays have utility in tracking the decrease in levels of toxicity in contaminated soil, thereby establishing the effectiveness of remedial treatment systems or natural degradative processes.

Table 3 summarizes the positive results of the Microtox and Ames assays for the total and $SA_mA_dA_pPA$ fractionated extracts on a qualitative basis. A '+' symbol in the Microtox assay column indicates that a 15-minute EC_{50} value of less than 25% by volume was reported for the particular water soluble fraction. This value is based on a remedial action criteria defined by Porcella[37] ($EC_{50} \leq 20\%$ by volume) and modified by Athey et al.[12] ($EC_{50} \leq 25\%$ by volume). A 15-minute EC_{50} Microtox value less than or equal to 25% by volume is an arbitrary value considered to be an indication for remedial action. Likewise, a '+' symbol in the Ames assay columns indicates a weakly mutagenic response in either the pilot study or the confirmation study in accordance with an arbitrary two-fold increase in revertants over the reference control.

It is evident from the total number of responses for each site that the creosote-contaminated site, Site 2, exhibited the greatest number of responses in the bioassays. Creosote is a complex mixture which includes many mutagenic and carcinogenic PAH and acutely toxic water-soluble phenolic compounds that contribute to the overall toxicity of the mixture. The presence of a substantial quantity of water-soluble organic compounds in a waste matrix would be expected to create a potential for a definite toxic response in the Microtox assay. Additionally, while higher molecular weight PAH, such as benzo[*a*]pyrene, are relatively insoluble in water in their pure form, mechanisms such as co-solvency, oil emulsions, and dissolved humic materials can enhance their presence in the aqueous phase.[23,29] Evidence of a high level of toxic organic compounds in the water phase at the creosote-contaminated site is reflected in the strong toxic response ($EC_{50} = 4.8\%$) of the water extracted at field capacity from the high-contamination soil. The elevated toxic responses from the soil-water extract and fractionated-oil extracts at Site 2 suggest that microbial growth in the soil may be inhibited, so bioremediation of this site may not be an effective option for cleanup. Physical treatment, containment, or removal of the waste soil might be the only plausible options for prevention of potentially harmful leachate migration.

The petroleum contaminated sites, 1, 3, and 5, exhibited a smaller number, 1, 2, and 2, respectively, of total responses in the bioassays (Table 3) when compared to the creosote-contaminated site. Additionally, the total extract and class fractions from Site 4 exhibited no toxic responses. Lower responses may be attributed to the relatively insoluble nature of components in the petroleum mixtures at the sites and imply that the chance of off-site transport of harmful contaminants is minimal. Site 3 revealed acute toxicity in the polar phase, whereas the combined extract exhibits no toxicity. Conversely, Site 5 displayed a Microtox toxic response in the combined extract and little or no response in the other fractions. While the effects of antagonism and synergism between potentially toxic compounds in the combined extracts may be acting, firm conclusions on such action cannot be drawn with the available information. An important point, however, is that a toxic response in a combined extract may signal potential hazards in the water-soluble fraction at the contaminated site, because the bulk oil phase exists in the environment in this combined condition. A non-toxic response in the combined extract, while its fractionated components reveal a toxic response, may indicate that components within the bulk oil phase inhibit dissolution of potentially toxic components by retaining them within the immobilized oil phase. Therefore, their off-site transport, contamination of groundwater, and exposure to biota are reduced.

As indicated by the Microtox and Ames bioassays, fractions that exhibit an acute toxicity or mutagenicity at the creosote-and petroleum-contaminated sites would likely require chemical analysis for further risk assessment. The polyaromatics at sites 1 and 2, the polar fractions at sites 3 and 5, and the asphaltenes at Site 2 exhibited some form of toxic response and should be examined by more specific analytical techniques to further characterize their associated health impacts. The majority of the total oils in the form of mono-and diaromatics, the saturates, and the asphaltenes remained relatively innocuous in the bioassays and probably do not require further scrutiny.

Pollard et al.,[8] using a tiered analytical protocol on the $SA_mA_dA_pPA$ fractions from these five sites, indicated that the creosote-contaminated Site 2 is significantly less weathered in composition than the other sites. This implies that the availability of water-soluble compounds is probably greater in this "fresher" creosote contamination. The polyaromatics class at Site 2 was found to be dominated by pyrenes/benzofluorenes, fluorenes, and the phenanthrenes/anthracenes, which may be possible causes for the mutagenic response in this class. A further chemical examination of the polar fractions at all the sites by GC/MS failed to identify potentially mutagenic compounds on an individual basis because of sample complexity and poor chromatographic resolution. Identification of the toxic components in the polars fractions at sites 3 and 5 would require further

chemical fractionation and possibly some derivitization for isolation of suspect compounds. Pollard et al.[8] also noted that while naphthenic acids in asphaltene fractions of petroleum wastes have been shown to exhibit aquatic toxicity, these compounds were not found in the asphaltene fraction from Site 2.

CONCLUSIONS

The Microtox and Ames assays were employed to measure acute toxicity and indicate potential mutagenicity of water-soluble components of class-fractionated oils extracted from one creosote-and four petroleum-contaminated soils. A water extracted directly from a creosote contaminated soil at field capacity was also subjected to Microtox evaluation. The mono-and diaromatics, the saturates, and most asphaltenes account for the majority of the bulk oil on a mass basis—and these exhibited low or no toxic response. The Microtox test revealed that potential acute toxicity resides mainly in the polar fractions at three sites, a factor attributable to the relatively higher water solubility of this fraction. Ames *Salmonella*/microsome testing indicated that the polyaromatic fractions at two sites exhibit weak mutagenicity with enzymatic activation, while the polar fractions at two sites are weak direct-acting mutagens requiring no metabolic activation. The bioassays demonstrated that further chemical characterization of the polar and polyaromatic fractions would be required to more completely assess the potential of health risks at the creosote-and petroleum-contaminated sites exhibiting the associated toxic response.

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About the Authors

Michael G. Zemanek is an environmental engineer at Contaminated Sites Decommissioning Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, 9820-106 Street, Edmonton, Alberta, T5K 2J6, Canada. Simon J. Pollard is policy advisor for contaminated land, Environmental Strategy Directorate, Scottish Environment Protection Agency, Stirling, Scotland, FK9 4TR, United Kingdom. Sandra L. Kenefick is an instructor in the Department of Chemistry, Okanagan University College, 3333 College Way, Kelowna, British Columbia, V1V 1V7, Canada. Steve E. Hrudey (corresponding author) is professor and eco-research chair in environmental risk management, Environmental Health Sciences Program, Department of Public Health Sciences, Faculty of Medicine and Oral Health Sciences, University of Alberta, Edmonton, Alberta, T6G 2G3, Canada.

Characterization of Refractory Wastes at Hydrocarbon-Contaminated Sites: 1. Rapid Column Fractionation and Thin Layer Chromatography of Reference Oils

Martin Whittaker and **Simon J.T. Pollard***

Key Words:

Refractory wastes
Hydrocarbon contamination
TLC-FID
Column fractionation

Summary

Effective risk management of hydrocarbon-contaminated sites often necessitates the detailed characterization of residual wastes and identification of potential sources of contamination. Details of a rapid, reliable protocol for the component class analysis of seven weathered reference oils are presented as an initial stage of the characterization of refractory hydrocarbon wastes. The procedure features initial removal of asphaltenes by precipitation with *n*-pentane, with subsequent flash chromatographic fractionation of maltenes using a solvent scheme comprising *n*-pentane (for elution of saturated compounds), toluene (mono-, di- and polyaromatic compounds), dichloromethane (moderately polar compounds), methanol (strongly polar compounds), and additional resolution of the saturated compounds by classical column chromatography. Gravimetric analysis of each fraction has enabled component class characterization for each reference oil. Subsequent component class analysis of neat reference oils and individual class fractions by thin layer chromatography with flame ionization detection (TLC-FID) validates the utility of TLC-FID as a screening tool and the integrity of the column fractionation scheme.

1 Introduction

The effective assessment and management of risk at hydrocarbon-contaminated sites increasingly necessitates characterization of the underlying waste – soil matrix. Elucidation of the fundamental physiochemical and toxicological properties of waste components and the distribution of individual contaminants throughout the waste – soil – groundwater matrix, enables remediation experts to evaluate more accurately the environmental risks associated with a contaminated site, to select appropriate, realistic remedial treatment technologies in the light of this information, and to fingerprint wastes in order to identify the sources of the contamination [1].

Conventional methods for characterizing hydrocarbon-contaminated sites, that rely on determining the extent of solvent-extractable organic compounds (the surrogate "oil and grease" parameter), provide no information on waste composition and distribution; they are, therefore, inadequate for quantitative risk assessment when used in isolation [2]. Unfortunately, the prevalence of mixed wastes and refractory compounds at many sites is such that extended characterization of the underlying waste – soil matrix requires the use of expensive and time-consuming analytical instrumentation [3]. Given the limited availability of resources for contaminated site investigation and remediation, this represents a significant constraint on the efficacy of risk assessment and risk management programs.

In response, attention has focused on the development of flexible, tiered analytical approaches which utilize a combination of techniques, facilitating both the rapid screening and detailed compositional analysis of waste streams, in accordance with specific site investigation needs [1]. Such approaches enable selective application of more costly, time-consuming analytical techniques, thereby promoting effective utilization of site clean-up resources and enabling remediation experts to develop a sound analytical basis for subsequent "clean-up" decisions.

M. Whittaker, Department of Chemistry, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh EH9 3JJ, UK; and S.J.T. Pollard, Aspinwall and Company, 13 Melville Street, Edinburgh EH3 7PE, UK.

Spiked urine samples were used to determine the linearity of the method in the range 0.2–2.6 μg EA-HS. The regression equation was $Y = 0.5790 \cdot X - 0.0145$, where Y is the ratio [peak area EA]:[peak area IS] and X is the amount applied [μg]. Five different concentrations were investigated; the number of analyses was 14, the correlation coefficient was 0.9822, and the standard error of the estimate $S_{Y,X}$ was 0.0970. The limit of quantification of EA in urine at a signal-to-noise ratio of 4 was 25 ng, which corresponded to 5 μg/ml urine. **Figure 3** shows densitograms of blank urine (A), urine spiked with EA and IS (B), and of a real urine sample, taken 3 h after oral administration of 250 mg erythromycin capsule (C).

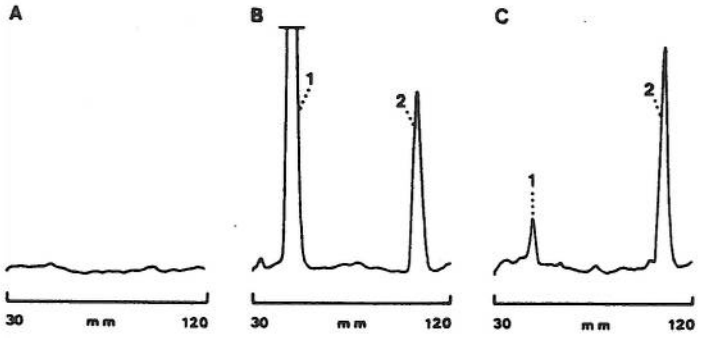


Figure 3

Densitograms obtained from blank urine (A), urine spiked with 6 μg EA (B), and a urine sample taken 3 h after oral administration of a 250 mg erythromycin capsule (C). 1, EA (0.3 μg); 2, IS (troleandomycin).

For plasma samples, an extraction procedure was necessary for reasons of sample clean-up and concentration. When blank plasma was extracted and analyzed, an endogenous compound coeluted with troleandomycin, used as IS for urine samples. For this reason, EANO, a substance related to EA which had not been detected in plasma samples, was used as IS.

Chromatograms of blank plasma after extraction, an extracted plasma spiked with EA and some of its metabolites, and a sample taken 3 h after oral administration of a 250 mg erythromycin capsule are shown in **Figure 4**. Whereas unchanged EA was detected in all the samples, the presence of dMeEA was detected in some of the samples.

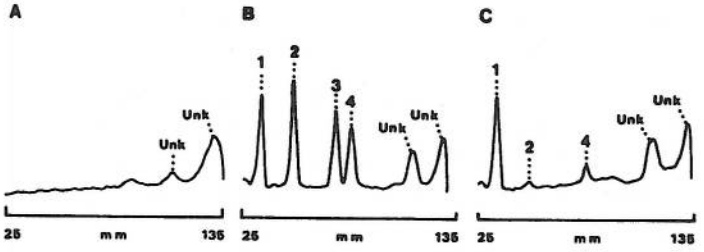


Figure 4

Densitograms obtained from blank human plasma (A), plasma spiked with EA and some of its metabolites (B), and a plasma sample taken 3 h after administration of a 250 mg erythromycin capsule (C). 1, EANO (IS); 2, dMeEA; 3, AEA; 4, EA (60 ng in C); Unk, unknown plasma interference.

4 Conclusion

Quantitative TLC using xanthydrol as detection reagent for erythromycin is quite simple and sensitive. As the limit of detection is 25 ng the method is 40 times more sensitive than LC with UV detection. Because this method requires less sample preparation than LC it may be a useful alternative to the latter technique for preparations containing erythromycin. This method can also be used for rapid and simple quantitation of the main component (EA) in urine and plasma samples but it is not sufficiently sensitive for detection of minor metabolites in biological samples.

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CHARACTERISATION OF REFRACTORY WASTES AT HEAVY OIL-CONTAMINATED SITES: A REVIEW OF CONVENTIONAL AND NOVEL ANALYTICAL METHODS

MARTIN WHITTAKER[1], SIMON J. T. POLLARD[2]* AND TONY E. FALLICK[3]

[1]Environmental Chemistry Unit, University of Edinburgh, King's Buildings, West Mains Road, Edinburgh, UK EH9 3JJ.
[2]Aspinwall & Company, 13 Melville Street, Edinburgh, UK EH3 7PE.
[3]Isotope Geosciences Unit, Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow G75 0QU, UK

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ABSTRACT

Methods for the analysis of petroleum hydrocarbons in contaminated soil and water are subject to a range of constraints arising from the complexity of waste-soil-groundwater matrices, the inherent chemical diversity of the spilled product and the requirements of the site investigation. The analytical uncertainties associated with refractory weathered contaminants, which exist as pockets of residual saturation in the contaminated subsurface are a major problem. Adoption of a transparent, phased approach to waste characterisation significantly mitigates these constraints and improves the use of site investigation resources. Moreover, the use of biomarker monitoring and gas chromatography-stable carbon isotope ratio mass spectrometry within such a scheme is likely to be of significant benefit to remediation experts in the elucidation of waste source terms and the selection and monitoring of remedial treatment technologies.

Keywords: Contaminated soils, hydrocarbon wastes, analytical constraints, biomarkers, GC-IRMS

INTRODUCTION

Many industrialised countries have now identified the issue of contaminated land as a subject of major social, legal, environmental and economic concern. In the UK alone, a recent report suggests that there may be up to 250,000 hectares of contaminated land carrying a potential cleanup cost of almost £20 bn. (1). Such estimates unfortunately shroud the underlying and largely unresolved complexities of "When is a site contaminated?" (environmental quality criteria, their development and use), "Who pays for the remediation of historical contamination?" (tracking liabilities and the role of the taxpayer) and "How clean is clean?" (the technical and economic viability of remedial techniques with reference to environmental quality criteria). In an arena where uncertainties about the extent and type of contamination often outweigh the certainties, it is entirely correct that the rational prioritisation of resources and remediation of identified contaminated sites is focused on considering the associated risks to human health and the environment within a risk assessment framework (2).

As stakeholder perception of the issues which surround the identification and management of contaminated land heightens, the analytical integrity of site investigation strategies are becoming the focus of intense scrutiny. Consequently, increasing emphasis is being placed on the elucidation of the fundamental physicochemical and toxicological properties of waste components and the distribution of individual contaminants throughout the waste-soil-groundwater matrix. In addition to enabling remediation experts to evaluate more accurately the environmental

risks associated with a contaminated site (3), this information is crucial to the elucidation of waste source terms and the selection and monitoring of remedial technologies (4,5).

The prevalence of mixed wastes and refractory compounds at many hydrocarbon-contaminated sites presents particular environmental and analytical problems. At such sites, the movement of heavy, non aqueous-phase liquids (NAPLs) throughout the unsaturated zone can result in pockets of recalcitrant, oily material in the contaminated subsurface. Contamination of this kind is commonly referred to as residual saturation, and is typical at sites featuring terrestrial deposition of coal tars, acid tar wastes and heavy petroleum products (e.g., No.6 fuel oil) (6). Of specific concern to risk assessors is the propensity of residual saturation to release contaminants into the surrounding soil and groundwater (7). This problem is particularly acute at sites where rebounding groundwater floods the unsaturated zone to mobilise and disperse environment long after the removal of the bulk previously quiescent contaminants (8). Furthermore, in many cases, the hydrophobicity, inaccessibility and microbial recalcitrance of heavy oil components impose particular constraints upon the application of biological treatment processes (6,9,10) and conventional groundwater cleanup systems (7). The chemical complexity of this material represents a substantial challenge to the environmental chemist since the number, diversity, high molecular weight, and low volatility of the contaminants can severely limit the application of conventional analytical techniques.

An important factor determining the compositional complexity of petroleum products in the soil environment is the extent of weathering experienced by the source term (11,12). The physical, chemical and biological processes that occur during weathering often combine to dramatically alter the fundamental composition of the waste-soil-groundwater matrix. An analytical evaluation of the nature of the changes that occur during weathering may therefore, be extremely beneficial to effective site characterisation. A result of the difficulties associated with analysis of refractory contaminants is that in place of a complete elucidation of the compositional changes associated with weathering, some workers are characterising waste source terms and weathered state using individual environmentally persistent waste components, or biomarkers (5,13,14). The documented microbial recalcitrance of certain biomarkers has facilitated their use as internal mass balance indicators for assessing the degradation of more susceptible waste components during both natural weathering (13) and controlled bioremedial activities (14).

Efforts to address the constraints which surround the analysis of complex mixtures of organic contaminants in terrestrial and aquatic environments continue to evolve. An approach which has proved particularly useful in the characterisation of marine oils in terms of oil source, maturity, migration and depositional environment involves bulk fraction and compound specific isotope analysis (15-21). The application of this approach to the characterisation of hydrocarbon-contaminated soils is poorly understood, even though it may provide a valuable adjunct to conventional gas chromatography-mass spectrometry (GC-MS) and an alternative means of biomarker fingerprinting (22).

This paper reviews current analytical methodologies for the characterisation of heavy oil-contamination extracted from the waste-soil matrix. The applications and limitations of a variety of conventional and novel techniques for the rapid screening and extended analysis of refractory petroleum waste streams are discussed. Particular emphasis is placed on a critical evaluation of the potential use of bulk and compound specific stable carbon isotope ratio mass spectrometry in the elucidation of waste source terms and extent of weathering.

EXISTING ANALYTICAL TECHNIQUES ANDTHEIR LIMITATIONS

The detailed characterisation of wastes at hydrocarbon-contaminated sites is of key importance to: (i) the effective assessment of risks posed by a site to human health and the environment; (ii) the evaluation of bioavailability and distribution throughout the waste-soil-groundwater matrix; (iii) the selection, allocation and monitoring of appropriate remedial technologies, if required; and (iv) the identification of multiple waste source terms, particularly for incidents of cross boundary contamination (23). At many sites, such a detailed appraisal is prevented by the heterogeneity of the subsurface and the presence of refractory contaminants discharged to the soil environment from a variety of different sources over an unspecified period of time (24). Post-

depositional biodegradation of assimilable hydrocarbons during weathering can also severely augment the matrix complexity, resulting in the gradual predominance of recalcitrant aromatic, polar and asphaltic contaminants that are analytically problematical and resilient to biological treatment (9,25,26).

Current analytical methodologies embody a range of inherent limitations when applied to the vastly complex waste streams encountered at sites featuring heavy oil contamination and residual saturation. Recently, attention has focused on the development of flexible, tiered analytical approaches which facilitate the rapid screening and detailed compositional analysis of waste streams in accordance with specific site investigation needs (22,23,27-31). These approaches promote effective allocation of site cleanup resources and enable risk assessors and remediation experts to develop a sound analytical basis for subsequent cleanup decisions.

The wide variety of techniques used in the analysis of petroleum hydrocarbons in soils and water can be divided into three categories, depending on their point of application and the level of analytical detail: field screening techniques, conventional non-specific methods and methods for detailed component analysis (32). In formulating an effective, financially viable analytical strategy, an accurate understanding of the capabilities and limitations of individual techniques, particularly with respect to the operational parameters and the ultimate goals of the site investigation, is of utmost importance.

Field Screening Techniques

Field monitoring at contaminated land sites is carried out primarily to facilitate the rapid on-site assessment of soils, groundwater and soil gases. Information is used to provide a preliminary indication of the extent and nature of contamination and, more importantly, to direct further sampling and analysis, thereby saving time and expenditure. This allows site characterisation programmes to become more focused and remedial efforts to be optimised (32).

The majority of field screening methods depend upon the measurement of vadose zone soil vapours by either in situ soil gas measurements or head space analysis (27,33), e.g. field gas chromatographs equipped with flame ionisation detectors (FIDs) and photoionisation detectors (PIDs). These techniques are largely ineffectual at contaminated sites involving heavy, refractory oils, due to the absence of sufficiently volatile organic compounds. Moreover, at sites where extensive hydrocarbon contamination has occurred, a number of additional problems can arise which further diminish the efficacy of field screening techniques. These include: (i) the presence of refractory, toxicologically-important compounds (e.g., 5 - 6 ring polynuclear aromatic hydrocarbons (PAHs), which often possess very low vapour pressure (Pv), high octanol-water partition coefficients (K_{ow}) and high organic carbon-water partition coefficients (Koc) values and which remain undetected by portable GC methods; (ii) the physical or chemical sorption of hydrophobic contaminants to subsurface humic matter; (iii) residual saturation of subsurface matrix pores with non-aqueous phase liquid (NAPL); (iv) the inability of rapid spectrophotometric field screening techniques to sufficiently resolve and determine components exhibiting similar structural and chemical properties (32).

Faced with a diminution of field monitoring capabilities and the high costs associated with more sophisticated analytical techniques, many site assessors are turning to generic methods for characterising contaminated sites (3,34). This approach involves the collective measurement of all hydrocarbon constituents over a particular detection range, which may or may not be defined. If used in isolation rather than as part of a disperse analytical framework, these methods present a greatly over-simplified picture of the nature and distribution of contaminants which can lead to potentially damaging and expensive miscalculations during site remediation programmes.

Conventional Techniques

Three techniques are routinely used in the analysis of petroleum hydrocarbons in soils and water: gravimetric analysis, measurement of Total Petroleum Hydrocarbons (TPH) by infrared spectroscopy (EPA Method 418.1) and high resolution gas chromatography with flame ionisation detection (GC-FID). All three become subject to significant limitations when applied to heavy or weathered residual hydrocarbon contamination.

(i) Gravimetric determination of solvent-extractable organics:

Useful for determining the total load of solvent-extractable organics within a sample, the

surrogate "oil and grease" parameter (35) precludes elucidation of either the composition of the extracted organics or the distribution of target contaminants within the organic phase (3) and is completely method-dependent (36). In addition, poor extraction efficiencies (28) and superfluous analysis of co-extracted natural organic matter (37) can result in considerable inaccuracies in reported contaminant loads.

ii) Total Petroleum Hydrocarbons (TPH) by infrared spectroscopy (IRS)(EPA Method 418.1):

Measurement of the infrared absorbance of freon-extracted hydrocarbons at 2930 cm^{-1}, the wavenumber corresponding to the aliphatic CH2-stretch is potentially vulnerable to both positive and negative analytical bias (27,28). The central constraint concerns the insensitivity of the technique to extracted waste components not exhibiting detectable absorption bands at the monitoring wavenumber, i.e., non-saturate class components. At sites incorporating highly weathered hydrocarbon contamination in which saturate class constituents have been essentially dissipated, this is clearly a major drawback. In addition, samples are quantified against a standard hydrocarbon mixture and not the actual spilt material. Since different hydrocarbons exhibit different responses to IRS, such a comparison cannot be relied upon to produce true contaminant concentrations (34).

(iii) Gas chromatography with flame ionisation detection:

The use of methods modified from EPA Method 8015 Total Petroleum Hydrocarbon (TPH) analysis by gas chromatography with flame ionisation detection (GC-FID) has found widespread use in the screening and further analysis of petroleum hydrocarbons in soil and water. GC-FID screening of extracted organic contaminants, generally involves a qualitative correlation of retention time windows for sample and standard chromatograms over the total detectable carbon number range (38). More commonly, however, GC-FID analysis is used for determining Total Petroleum Hydrocarbons (TPH) over the whole range of detection, TPH over defined hydrocarbon ranges (usually diesel range or gasoline range organics), or target compounds, e.g., BTEX (benzene, toluene, ethyl benzene and xylene) or pristane/phytane (13) (see Figure 1a). Quantitation is generally achieved using calibrated, representative standard hydrocarbon mixtures, internal standards or both.

GC-FID has become the most widely adopted tool for analysing crude oils and associated products. In a very recent report, Fan *et al.* (34) describe seven new analytical methods, all based on GC-FID, which have been developed for the determination of gasoline and diesel range organic compounds in petroleum-contaminated soils in the states of Tennessee and Wisconsin. Hydrocarbon fingerprinting by GC-FID is frequently used to determine the nature and possible source of unknown contaminant mixtures, although identification of contaminant type is usually facilitated by comparison with representative chromatograms (36). Bruce and Schmidt (39), in a recent review of hydrocarbon fingerprinting techniques, characterised a range of *n*-paraffin GC profiles by overall shape, symmetry, and fuel additive abundance to distinguish between crude oil types, condensates, refined products and weathered oils. Similarly, Baugh and Lovegreen (40), differentiated between crude and refined petroleum products using peaks above the diesel range, reported together as C_{20} - C_{30} hydrocarbons. Rhodes *et al.* (36) adopted a more quantitative approach, returning gasoline TPH of 50 to 50 000 mg TPH g^{-1} following *n*-tetradecane extraction hydrocarbons from gasoline-contaminated soils. Douglas *et al.* (28) also used GC-FID to evaluate petroleum hydrocarbon contaminant concentrations in water and soil samples (total hydrocarbons reporting limits: 50 mg l^{-1} and 10 mg kg^{-1}, respectively) and, following a comparison of sample and suspected source term chromatogram peak patterns, unresolved complex mixtures and pristane/phytane ratios, to identify fresh to moderately degraded diesel oil and coal tar samples.

The utility of target compound analysis by GC-FID has also been shown to be of value in characterising spilled hydrocarbons. For unweathered or lightly weathered petroleum contaminants, distinctive *n*-alkane peak patterns and C_{17}/pristane; C_{18}/phytane; pristane/phytane ratios can be used along with the distribution of the unresolved complex matter (UCM) to provide compelling evidence for source correlation purposes (41). In an investigation of residual oil source terms, Glover and Bullin (42) quantitatively compared the pristane/phytane ratios and the *n*-paraffin (C_{15} - C_{31}) and isoprenoid gas chromatogram peak height profiles of seven unweathered heavy oil samples. Peak profiles were calculated by dividing individual *n*-alkane and isoprenoid peak heights by the sum of all of the *n*-alkane peak heights.

Using additional data from GC-MS and statistical analysis, four oil pairs were identified, with commonality assigned when a 10 % agreement was observed in oil pristane/phytane ratios and corresponding peak profile values.

For more weathered samples, featuring extensive *n*-alkane degradation, the use of the relatively recalcitrant pristane and phytane as internal mass balance indicators allows the extent of degradation of amenable hydrocarbons to be estimated. Senn and Johnson (13) analysed samples taken from three observation wells in the vicinity of a distillate leakage to determine the source of contamination. The sample from the first well was a weathered distillate with a C_{17}/pristane ratio of 0.2 and a C_{18}/phytane ratio of 0.3. The second sample was a slightly fresher product with a C_{17}/pristane ratio of 1.4 and a C_{18}/phytane ratio of 1.4. The sample from the third well was the least degraded, reflected by C_{17}/pristane and C_{18}/phytane ratios of 1.8 and 2.7, respectively. The authors concluded that the third, least degraded sample was closest to the source and, following an examination of groundwater flow, determined the source of contamination. More recently, Christensen and Larsen (43) investigated the relationship between the ages of 12 diesel oil spillages and degradation ratios calculated from the peak height ratios of C_{17}/pristane, C_{17}/ norpristane, C_{18}/phytane and C_{18}/norpristane, respectively. Linear correlation coefficients (r^2) ranged from 0.52 to 0.89 (based on the 12 data points), with the highest correlation with age found to be for the average C_{17}/pristane ratio. This result enabled the authors to estimate the age of spilled diesel to within approximately two years. However, evidence demonstrating the eventual biodegradation of pristane and phytane by some microbial populations suggests that their use in the characterisation of severely degraded refractory wastes may be unreliable (44).

Unfortunately, the use of GC-FID in the detection and measurement of subsurface contamination is often subject to a number of constraints (38). These include; (i) over-recoveries, caused by carry over or memory effects from high boiling residual components on the column, column bleed and mass discrimination of high molecular weight hydrocarbons in the injection port and/or syringe; (ii) under-recoveries, caused by the use of overly diverse hydrocarbon component standards; and, (iii) the presence of large unresolved complex mixtures (UCM) (41), which impede component detection and may cause high or low recoveries, through individual peak and baseline interferences, respectively.

Conventional chromatographic techniques are unable to resolve a large proportion of UCM, even after extensive cleanup of oil extracts (Figure 1b). Characterised as a broad 'hump' in GC chromatograms, the presence of a large UCM often obscures individual contaminant peaks and significantly restricts the analysis of specificcompounds and groups of compounds. Work by Gough and Rowland (41,45) and Gough *et al.* (46) has indicated that some UCMs consist in part of uncomplicated monoalkyl-substituted "T"-branched alkanes, and that chemical oxidation of the UCM yields > 90 %w/w functionalised products, including ketones, lactones and carboxylic acids, of which *ca.*15 %w/w were resolved by GC. However, the inability of GC-coupled analytical techniques to adequately resolve heavy, weathered oils, which may contain significant UCM and high-molecular weight components, remains a major obstacle to the effective analysis of residual hydrocarbon wastes.

Alternative Screening Techniques

The difficulties associated with conventional techniques used in the analysis of crude oil and petroleum product contaminants has resulted in the emergence of a range of alternative analytical approaches:

(i) Simulated distillation gas chromatography (GC-SIMDIS):

GC-SIMDIS is a well-established method which facilitates characterisation of hydrocarbons in terms of carbon number distribution and boiling range. GC-SIMDIS is particularly suited to the analysis of heavy oil contaminants since it requires much smaller sample sizes, is more rapid than regular distillation and can be used for very high boiling samples (up to *ca.*540 °C) (47). Recently, the technique was used by Pollard *et al.* (23) to rank petroleum- and creosote-contaminated site extracts in terms of their boiling point distribution. By correlating the SIMDIS profiles of various extracted fractions with boiling points of the *n*-alkanes (C_4 - C_{100}), the authors were able to determine the carbon number distributions within each fraction, the associated atmospheric equivalent boiling point distributions and, consequently, the proposed relative recalcitrance of the sampled wastes and their class fractions.

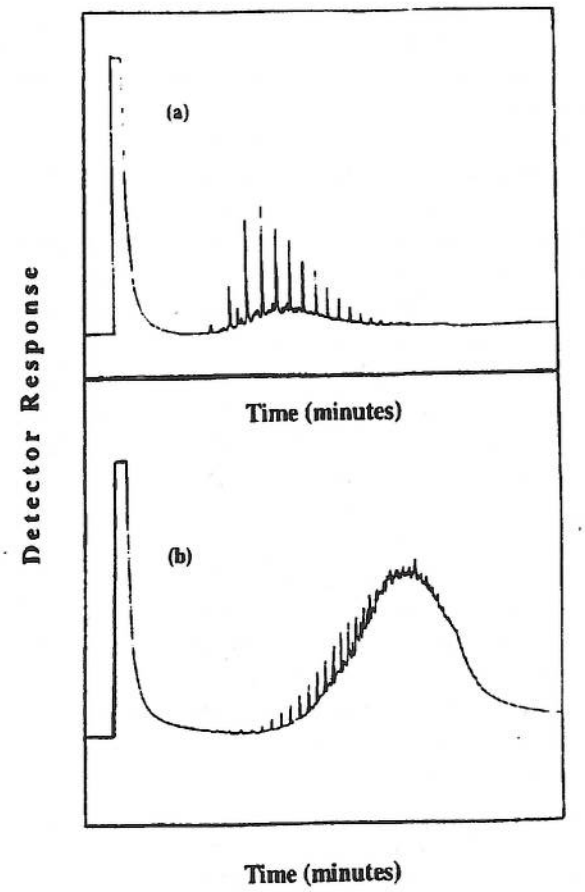


Figure 1. Typical GC-FID profiles of saturate fractions for: (a), a light oil, with *n*-alkane peaks clearly prominent; and (b), a heavy oil containing a significant UCM 'hump'.

(ii) Thin-Layer Chromatography with Flame Ionisation Detection:

A screening technique finding increasing application in the characterisation of weathered hydrocarbon wastes is IatroscanTM thin layer chromatography with flame ionisation detection (TLC-FID). By facilitating the rapid component class fingerprinting of a wide variety of solvent extractable organics from soils at petroleum- and coal tar-contaminated sites, TLC-FID allows entire waste extracts to be classified according to their composition. This is particularly valuable at weathered, heavy oil-contaminated areas, where the relative abundance of component types provides important information as to the treatability and weathered state of the waste stream (3). The use of TLC-FID screening at problematic, refractory waste sites may be especially appropriate, due to its documented reliability, speed, cost-effectiveness and its aptitude for analysing refractory wastes of negligible volatility (48). The latter property is important since it allows a significant drawback of the technique, namely loss of low boiling compounds during the chromatography phase, to be avoided. It is also important to recognise that component class results are heavily dependent upon the solvent scheme employed and are at best semi-quantitative in nature. Karlsen and Larter (49) and Volkman and Nichols (50) provide a detailed description of the key technical elements of TLC-FID analysis.

TLC-FID has been used extensively in the component class characterisation of various heavy whole oils and oil fractions (48-51). Poirier and George (51) used TLC-FID to separate the maltenes and asphaltenes in bitumens, selected heavy oils and synthetic fuel residues. Asphaltenes (wt %) were quantified by comparison of integrated peak areas with those from an Athabasca asphaltene standard, with malthene comprising the difference. Maltene/asphaltene values varied between 74.3 % w/w / 25.7 %w/w for a Lloydminster 4LL79

feed sample to 99.4 % w/w / 0.6 % w/w for a Medicine River residue.

A more detailed analysis of heavy oil and bitumen processing residues was carried out by Fuhr *et al.* (48), who used TLC-FID to determine the amounts of saturates, aromatics, polars 'A' (lower molecular weight, light to moderately polar heteroatom-containing compounds) and polars 'B' (higher molecular weight, highly polar material, including asphaltenes) in a series of residue samples taken from solvent deasphalting and cracking processes. Calibration was achieved using an Athabasca bitumen with a component class composition (based on 41 separate analyses over a six month period) of: saturates, 20.7 %w/w (RSD 6.8 %); aromatics, 43.1 %w/w (RSD 4.4 %); polars A, 18.2 %w/w (RSD 8.8 %); and polars B, 18.1 %w/w (RSD 9.4 %). Component class fingerprints indicated the high saturate and aromatic contents of cracking process residues (average values *ca.*20 %w/w and 50 %w/w, respectively) and the high polar contents of solvent de-asphalting process residues (average polars 'A' and polars 'B' values *ca.*20 %w/w and 40 %w/w, respectively). By using a modified solvent system, the authors were able to separate and quantify aromatics of three or less rings and those with four or more, reporting higher contents of the latter in heavily polar samples and higher contents of the former in samples featuring high saturate contents.

TLC-FID was used in an alternative capacity by Volkman and Nichols (50), who analysed two sediment samples for total hydrocarbon content. The total concentration of hydrocarbons in the two sediments was found to be 70 mg g^{-1} and 6 mg g^{-1}. Additional analysis of the samples by capillary GC revealed the presence of a large amount of UCM in the former sample, thus indicating a high level of contamination by weathered, petroleum hydrocarbons. More recently, TLC-FID has been used specifically for the screening of refractory oily wastes by Pollard *et al.* (3), who used TLC-FID to fingerprint a variety of residual hydrocarbon-contaminated soil extracts from petroleum- and creosote-contaminated sites. By using variations in TLC solvent schemes to focus on the aromatic and polar components of waste samples, the authors were able to correlate observed waste class composition with the extent of weathering experienced by the wastes. Whittaker and Pollard (52) utilised TLC-FID to provide class compositional distributions of 7 selected, representative heavy oils as an initial stage in an investigation of source terms and the weathered state of residual saturation at hydrocarbon-contaminated sites. Oils were characterised according to saturate, aromatic, combined polars and asphaltene content. Reported class compositions for lighter ballast and API separator oils containing *ca.*80 %w/w saturates contrasted sharply with those for heavier bitumen and Bunker C samples containing *ca.*15 % w/w asphaltenes and *ca.*25 % w/w combined polars (Figure 2).

(iii) High-Performance Liquid Chromatography (HPLC):

This technique has been shown to have some utility in the rapid separation of crude oil components, although several difficulties still arise due to the strong adsorption of polar compounds on polar stationary phases and, for reversed phase HPLC, the poor solubility of many petroleum constituents in aqueous mobile phases. Li *et al.* (53) addressed the former problem and characterised a variety of de-asphalted crude oils by GC-MS and GC with nitrogen phosphorous detection (GC-NPD) following successful isolation of pyrrole and pyridine components by normal phase HPLC. Previously, irreversible adsorption of nitrogen-containing heterocycles onto polar stationary phases (e.g., unmodified silica and basic alumina) had precluded further analysis of the separated nitrogen species. Using a polar aminocyano-bonded silica column, the authors successfully resolved pyridine nitrogen heterocycles and pyrrole nitrogen heterocycles from light crude oils containing as low as 0.1 %w/w nitrogen content. The reported recoveries of nitrogen-containing standards were over 98 % w/w.

In recognition of the excessive costs associated with extensive analysis of environmental samples by GC-MS, Krahn *et al.* (54) determined the distribution of spilled crude oil in Prince William Sound, Alaska, by the rapid HPLC screening of over three thousand sediment samples. Following sonic extraction and size-exclusion HPLC separation of aromatic compounds, the authors determined the concentrations of alkylated naphthalenes and dibenzothiophenes (at 290 / 335 nm, 1 naphthalene), and alkylated phenanthrenes (at 260 / 380 nm, 1 phenanthrene) by fluorescence detection. A correlation of these results with the quantitative results obtained by GC-MS for the same polynuclear aromatics appeared favourable (r = 0.726 and 0.731 for phenanthrene and naphthalene groups, respectively). The distinctive chromatographic patterns of different

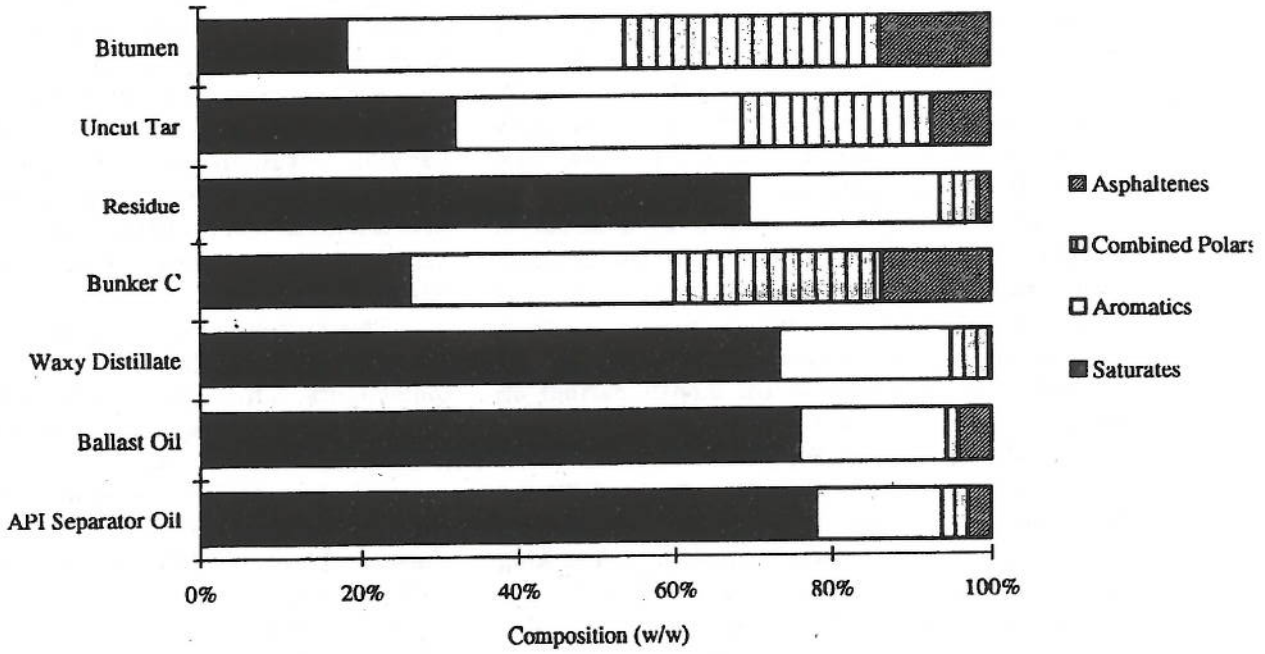


Figure 2. Component classs fingerprints of typical heavy oils by TLC-FID

crude oils and crude oil fractions also demonstrated the utility of the technique in distinguishing between contaminant source terms and, tentatively, the extent of weathering.

(iv) Laser desorption laser photoionisation time-of-flight mass spectrometry (L^2TOFMS):

Recently, Dale *et al.* (55) adapted L^2TOFMS to the analysis of individual PAHs at the parts per million (ppm) level directly from contaminated soil matrices. The technique avoids lengthy sample preparation procedures, producing well-resolved mass spectra for the semi-quantitative determination of a range of PAHs, from phenanthrene/anthracene (m/z 178) and 4H-cyclopentaphenanthrene (m/z 190) to coronene (m/z 300). Although L^2TOFMS is unable to distinguish between equivalent mass species, cannot identify organic species which do not contain a UV chromaphore (due to the use of UV radiation for ionisation) and has not yet been adapted for use in the field, it remains a potentially effective adjunct to more conventional screening methods.

Detailed Component Analysis

EPA GC-MS Methods 8270 and 625 remain routine procedures for analysing volatile and semi-volatile petroleum products, despite criticisms regarding their lack of sensitivity (caused by the relatively high reporting limits) and over-narrow analyte specifications (28). Douglas *et al.* (28) highlight these shortcomings by measuring PAHs in water-soluble fractions of JP5 jet fuel and diesel fuel. Analysis by EPA Method 8270, at a reporting limit (RL) of 10 ug g^{-1}, detected three PAHs (naphthalene, C1-naphthalene and phenanthrene) at concentrations of 10 - 20 ug l^{-1}. Analysis by the modified method, using a RL of 0.01 mg l^{-1} and a wider analyte list, revealed the presence of an additional 17 PAHs, mostly alkylated naphthalenes, fluorenes, phenanthrenes and anthracenes, at concentrations of up to *ca.* 80 mg l^{-1}. Unfortunately, however, for residual oils of negligable volatility the use of GC-MS can be impeded by poor chromatographic resolution of high boiling components, lengthy sample preparation procedures and resultant high costs.

In essence, there are two possible approaches to GC-MS analysis, the difference between them being the manner in which the analyte is ionised in the mass spectrometer (56). Fragmentation methods, such as electron impact mass spectrometry (EI MS), bombard the analyte with a stream of electrons to produce both parent and fragment ion peaks. Nonfragmenting or

soft-ionisation methods, such as chemical ionisation mass spectrometry (CI MS), produce predominantly parent ion peaks. In choosing which approach is most appropriate for heavy or weathered petroleum samples, it is important to consider the underlying chemistry of the analytes in question, as well as the ultimate goals of the analysis. These decision criteria are discussed in the following sections.

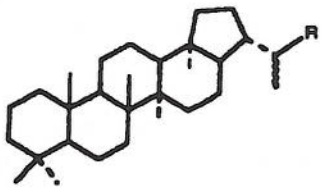
(i) Target analysis by GC-EI MS:

When a general analysis of all component types within a particular sample is required, GC-EI MS patterns can be far too congested to be of realistic analytical value. In this respect, nonfragmenting methods can be favourable, since they produce relatively straightforward patterns of parent ion peaks. However, for complex, refractory petroleum samples, soft ionisation techniques often produce ambiguous results, since many of the analytes within such samples have identical parent ion peaks, and therefore lack the high degree of specificity required to accurately determine sample constituents and source terms (56). In light of these considerations, the approach most suited to the characterisation of heavy or weathered oil samples is selective ion monitoring by GC-EI MS (57). Analysis of selected ion peaks produced by characteristic, environmentally-persistant biomarker compounds, for example, generates information of great importance in determining contaminant source terms, weathered state and potential treatability. The structures of a selection of biomarkers are shown in Figure 3.



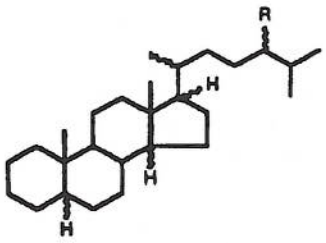
Pristane (R = Methyl)

Phytane (R = Ethyl)



Hopanes

(17α/β, 21 α/β ,22R/S; R = H, Methyl, Propyl, Butyl)



Steranes

(5α/β, 14α/β, 17α/β, 20R/S; R = H, Methyl, Ethyl)

Figure 3. Molecular structures of selected biomarkers (pristane, phytane, hopanes and steranes).

Target analysis is particularly attractive for complex petroleum wastes since the majority of biomarkers (hopanes, steranes, etc.) report in the analytically amenable saturate class fraction. One major advantage of this approach is that the alicyclic biomarkers, that do not biodegrade significantly under normal conditions, can be easily identified as conserved internal indicators (14,44). In some instances, where samples are sufficiently light to respond to GC analysis, target EI-GC-MS can avoid the prolonged cleanup requirements often associated with complex hydrocarbon wastes.

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Biomarker fingerprinting has historically been used extensively in petroleum geochemistry in the characterisation of marine oils in terms of source rock, genetic family, migration and maturation properties and general source depositional environment (17,21). A wide variety of biomarkers have been identified as being of use in the characterisation of crude oils and oil fractions (57-59), including pentacyclic hopanes (m/z 191), methylhopanes (m/z 205), steranes (m/z 217, 218) and diasteranes (m/z 217/259). Recently, biomarker fingerprinting has also been successfully used in contaminant source term identification (5) and in determining the extent of biodegradation undergone by spilled crude oil (14, 29). Volkman *et al.* (5), for example, determined the distribution of hopanes, methyl hopanes, steranes and diasteranes in a range of aquatic and sediment samples to confirm the presence of oil contamination and identify possible source terms (Figure 4).

Oil characterisation is not limited to the qualitative comparison of biomarker distributions. The ratio of one individual biomarker to another is also useful for fingerprinting purposes. Wang *et al.* (59) describe the identification of 53 biomarker compounds in Alberta Sweet Mix Blend oil, presenting mass fragmentograms and quantitative analysis of the hopane and sterane distributions. The authors note the greater abundance of both the pentacyclic C_{30}- and C_{29}-α,β-hopanes and the C_{27} and C_{29} steranes, and characterise the oil by calculating a range of triterpane/triterpane and sterane/sterane ratios. However, when a quantitative analysis of individual biomarkers is sought, it should be noted that the response factors of individual compounds can differ due to different fragmentation behaviour (60).

Butler *et al.* (30) used 17α(H),21β(H)-hopane (m/z 191), a pentacyclic alkane ubiquitous in petroleum oils, to evaluate the depletion of nC_{18}, phytane and total hydrocarbons (THC) in degraded Prudhoe Bay crude oil as a means of quantifying the extent of biodegradation undergone by beached oil from the Exxon Valdez spillage. Relative to the hopane, nC_{18} depletion increased from *ca.*65 % in the least degraded oil to > 95 % in the most degraded. Similarly, phytane and THC depletion also increased, from *ca.*25 % to *ca.*85 % and from < 10 % to *ca.*49 %, respectively. In contrast, the traditional weathering indicators, C_{18}/phytane and C_{17}/pristane, revealed little distinction between samples. Prince *et al.* (14) later confirmed that 17α(H),21β(H)-hopane was neither consumed nor produced during microbial degradation and was therefore a valid internal conserved mass-balance indicator.

A more thorough quantitative evaluation of the relative degree of biodegradation of crude oil samples using biomarker ratios was carried out by Pande *et al.* (61). The authors calculated the ratio of C_{30} 17α(H),21β(H)-hopane (the most abundant and degradation resistant pentacyclic alicyclic biomarker) to pristane and the ratio of bicadinane T (an uncommon plant-derived C_{30} hopane) to pristane, using the integrated peak areas in reconstructed ion chromatograms, in 7 oils. From least to most degraded oil, both parameters increased: the former from 0.5 to 0.7, 0.9, 4.4, 23.3, 22.0 and 22.6, and the latter from 3.6 to 5.8, 7.0, 37.4, 21.5, 168.0 and 194.0.

Wang *et al.*, (29) identified 8 tricyclic terpane, 4 tetracyclic terpane, 20 pentacyclic terpane and 15 sterane biomarkers in 22-year-old no.6 fuel oil spilled from the tanker Arrow. Concentrations of hopanes ranged from 5 to 203 mg g^{-1} of total solvent extractable material (1:1 hexane/dichloromethane and neat dichloromethane). C_{29} and C_{30} hopanes were found to be both the most abundant and degradation-resistant biomarkers; the C_{29}/C_{30} ratio was therefore considered to be the most

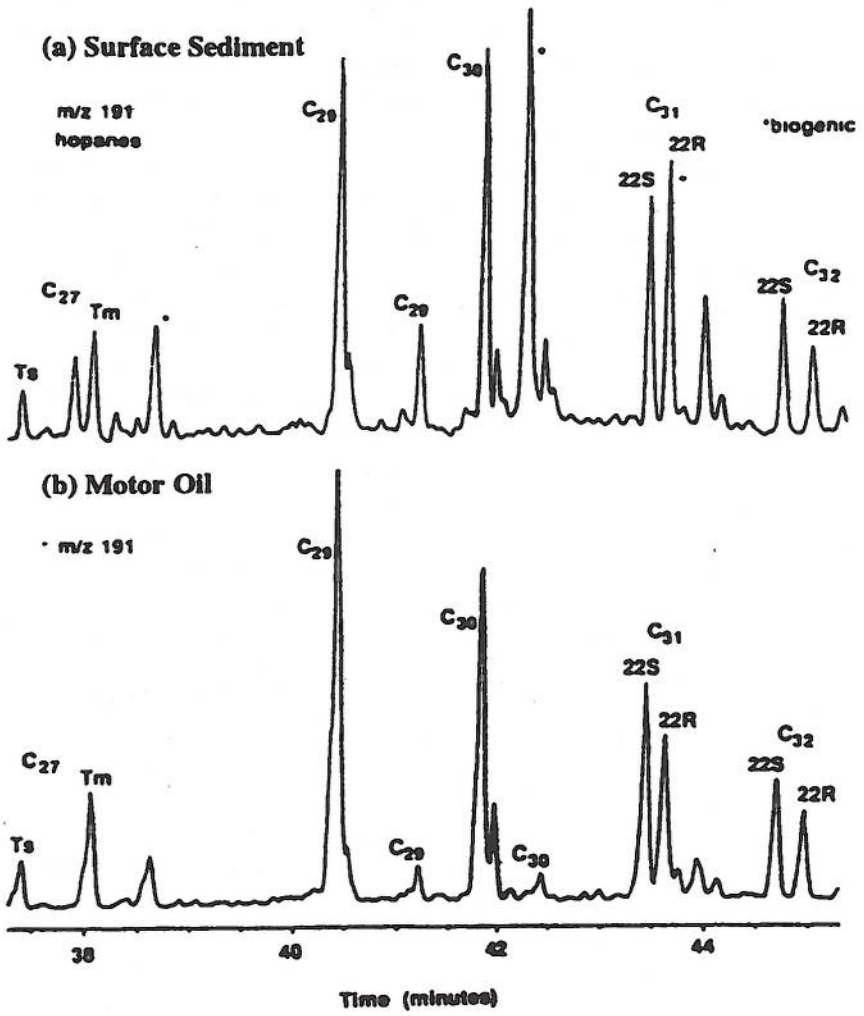


Figure 4. Mass fragmentograms for m/z 191 showing the similarity in hopane distribution between (a) an estuarine sediment sample, and (b) a common motor lubricating oil. (Adapted from Volkman *et al.* (5)).

reliable source indicator in this case. For the steranes, degradation resistance increased with increasing carbon number from C_{27} to C_{29}.

An understanding of the effects of biodegradation on these and other biomarkers is clearly of great importance if their utility as conserved internal signatures is to be widely accepted. This was investigated by Williams *et al.* (62), who observed slight degradation effects amongst C_{29} and C_{30} 17α(H) hopanes, no effects amongst remaining pentacyclics and steranes, and, in one severely degraded oil, complete demethylation of pentacyclic triterpanes. Wehner *et al.* (17) examined the in vitro effect of mixed and pure microbial populations on biomarkers within the various petroleum fractions. The fingerprint patterns of triterpanes and steranes showed no changes during biodegradation by mixed cultures, despite extensive saturates loss (including pristane and phytane) and concomitant polar and asphaltene accumulation, and were, therefore, useful in correlating degraded and non-degraded oils.

In rare cases, triterpane distributions cannot be used to draw conclusions on oil behaviour and source. For example, Chen *et al.* (63) used the steranes as indicators of crude oil maturity and depositional environment, observing an abundance of short chain steranes in mature samples and depositional variations in the carbon number distributions of monoaromatic steroids, in particular. In this case, pentacyclic terpanes were found to be less sensitive indicators of oil maturity and of greater use as measures of the salinity of depositional environment. In examining the

biodegradability of Gifhorn Trough crude oils, Teschner and Wehner (64) used the m/z 253 fragment ion peak associated with recalcitrant monoaromatised steranes (C27 -C29) as an internal reference against which peaks of biodegradable *n*-alkanes could be correlated. GC-MS patterns for tetracyclic steranes and pentacyclic triterpanes within these crude oils remained unchanged following biodegradation.

The fractionation behaviour of biomarkers during oil migration was investigated by Philp and Engel (65), who simulated the migration of a series of crude oils through successive glass columns of alumina, silica and montmorillonite. Although the relative degrees of class component fractionation remained consistent, the extent of fractionation observed was much greater through alumina. GC-MS analysis demonstrated that rearranged steranes migrated more rapidly than regular steranes, that the tricyclic terpanes migrated much more rapidly than the pentacyclic terpanes, and that for the tetracyclic terpanes, migration time increased with carbon number.

Given the depth of understanding that now surrounds the application of biomarker fingerprinting in fresh and weathered crude oil characterisation, it would seem advantageous for this approach to be put to similar use in the characterisation of heavy oil-contaminated land.

(ii) Conventional chemical ionisation (CI) GC-MS:

GC-CI MS is a nonfragmenting or soft ionisation method which has found marked utility in the analysis of samples featuring components less susceptible to fragmentation, particularly PAHs and polar heterocompounds (56). The distribution of parent ion peaks within such samples allows the analyst to elucidate the class component configuration within extremely complex waste streams, although the problem of corresponding parent ion peaks alluded to earlier should not be overlooked. For example, Pollard *et al.* (23) associated PAH and saturate class component distributions with weathered state in the characterisation of petroleum-contaminated sites, noting the prevalence of 3 and 4 ring alicyclics in the saturate fraction and pyrenes/ benzofluorenes, fluorenes and phenanthrenes/anthracenes in the aromatic fraction (Figure 5). In addition to providing information on the weathered state and remediation potential of waste-soil-groundwater matrices, this approach can tentatively used to infer the potential toxicity of the contaminants, since the majority of hazardous compounds are believed to reside in the highly aromatic, polar and asphaltenic fractions (66).

Douglas *et al.* (28) used PAH distributions by GC-MS of fresh and degraded diesel oil to elucidate sample source terms and quantitatively estimate biodegradation. Using C4-alkylated phenanthrene as a conserved analyte, the percent depletion of the oil was estimated from the ratio of C4 phenanthrene in the degraded oil to that in the source oil (or, if the source oil is anonymous, in the oil prior to the application of bioremedial treatment) and the percent of individual analyte depletion from the C4 phenanthrene concentrations and the individual analyte concentrations. However, in their study of a heavily weathered No.6 fuel oil, Wang *et al.* (29) concluded that the aromatic class components had undergone such alteration and degradation during weathering that, when used in isolation, their distribution patterns were an insufficient basis on which to draw conclusions regarding source terms. A quantitative evaluation of toxic PAH compounds revealed that naphthalene homologues were most easily degraded (over 95 %w/w in most samples), followed by phenanthrenes and dibenzothiophenes (*ca.*50 %w/w lost on average) with chrysene concentrations remaining constant (at approximately 190 mg g^{-1} of total solvent extractable material) due to their very low water solubilities and microbial recalcitrance. The ratios of alkylated chrysenes to alkylated phenanthrenes and dibenzothiophenes were used by the authors as a rough indication of weathered state, with most highly weathered samples displaying ratios of up to 6.7 and 55.0, respectively, compared to source oil ratios of 0.13 and 0.19.

Despite the reported unpredictability of aromatic biodegradation patterns (62), several authors have used conserved internal indicators within the aromatic fraction of petroleum wastes to assess the weathered state of the waste and the overall load of aromatic contaminants (28,54). Chen *et al.* (63) corroborated sterane-derived oil maturity data using the selective degradation of trimethylnaphthalenes and Williams *et al.* (62) observed that selectivity in the biodegradation of 2- and 3-ring aromatics was dependent upon ring number and length and position of alkyl substituents. Teschner and Wehner (64) perceived a decrease in the di- and trimethylnaphthalene concentrations during biodegradation of crude oils, although they reported that the biodegradation pattern followed

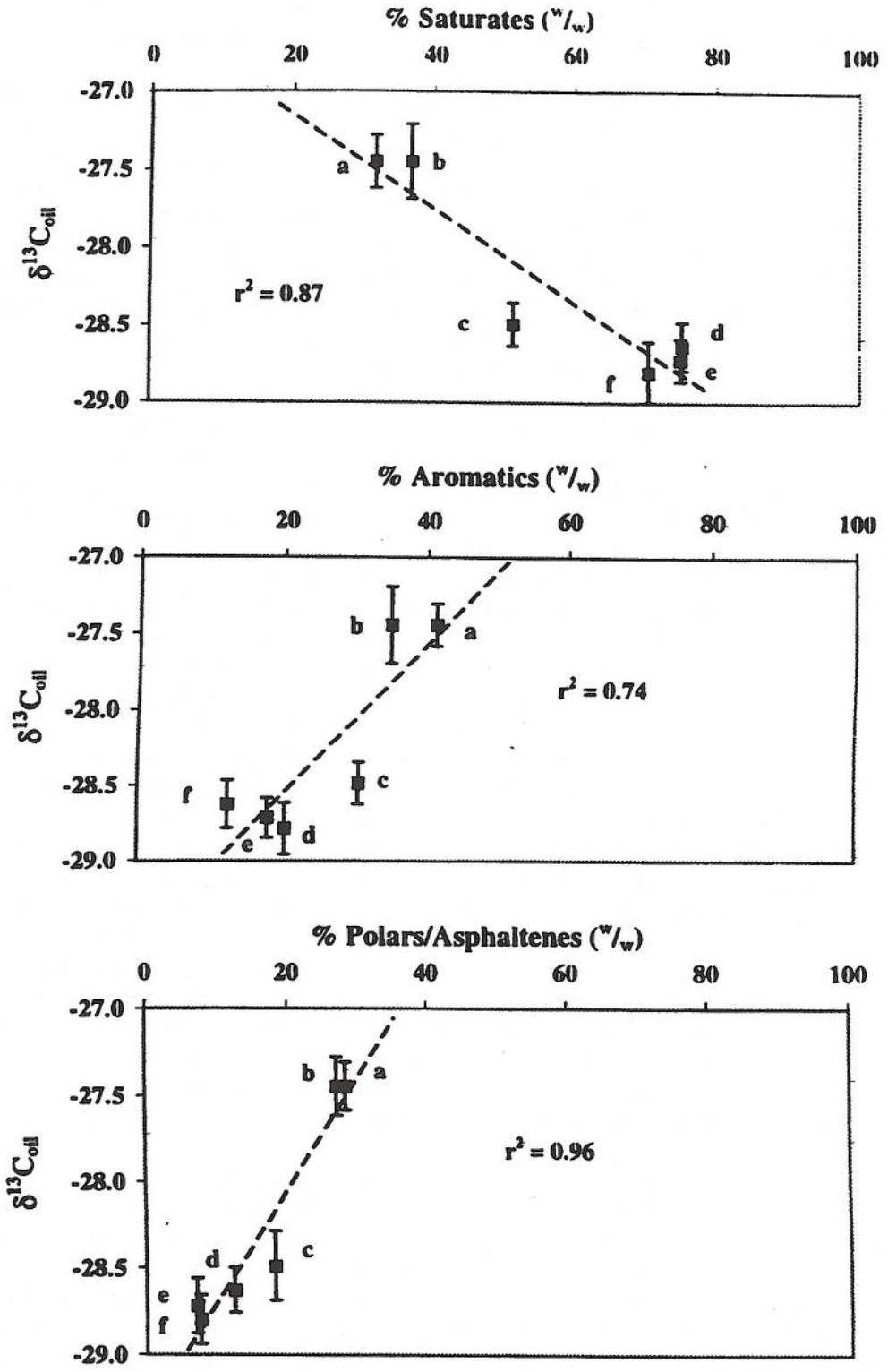


Figure 5. Variation of whole oil isotopic composition (δ^{13}Coil) with class abundance for bitumen (a), No.6 fuel oil (b), API separator oil (c), ballast oil (d), waxy distillate (e) and residue oil (f). The error bars represent the standard deviations of triplicate analyses. The linear correlation coefficient (r2) for each plot is shown.

was not influenced by the experimental conditions and that, therefore, explicit biodegradation of the aromatics could not be confirmed.

(iii) Fast atom bombardment mass spectrometry (FAB-MS):

FAB-MS is a soft ionisation technique. especially suited to the analysis of compounds of high molecular weight. Fan (67) reported the use of FAB-MS in the analysis of naphthenic acids isolated from various crude oils by preparative ion-exchange column chromatography. By obtaining the M^{-1} ion spectra of separated naphthenic acids in a triethanolamine (TEA) matrix, the author was able to determine carbon number distributions within various homologous series of carboxylic acids. The author also examined the relationship between the distribution of naphthenic acids within the selected oils and the oil source terms and degree of maturity, noting (i) the similarity of naphthenic acid distributions in oils from the same source, (ii) the abundance of low-molecular weight aliphatic carboxylic acids in immature oils, and (iii) that biodegradation complicates specific carboxylic acid distribution but not necessarily the bulk naphthenic acid characteristics. The ability of this technique to analyse distributions of higher boiling components of oily wastes suggests that it could make a useful adjunct to CI-GC-MS in extended characterisation of hydrocarbon wastes.

Generally, GC-MS analysis can provide a good deal of information on the underlying physico-chemical properties of petroleum contaminants, their potential source terms, perceived toxicological significance, the extent of weathering they have undergone and their possible means of treatment. Nevertheless, when the use of GC-MS analysis is curtailed, either due to the nature of the analyte (e.g., for complex, high-boiling species, or samples which have undergone extensive molecular transformation) or due to external issues such as excessive costs or prolonged sample preparation procedures, the need for alternative analytical approaches becomes a compelling priority.

CHARACTERISATION OF HYDROCARBONS BY STABLE CARBON ISOTOPE RATIO ANALYSIS

Bulk Fraction Isotope Analysis

The stable carbon isotopic composition of crude oils and their related products is essentially a manifestation of the myriad physical and biogeochemical processes that influence oil formation and refinery. The complex isotopic fractionation patterns induced by these processes result in characteristic $^{13}C/^{12}C$ ratios that can be interpreted to elucidate oil depositional environment, maturity, migration and biodegradation (e.g., 15,68). In practical terms, the technique involves combustion of samples to CO_2 followed by analysis by mass spectrometry to determine the relative amounts of $^{44}CO_2$, $^{45}CO_2$ and $^{46}CO_2$ present. After correcting for ^{17}O contributions, the ratio of $^{13}C/^{12}C$ is then determined, expressed in terms of $\delta^{13}C$ values which are measured in per mil (o/oo) and calculated relative to a standard Cretaceous peedee belemnite (PDB). Bulk isotopic analysis is used primarily for determining the $\delta^{13}C$ of whole oil samples or component class fractions. Individual compound $\delta^{13}C$ values can also be obtained by this approach, but this entails lengthy and unreproducible separation techniques and, with the advent of compound specific isotope analysis (discussed in the next section), is no longer commonly practiced (69).

Few studies have been devoted to evaluating the utility of the technique in hydrocarbon-contaminated land characterisation. Fan *et al.* (34) include a brief summary of the technique in a recent review of analytical methodologies commonly used for determining petroleum hydrocarbons in soil. They suggest that the primary advantage of the technique lies in the analysis of samples that have undergone extensive molecular transformation, since the whole oil isotope ratio usually remains largely unaffected and can therefore still be used as a correlation parameter. This was demonstrated recently by Hostettler and Kvenvolden (70), who used similarity in isotopic composition as further evidence of correlation between beached oils in Prince William Sound ($\delta^{13}C$ = -29.1 to -29.4 o/oo) and oil taken from the Exxon Valdez tanker ($\delta^{13}C$ = -29.2 o/oo). Other examples of the use of bulk IRMS in this capacity are almost exclusively limited to the characterisation of marine oils.

Following the division of the $\delta^{13}C$ values of 621 crude oil samples into three discrete ranges, Chung *et al.* (68) were able to distinguish four groups of oils based on the age and nature of oil source rock and the environmental conditions at, and prior to, oil generation. $\delta^{13}C$ values higher

than -23.5 o/oo were identified as marine shale oils of Miocene origin, those between -23.5 o/oo and -28.0 o/oo as either Mesozoic carbonate oils or terrestrial-derived deltaic oils of varying age, and those with $\delta^{13}C$ values of -28.0 o/oo to -32.0 o/oo as pre-Oligocene marine shale oils. The stable carbon isotope distribution of the asphaltene fraction of beach tars has also been used to evaluate possible natural and anthropogenic source terms (71). Although $\delta^{13}C$ data alone were insufficient to indisputably identify source terms, with the natural seepage oil $\delta^{13}C$ ranges (-22.51 to -23.20 o/oo) overlapping slightly with the $\delta^{13}C$ range of possible offshore anthropogenic sources (-22.10 to -22.85 o/oo), when the bivariant distributions of $\delta^{34}S$ and % (w/w) S were analysed simultaneously it was apparent that 81 % of beach tars originate from natural seepages. A similar study (16) of beach tar sources targeted the stable carbon isotope ratios of the bulk crude material and the aliphatic, aromatic and NSO (nitrogen-, sulphur- and oxygen-containing) component classes of the crudes. The stable carbon isotope signatures of these fractions matched those from samples taken from the sources of two major oil spills, although the speculative allocations of sourceterms to 16 other distinct signatures was indicative of the complexity of fingerprinting unknown source hydrocarbons.

Isotopic fingerprinting may be particularly useful for the characterisation of heavy oil-contaminated land since it does not rely upon GC resolution of waste components and therefore avoids the primary analytical constraint associated with refractory wastes. Whittaker and Pollard (72) investigated the potential utility of IRMS as a screening tool for sites featuring residual hydrocarbon contamination. Heavy oils containing a significant proportion of polar and asphaltenic compounds, were found to display isotope ratios 1.0 - 1.5 o/oo more positive than lighter oils exhibiting higher concentrations of isotopically lighter saturate class compounds. This suggests that the prevalence of either saturates or polars/asphaltenes can be inferred from unusually low (for saturates) or high (for polars/asphaltenes) whole oil $\delta^{13}C$. The nature of this relationship was confirmed by plots of oil $\delta^{13}C$ vs. saturate and polars/asphaltene content, which produced linear correlation coefficients (r^2) of 0.93 and 0.99, respectively (Figure 6).

These results are significant since information on unknown waste streams indicating a predominance of either saturates or asphaltenes would allow the use of bioremedial technologies, the success of which depends partly on the presence of waste constituents susceptable to microbial transformation.

A more discriminating means of isotopic fingerprinting is achievable by analysis of component class $\delta^{13}C$ values. Sofer (15) describes in some detail the limitations and capabilities of stable carbon isotope analysis of saturate and aromatic crude oil fractions, quantifying the isotopic relationship between the saturate and aromatic fractions in distinguishing between crude oils of marine and terrigenous origins (for terrigenous oils, $\delta^{13}C_{aro} = 1.12\,\delta^{13}C_{sat} + 5.45$; for marine oils, d13Caro = $1.10\,\delta^{13}C_{sat} + 3.75$).). Whittaker and Pollard (72) provided additional evidence of isotopic fractionation between oil classes, reporting a gradual isotopic enrichment of ^{13}C in heavy oil class fractions in the order: saturates < aromatics (≡ bulk oil) < polars < asphaltenes, with $\delta^{13}C_{sat}$ generally 0.2 - 2.5 o/oo lower than $\delta^{13}C_{pol}$ and $\delta^{13}C_{asp}$. This is in close agreement with the class isotopic differences observed by previous workers (15,16,18).

However, whilst characteristic isotopic fingerprints based on whole oil and class fraction $\delta^{13}C$ values may provide a more efficient means of differentiating between possible source terms than the measurement of whole oil $\delta^{13}C$ alone, the effect of microbial action on the $\delta^{13}C$ of class fractions must not be overlooked.

Stahl (18) examined the nutrient-enhanced bacterial degradation of crude oil over 42 days by determining resultant compositional and stable carbon isotope variations within component class fractions. Although the aromatic and heterocompound (NSO) fraction $\delta^{13}C$ values remained constant (at -27.6 o/oo and - 27.1 o/oo, respectively) throughout the experiment, the saturate fraction became isotopically heavier by 0.7 o/oo and the asphaltene fraction isotopically lighter by 1.1 o/oo. In general, it would appear that biodegradation causes the $^{13}C/^{12}C$ ratio to shift in favour of ^{13}C in the saturate fraction, to remain unchanged in the aromatic fraction, to shift in favour of the lighter ^{12}C isotope in NSO and asphaltene fractions, and to change in favour of ^{13}C in the bulk crude oil, although other workers have reported no variation in isotopic composition during biodegradation (64).

The effect of oil migration through various stationary phases on the stable carbon isotopic composition of oils and component classes has also been recognised. Bonilla and Engel (73) showed in simulated migration experiments that

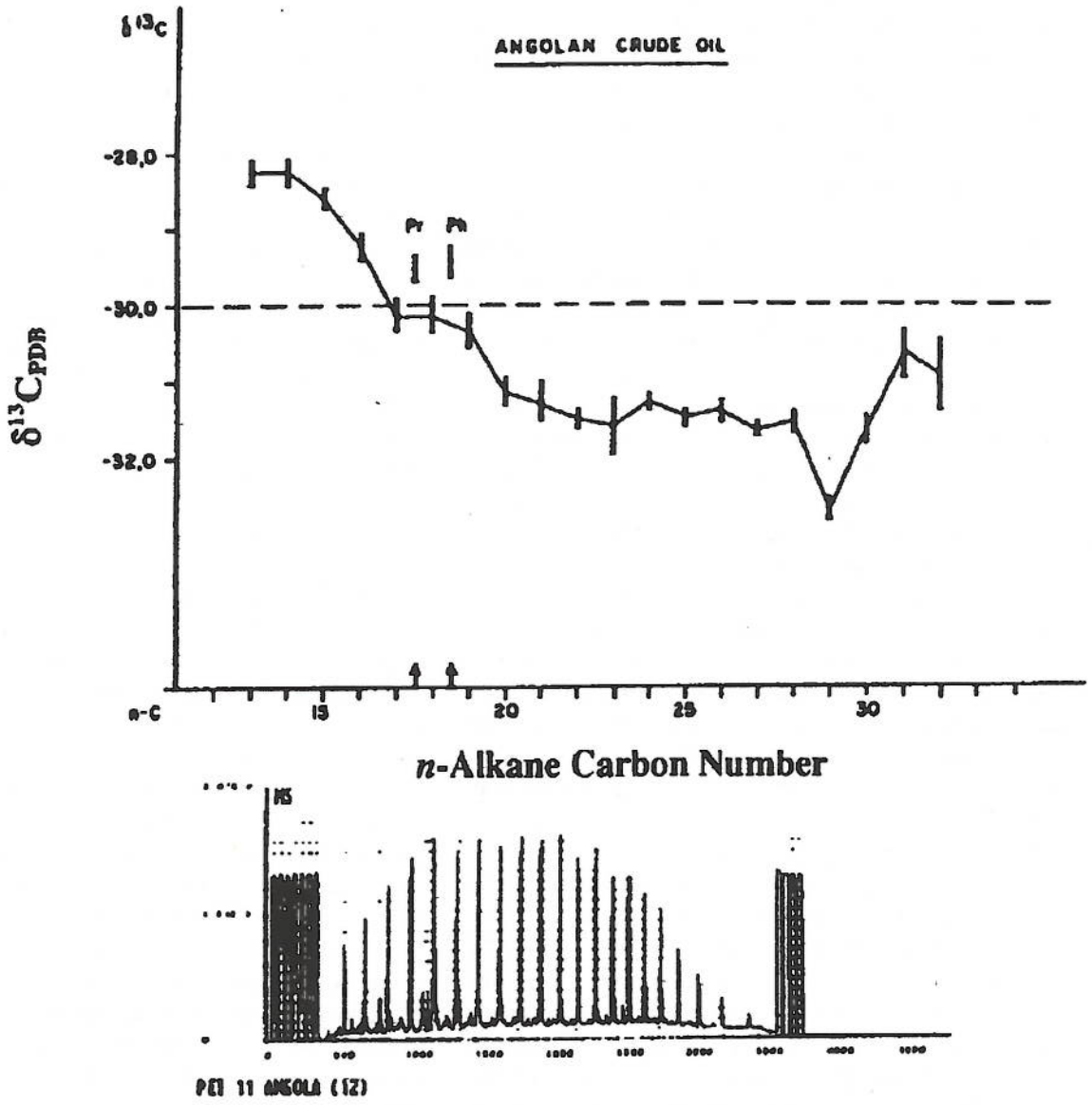


Figure 6. Isotopic fingerprint of a typical crude oil determined by GC-IRMS (GC-IRMS profile shown in lower diagram). Pr = pristane, pH = phytane. (Adapted from Mycke *et al.* (88)).

both the saturate and NSO fractions of selected crude oils became depleted in ^{13}C by up to 2.26 o/oo and 1.85 o/oo, respectively, as a result of 10 to 50 cm migration through coarse and fine sands (flow rate 0.13 ml min^{-1}: total time of elution *ca.* 12 hr), whilst the aromatic fraction ^{13}C content remained unaffected. The observed carbon isotope fractionation was attributed to the redistribution of *n*-alkanes during migration. Philp and Engel (65) modelled the migration of crude oils through various stationary phases under identical flow conditions as described above. Although little change was observed in $\delta^{13}C$ values for all four class fractions when a coarse (125 - 250 mm) quartz sand was used, addition of 10 % montmorillonite induced pronounced $\delta^{13}C$ depletions of 1.9 o/oo, 2.6 o/oo and 1.5 o/oo in the saturate, NSO and asphaltene fractions, respectively, after migration. For the saturate fraction, this was thought to be due to preferential migration of *n*-alkanes. The $\delta^{13}C$ values for isolated aromatic fractions remained

unchanged.

In practice, however, the most useful applications of bulk IRMS to studies of hydrocarbon-contaminated land have been limited to the analysis of soil gas CO_2, and in particular to the isotopic fractionation effects that occur as a result of hydrocarbon biotransformation. The most comprehensive of these studies was carried out by Aggarwal and Hinchee (74), who assessed the aerobic in-situ biodegradation of hydrocarbons at three jet fuel-contaminated sites by determining the stable carbon isotopic composition of CO_2 from contaminated and uncontaminated soil. Natural hydrocarbon degradation of soil organics resulted in high soil CO_2 concentrations (33 %) which were depleted in ^{13}C relative to uncontaminated samples by between 5.6 and 5.9 o/oo. $\delta^{13}C$ values of CO_2 from contaminated locations decreased by *ca.* 4 - 5 o/oo as CO_2concentrations increased up to 5 %, but did not change as CO_2 concentrations increased above this. Fresh jet fuel vapour ($\delta^{13}C$: -26 o/oo) injected into previously uncontaminated soil for 8 hours produced soil gas CO_2 $\delta^{13}C$ values of between -22.8 and 23.2 o/oo, against background soil gas CO_2 $\delta^{13}C$ of -18.1 to -18.7 o/oo. Thus, in this case, the authors concluded that microbial degradation of jet fuel resulted in the preferential fractionation of the heavier isotope into soil gas CO_2. Unfortunately, the isotopic and chemical composition of the spilled fuel could not be determined and so the authors could not attenuate the observed isotopic variations to changes undergone by the fuel itself. These results are in conflict with those reported by Stahl (18), who found that during the microbial degradation of crude oil the stable carbon isotopic composition of the head space gas above the reaction vessel decreased from +1.9 o/oo to -20 o/oo after 42 days, implying that the CO_2 produced during the reaction was richer in the lighter isotope. Since the former study was carried out under field conditions, with likely interference by plant respiration or atmospheric CO_2, a direct comparison of these two observations may not be entirely valid.

Suchomel *et al.* (75) revealed that soil gas taken at various depths from a site contaminated by a variety of organic solvents (predominantly trichloroethylene, 1,1,1-trichloroethane and degradation products) produced $\delta^{13}C$ values of between -23.27 and -24.70 o/oo, 4 - 6 o/oo lower than samples taken at the same depths from an uncontaminated area nearby. The authors cautiously interpreted this reduction to be evidence of in-situ biodegradation of the solvents, since the contaminated soil gas $\delta^{13}C$ are similar to that of CO_2 produced by the bacterial oxidation of petroleum in a previous study (18). These conclusions were somewhat tentative, however, because of a general lack of understanding of the broader issue of the effect of bacterial action on organic isotopic composition and, more specifically, to a paucity of data on either non-biodegradative sources of carbon in the soil gas or the isotopic composition of fresh solvent.

Compound Specific Isotope Analysis

The advent of compound specific isotope analysis (CSIA) for carbon in crude oils and crude oil fractions by gas chromatography-coupled isotope ratio mass spectroscopy (GC-IRMS), first developed by Sano *et al.* (76) and Matthews and Heyes (77), and technically examined recently by Eakin *et al.* (78), Ricci *et al.* (79) and Merrit *et al.* (80), has elevated characterisation of petroleum hydrocarbons to a level of sensitivity and detail unobtainable by conventional IRMS. The extensive, time-consuming and often unreproducible fractionation procedures required for reliable IRMS analysis of individual class components are removed, facilitating the fractionation and examination of samples in less than two hours. In particular, the now routine exploration of links between the isotopic composition of individual oil components and the physical and biogeochemical forces that govern them has led to significant developments in the understanding of marine oil evolution. The isotopic fingerprint of an Angolan crude oil shown in Figure 6 represents a typical GC-IRMS trace.

Bjorøy *et al.* (69) describe in detail the principal features of the instrumentation and report $\delta^{13}C$ values of individual *n*-alkanes and acyclic isoprenoid alkanes in standard mixtures and in two light North Sea crude oils. A comparison of $\delta^{13}C$ values obtained by GC-IRMS with those obtained by dual inlet IRMS for a standard mixture of even carbon number *n*-alkanes (nC_{12} - nC_{32}), pristane and phytane show good agreement, with the two techniques producing mean $\delta^{13}C$ values of within 0.3 o/oo in most cases. For a Statfjord reservoir oil, the $\delta^{13}C$ values became higher by 1.1 o/oo as the alkane boiling range increased between 50 °C and 100 °C, returning to the original value of -29.4 o/oo as the boiling range increased further to 150 °C and above. This effect was reflected in the

sequential shifting of $\delta^{13}C$ values from -29.6 o/oo to -28.8 o/oo and back to -29.4 o/oo as *n*-alkane carbon number increased from C_6 to C_{11} and then to C_{19}. In an Ekofisk reservoir oil the $\delta^{13}C$ values remained uniform over a similar range of carbon numbers and boiling ranges. A surprising phenomenon was the conflicting variations in isotopic composition of the acyclic isoprenoids and the *n*-alkanes between the two oils: the Statfjord and Ekofisk oils contained isoprenoids which were isotopically lighter and heavier, respectively, than their corresponding *n*-alkanes.

Elucidation of the factors that influence the isotopic compositions of oil components remains one of the key applications of CSIA. Bjorøy *et al.* (81) demonstrated that the isotopic compositions of isoprenoids and *n*-alkanes are influenced by a variety of factors, including anoxicity of depositional environment and type of source rock organic matter, and do not follow easily predictable trends. Thus, whole oil isoprenoids could either be isotopically heavier or lighter than the corresponding *n*-alkanes, depending on the oil source environment and genetic make-up. For increasing maturity, both whole oils and saturate fractions became isotopically heavier. For increasing *n*-alkane molecular weight, however, whole oils isotopic signatures tended to become isotopically heavier, whilst condensate samples became isotopically lighter. This suggests that co-eluted components within the strongly aromatic whole oil can exert an influence on observed $\delta^{13}C$ distributions. Moreover, marine-derived, terrestrially derived and lacustrine oil *n*-alkanes and isoprenoids were found to display disparate isotope ratios which exhibit contrasting dependencies on compound carbon number. This suggests that genetically-related oils display similar *n*-alkane isotopic patterns, in agreement with the results of Sofer *et al.* (82).

Clayton and Bjorøy (83) examined isotope ratios of individual compounds (including *n*-alkanes, isoprenoids, branched and cyclic alkanes, and aromatics) from four North Sea oils of variable thermal maturity and facies. The former parameter accounted for 50 - 90 % of the observed isotopic spread with a maturity-related ^{13}C-enrichment of 2 to 3 o/oo associated with progression from oil in the early generation stage through to the very early stage of cracking to gas. Low molecular weight aromatic hydrocarbons were noted to have high $\delta^{13}C$; interestingly, this was attributed to a larger component from a secondary terrestrial-influenced source. The effect of evaporation on the isotopic composition of the C_4 - C_{20} fraction of various oils and condensates has also been recently studied (84). No significant isotopic changes were observed between oil samples removed from an open beaker stored at 30 °C after 2, 4, 8, 24 and 48 hrs. This result implies that isotopic fractionation due to lengthy sample storage is negligible and that the isotopic composition of this fraction can serve as a useful correlation parameter.

CSIA has also been utilised to considerable effect in the determination of the source terms of oils and other organic matter. For example, Rieley *et al.* (85) used GC-IRMS to determine the source terms of lake sedimentary carbon. A correlation of the $\delta^{13}C$ values for *n*-alkanes extracted from lakeside tree leaves (-30.1 to -38.7 o/oo) with those obtained for sedimentary *n*-alkanes (-30.1 to -35.9 o/oo) suggests that the nearby trees may be a significant source of sedimentary lipids. From a study of $\delta^{13}C$ of extractable *n*-alkanes (C_{16} - C_{28}) from the Eocene Green River Formation (Colorado), Collister *et al.* (86) deduced that at least five distinct sources were required. Moreover, Bakel *et al.* (87) directly examined the relationship between differences in C_{19} - C_{24} *n*-alkanes $\delta^{13}C$ between water column particular organic matter and surface sediment and noted that the water column values depended on productivity. They suggested that the observed $\delta^{13}C$ differences of up to 1 o/oo were partly attributed to source effects, and partly to degradation processes in both water column and sediment.

In many cases, CSIA of oil biomarkers, as well as *n*-alkanes and isoprenoids, has provided a valuable additional set of correlation parameters. Bowler *et al.* (21) studied a variety of source depositional and maturity effects on nC_{12} - nC_{31}, pristane, phytane and 17α(H), 21β(H) hopane isotopic signatures in non-marine- and marine-derived oil saturate fractions. General trends observed were a depletion of ^{13}C with increasing carbon number (possibly due to contribution from a ^{13}C depleted biogenic source) and decreasing maturity, in support of some previously observed trends (81). The authors also provided further evidence that the disparity between isoprenoid and *n*-alkane isotopic composition varies amongst oils. Bjorøy *et al.* (20) investigated the changes in stable carbon isotope ratios of *n*-alkanes, isoprenoids and terpenoids (e.g., hopanes, homohopanes and norhopanes) with simulated maturation by hydrous pyrolysis. For kerogen source oils, an

increase in maturity and molecular weight was accompanied by a minor (1 - 3 o/oo) *n*-alkane and isoprenoid $\delta^{13}C$ shifts in favour of ^{13}C, whereas for a carbonate source oil, increasing maturity and molecular weight brought about a proportionate depletion of ^{13}C.

This was in agreement with Sofer *et al.* (82), who observed no change in the isotopic composition of individual *n*-alkanes of a variety of crude oils with oil maturity or biodegradation. The terpenoids, however, exhibit distinct isotopic fingerprints which changed significantly with increasing maturity towards those of other saturated hydrocarbons to become gradually more indistinguishable and, ultimately, ineffectual as diagnostic indicators. For example, the $\delta^{13}C$ values of 17α(H),21β(H) and 17β(H),21α(H) isomers of C_{29} - C_{30} triterpanes, biomarkers used recently in the evaluation of bioremediation treatment (14), shifted markedly during pyrolysis treatment from original values of between -36.3 to -43.2 o/oo to approximately -26.0 o/oo. The $\delta^{13}C$ shifts of other artificially matured terpenoids ranged from less than 1 o/oo to over 15 o/oo.

Schoell *et al.* (19) determined the carbon isotopic compositions of several biomarkers, including 28,30-bisnorhopane (-31.9 to -32.8 o/oo), C_{30} 17α(H) hopane (-25.8 o/oo), C_{27} cholestane (-25.9 o/oo), pristane (-26.3 o/oo) and phytane (-25.7 o/oo), in an immature, tar-like oil. Possible biological precursor organisms for 28,30-bisnorhopane, a distinctive biomarker often found to be the most ^{13}C-depleted compounds in marine-derived organic matter, were chemoautotrophic bacteria distinct from those of the other hopanes in that they appeared to preferentially utilise ^{13}C-depleted substrates. The isotopic similarity of the remaining isoprenoids (C_{29} - C_{35} hopanes, C_{27} steranes, pristane and phytane) is indicative of a common biological origin. Mycke and Leplat (88) obtained $\delta^{13}C$ values for a range of crude oil biomarkers, including pristane, phytane, tricyclic terpanes, hopanes and steranes, to draw conclusions on oil depositional environments and match oils from the same source rock.

The Role of CSIA in the Analysis of Terrestrial Hydrocarbon Contamination

The depth of research summarised in the preceeding section illustrates that as an analytical approach, CSIA has become a mainstay of petroleum research. However, like bulk IRMS, the potential adaptation of CSIA to the interrogation of oils in wider context, though recognised, has not yet crystallised. Despite this, parallels exist between the needs of the geochemist characterising a marine oil and the needs of the remediation expert characterising petroleum-contaminated land which suggest that if the uncertainties generated by such an extension can be embraced, the successful adaptation of GC-IRMS fingerprinting to the elucidation of source terms and weathering at refractory or heavy oil-contaminated sites is entirely possible.

For this to happen, an understanding of the way in which the various post-depositional processes affect the isotopic composition of individual compounds, and how observed isotopic changes are linked to changes at a molecular level, must be developed. For weathered heavy oils, there is a special need to investigate the isotopic behaviour of biomarkers, since this may facilitate a more reliable means of elucidating, and in some instances quantifying, the extent of weathering undergone. Primarily, this entails a rigorous examination of the isotopic fractionation that occurs as a result of microbial transformation. Similarly, for elucidation of the source terms of anonymous hydrocarbon waste streams, it is important not only to establish the presence of unique signature isotope ratios (44), but also to define how and why these signatures vary in-situ with time. Methods for addressing these matters are currently under development by Whittaker and Pollard (22,52).

Perhaps the most important factor influencing the success of CSIA in the determination of petroleum contaminants relates to the inherent limitations of all GC-coupled techniques when applied to weathered hydrocarbon wastes featuring significant UCM. Adequate resolution of waste components is a primary necessity if accurate, reproducible compound $\delta^{13}C$values are to be obtained. The GC-IRMS trace of a typical weathered heavy oil shown in Figure 7b illustrates this point well. This is especially so for alicyclic saturate biomarkers, which are usually present in low abundance. In some cases, physical separation of class components prior to GC-IRMS analysis is useful for isolating specific analytes of interest. For example, several authors have made use of molecular seives for separating *n*-alkanes from branched/cyclic alkanes in the determination of biomarker isotope ratios (19,82). Unfortunately, however, these methods are unable to remove UCM material and therefore are of limited usage for improving the resolution of heavy or

weathered hydrocarbon wastes.

In such situations, a variety of background subtraction techniques can be employed to mitigate the presence of baseline rise in GC-IRMS analyses (84,87). These include the introduction of internal standard compounds of known $\delta^{13}C$ onto the UCM, the use of computerised background subtraction techniques (82) and, if single components can be isolated, the selective, parallel analysis of samples by bulk IRMS. Sofer *et al.* (82) found that the difference between the isotopic composition of *n*-alkanes obtained with and without computerised baseline subtraction was most significant (up to 4 o/oo) in the C_{20} - C_{24} range for oils with a sizeable UCM. Bakel *et al.* (87) compared the d13C values of *n*-alkanes obtained by GC-IRMS and bulk IRMS. They observed a regular difference between the two techniques of 0.1 - 0.5 o/oo, with GC-IRMS-obtained values consistently lower. For peaks residing on UCM humps, this difference increased in some cases by up to 2 o/oo, although for the majority of peaks, the UCM did not cause $\delta^{13}C$ shifts of greater than 0.5 o/oo. The authors also reported no significant changes in $\delta^{13}C$ of *n*-alkanes during column silica gel-fractionation. This is particularly relevent to the analysis of residual hydrocarbon contamination, where sample cleanup by column fractionation is often necessary.

It is clear that if both bulk IRMS and GC-IRMS are to become of genuine use as tools for analysing petroleum hydrocarbons in the soil environment, emphasis must be placed on fortifying the technical aspects of CSIA alluded to above. A recent development that may facilitate the routine use of CSIA in this context is that of GC-MS-IRMS, which combines GC separation of analytes with simultaneous analysis by IRMS and EI- or CI-MS. (89,90). This technique holds considerable promise for the many areas of science that currently utilise isotopic analysis as a means of investigation. If these requirements can be fulfilled, it may be that isotopic fingerprinting of bulk organic extracts, component classes and biomarkers will become of considerable use in elucidating the source terms and weathered state of oily wastes in the soil environment.

SUMMARY

Environmental quality criteria are becoming increasingly stringent. One effect of this has been to accentuate the constraints and limitations which affect the integrity of the analytical techniques used for their measurement. For refractory hydrocarbon contaminants in the soil environment, the analytical constraints are exacerbated to such an extent that effective characterisation of the waste-soil-groundwater matrix necessitates the use of a suite of analytical techniques, varying in analytical capability, cost and operating time. The use of screening techniques to preliminarily delineate contaminants is of considerable importance in the wider site investigation process. The novel application of bulk IRMS may provide a useful adjunct to conventional GC-based screening techniques since it avoids the need for chromatographic resolution of refractory contaminants.

The use of conventional GC-MS for the detailed characterisation of waste extracts generally entails considerable time and expense, particularly for mixtures of highly weathered petroleum products comprising a tremendous diversity of individual (and largely unresolvable) chemical constituents. Switching the focus of analysis to extended individual, analytically-accountable biomarkers may allow the source terms of, and extent of weathering undergone by, refractory waste mixtures to be elucidated in a cogent, cost-effective manner. This may be achieved by determining characteristic biomarker distributions by EI GC-MS and by measurement of characteristic biomarker $^{13}C/^{12}C$ ratios by GC-IRMS. The latter technique has been used widely in the elucidation of marine oil source terms and post-depositional characterisation to the monitoring of alteration processes. Its successful adaptation to the characterisation of refractory wastes at heavy oil-contaminated sites may enable site investigators to assess more accurately contaminant type and toxicity, possible contaminant source terms and appropriate courses of remedial action.

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CHARACTERISATION OF REFRACTORY WASTES AT HYDROCARBON-CONTAMINATED SITES—II. SCREENING OF REFERENCE OILS BY STABLE CARBON ISOTOPE FINGERPRINTING

Martin Whittaker,[a]* Simon J. T. Pollard,[b]† Anthony E. Fallick[c] & Tom Preston[c]

[a]*Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh EH9 3JJ, UK*
[b]*Aspinwall and Company, Consultants in Environmental Management, 13 Melville Street, Edinburgh EH3 7PE, UK*
[c]*Scottish Universities Research and Reactor Centre, East Kilbride, Glasgow G75 0QF, UK*

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Abstract

The preliminary evaluation of stable carbon-isotope ratio mass spectrometry (IRMS) as a novel, alternative method for screening residual heavy or weathered petroleum wastes is presented. Seven well-characterised middle-to high-boiling range oils (predominant boiling range: 150–600°C) and their isolated class fractions were analysed by IRMS. Whole oil $\delta^{13}C$ values (which express the ratio of ^{13}C to ^{12}C within each sample) showed a small but significant decrease with decreasing oil asphaltene content, from −26.8‰ for heavier oils to −28.8‰ for lighter, predominantly paraffinic oils. In agreement with the conventionally observed trend, $\delta^{13}C$ values of isolated class fractions were found to increase in the following order: $\delta^{13}C_{sat}$ ($\approx\delta^{13}C_{oil}$) $< \delta^{13}C_{aro} < \delta^{13}C_{pol} < \delta^{13}C_{asp}$, with $\delta^{13}C_{sat}$ up to 2.5‰ more negative than $\delta^{13}C_{pol}$ and $\delta^{13}C_{asp}$. However, this variation was much less pronounced for the heavier oil samples. As a result, isotope type curves exhibited a clear distinction between heavier oils, which produced much flatter type curves, and lighter oils, for which type curves were characteristically sloping. From these preliminary results, IRMS would appear to have application as a potential method for identifying a predominance of asphaltene class fractions in residual hydrocarbon wastes and for distinguishing between heavy and light oily contaminants. © *1997 Elsevier Science Ltd. All rights reserved.*

Keywords: Stable carbon isotopes, contaminated land, heavy oils, type curves.

INTRODUCTION

The environmental analysis of waste residues at hydrocarbon-contaminated sites often presents substantial technical difficulties because of enormous waste complexity (Pollard *et al.*, 1994). By far the most common tool for screening hydrocarbon wastes is gas chromatography with flame ionization detection (GC–FID) (Fan *et al.*, 1994). Unfortunately, GC–FID is often restricted at sites featuring non-volatile, weathered oils, since sufficient analytical recovery and adequate resolution of the complex mixtures encountered cannot be readily achieved (Pollard *et al.*, 1992) (e.g. Figure 1). Refractory residues in neat soil extracts are invariably non-volatile and are generally only removed from the GC column following prolonged heating at elevated temperatures. Isolation and analysis of the lower boiling saturate class fraction can assist characterisation, although for extremely heavy or weathered oils, even extensive sample fractionation cannot always provide a suitably refined analyte. Hence, two analytical strategies have been developed over recent years for characterising oily wastes. The first focusses on improved methods of analytical clean-up and specialised chromatographic separation and detection procedures. The second addresses the waste matrix as a whole and seeks to provide information relating to the full range of compounds encountered in such samples. An example of the latter approach, with which this paper is concerned, is thin layer chromatography with flame ionisation detection (TLC–FID) (Pollard *et al.*, 1992; Whittaker & Pollard, 1994), which is now routinely used in contaminated soil analysis and has proved a valuable tool for assessing the broad composition of complex oils extracted from contaminated sites.

An additonal technique that has been widely used to examine and classify crude oils, petroleum products and tars in the marine environment for over 20 years is stable-carbon-isotope ratio mass spectrometry (IRMS) (Silverman, 1971; Stahl, 1977, 1980; Schoell, 1984; Sofer, 1984; Wehner *et al.*, 1986). This technique appears to be suited to the analysis of heavy or weathered oils because it can provide useful information on the bulk sample without the requirement for analytical clean-up. IRMS

*Present address: Golder Associates Ltd, 2180 Meadowvale Blvd, Mississauga ON, Canada L5N 5S3.
†To whom correspondence should be addressed at: Scottish Environment Protection Agency, Head Office, Erskine Court, Castle Business Park, Stirling FK9 4TR, UK.

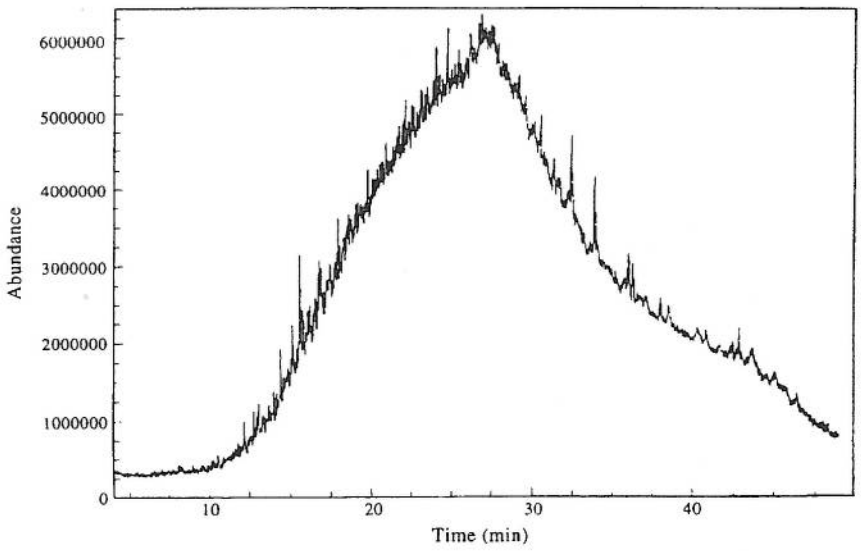


Fig. 1. GC profile of a contaminated soil extract showing a typical unresolved complex mixture.

entails quantifying the extent to which the stable isotopes of carbon (^{12}C and ^{13}C) in organic samples have fractionated during biological, chemical and physical transformation processes. Variations in isotope ratio between and within different crude oil families, and between individual chemical classes represented within an oil (specifically, the saturate, aromatic, polar and asphaltene (SAPA) class fractions), have been examined by many authors and are well documented, as have the effects of external factors, such as oil migration, maturation and biodegradation (e.g. Stahl, 1980; Schoell, 1984; Sofer, 1984; Philp & Engel, 1987). More recently, stable-carbon IRMS has been used to monitor biodegradation of contamination by jet fuel through analysis of soil gas CO_2 (Aggarwal & Hinchee, 1991) and to obtain information on the subsurface distribution of spilled solvent (Suchomel *et al.*, 1990).

To the present authors' knowledge, no studies have yet evaluated the utility of the technique in the direct analysis of terrestrial petroleum contamination. Given the range of constraints that currently afflict this area of environmental analytical chemistry, it seems appropriate in the first instance to investigate the potential utility of the technique as a means of screening heavy or weathered oils of the type that exist as residual contamination in the soil environment. This approach has potential use for contaminated soils, because there is evidence that recalcitrant polar and asphaltene class fractions become prevalent in heavy-oil-contaminated soils (Westlake *et al.*, 1974; Bossert & Bartha, 1984) and that the dominance of such fractions in oils may be evident from the oil isotopic composition (Silverman, 1971; Schoell, 1984; Whittaker *et al.*, 1995). Furthermore, by using characteristic stable-carbon-isotope values as a form of oil 'fingerprint', similar to that used for identification of marine oils and beach tars (Macko & Parker, 1983; Kvenvolden *et al.*, 1995), it may be possible to distinguish between possible sources of oily wastes at contaminated land sites.

The objective of the work described below was to assess the feasibility of IRMS for the characterisation of a set of heavy oils derived from the same crude-oil family. This work is an essential pre-requisite to the analysis of soil extracts, because of the need to evaluate the sensitivity and precision of the technique for genetically related oils. Six heavy oils (predominant boiling ranges, 50–>600°C), known to originate from North Sea crude oils, were chosen to represent typical terrestrial oil contaminants encountered in the UK (see Table 1). A seventh sample, an acid tar waste, represented an authentic heavy oil of unknown origin extracted from contaminated soil at a former lubricating oil recovery plant.

The SAPA class fraction distribution within each oil was determined gravimetrically following column fractionation (Whittaker & Pollard, 1994). Whole oil and individual class fraction $\delta^{13}C$ values (expressing the ratio of ^{13}C to ^{12}C) were then obtained to examine the correlation between oil stable carbon isotope ratio and oil class fraction distribution. Isolated saturate class fractions were also analysed by GC–FID to allow observed isotopic differences to be associated with differences in chemical composition.

EXPERIMENTAL

In this paper, the term 'class fraction' makes collective reference to all saturate, aromatic, polar or asphaltene compounds; the term 'class component' refers to the individual compounds that constitute each class fraction.

Column fractionation and isotope ratio mass spectrometry

Acid tar samples were first Soxhlet-extracted from soil subsamples (*ca* 30 g) for 16 h using HPLC-grade dichloromethane (DCM) (150 ml). DCM extracts were then reduced overnight at ambient temperatures in a

Table 1. Representative heavy oil properties, class fraction distribution and isotope ratios

Oil	Source description	Approximate boiling range (°C)	$\delta^{13}C_{oil}$[b] (‰)	Class distribution[a] and summarised isotope data[b]								Total calculated[c] $\delta^{13}C_{oil}$(‰)
				Saturates		Aromatics		Polars		Asphaltenes		
				%(w/w)	$\delta^{13}C_{sat}$[b]	%(w/w)	$\delta^{13}C_{aro}$[b]	%(w/w)	$\delta^{13}C_{pol}$[b]	%(w/w)	$\delta^{13}C_{asp}$[b]	
Acid tar waste	Contaminated site	200–>700	−26.8(0.3)	60.2	−26.9(0.0)	4.6	−26.4(0.0)	8.7	−26.9(0.2)	26.5	−26.7(0.1)	−26.8(0.0)
Bitumen oil	North Sea, heavy oil blend	200–>700	−27.4(0.2)	31.7	−27.4(0.1)	41.3	−27.3(0.3)	11.0	−27.2(0.0)	16.0	−27.3(0.1)	−27.3(0.1)
No.6 fuel oil	North Sea, heavy oil blend	150–600	−27.4(0.2)	36.7	−27.4(0.1)	34.9	−27.3(0.1)	12.6	−27.1(0.1)	15.8	−27.3(0.5)	−27.3(0.1)
API[d] separator oil	Refinery process run-off stream	20–400	−28.5(0.3)	51.3	−29.0(0.2)	30.7	−27.8(0.2)	14.9	27.7(0.1)	3.1	−26.7(0.0)	−28.4(0.1)
Ballast oil	Ship's discharge, variety of products	20–400	−28.6(0.1)	75.3	−28.8(0.0)	12.3	−27.8(0.1)	8.1	27.6(0.3)	4.3	−27.1[e]	−28.5(0.1)
Waxy distillate	North Sea, light oil blend	100–500	−28.5(0.6)	75.1	−28.8(0.0)	17.9	−27.9(0.0)	6.7	−27.9(0.3)	0.3	−27.4(0.4)	−28.6(0.1)
Residue oil	Mixed North Sea	150–600	−28.8(0.1)	71.8	−29.0(0.1)	20.7	−28.2(0.1)	5.9	27.7(0.3)	1.6	−27.7[e]	−28.7(0.1)

[a]Determined by adsorption column chromatography.
[b]Isotope ratios quoted are based on triplicate analyses (figures in brackets refer to standard deviations).
[c]Sum of weighted class fraction isotope ratios (figures in brackets refer to difference from measured value).
[d]American Petroleum Institute.
[e]Single measurement only.

forced draught fume cupboard. The experimental details of the column fractionation have been reported previously (Whittaker & Pollard, 1994). Conversion of whole oil and oil class fraction subsamples (*ca* 5 mg) to CO_2 for isotopic analysis was accomplished by dry combustion (850°C, 6 h) in sealed, evacuated quartz tubes containing excess fired cupric oxide as an oxygen source. Isotope ratio data were obtained on a SIRA 10 isotope ratio mass spectrometer (VG Micromass 602D) and are reported relative to the standard Pee Dee belemnite (PDB) with corrections made for ^{17}O contributions.

Isotope ratios are expressed in terms of $\delta^{13}C$ values, which are reported in per mil (‰), and calculated relative to the standard PDB, according to the following relationship: $\delta^{13}C = (R_S/R_R - 1)1000‰$, where R is the ratio of $^{13}C/^{12}C$ in the sample (R_S) and the reference (R_R). The reproducibility of the individual isotopic measurements, determined through repeated analysis of a laboratory standard graphite sample, was $\pm 0.05‰$ (1σ); for each sample, the isotopic composition was determined in triplicate, with standard deviations generally less than 0.3‰.

Gas chromatography with flame ionisation detection (GC–FID)

Analysis by GC was performed on an AI Model 93 gas chromatograph equipped with a 25-m, high-temperature aluminium-clad phenyl:siloxane carborane (5:95) column (SGE HT5) with 0.53 mm i.d. and 0.15 micron film thickness. Oil saturate fractions were made up to a concentration of approximately 10 mg ml^{-1} in DCM. Aliquots 2 μl were injected in splitless mode. A linear temperature gradient was employed, the column temperature being held at 75°C for 2 min following injection, ramped at 10°C min^{-1} to 350°C, then held at this temperature for a further 10 min. The injector and detector temperatures were set at 400°C. A helium carrier gas was used at a flow rate of 7.5 ml min^{-1}. *n*-Alkane peaks were identified by comparing sample GC–FID retention data with that obtained for a standard solution of five *n*-alkanes containing C_{15}, C_{20}, C_{25}, C_{30} and C_{40}.

RESULTS AND DISCUSSION

Column fractionation

Results of the SAPA column fractionation (Table 1) show that the ballast oil, waxy distillate and residue oil are predominantly paraffinic, containing > 70% w/w saturates and < 13% w/w combined polars and asphaltenes. The API separator oil (51.3% w/w saturates, 18.0% w/w combined polars and asphaltenes), No. 6 fuel oil and bitumen (both < 40% w/w saturates and > 25% w/w polars and asphaltenes) exhibit sequentially higher polar and asphaltene contents, characteristic of heavier oils (Altgelt & Boduszynski, 1994). The acid tar samples, despite the predominance of the saturate class fraction (60.2% w/w), were the heaviest of the oil samples, containing the largest polar/asphaltene fraction (35.2% w/w).

GC–FID

The API separator oil, ballast oil and No. 6 fuel oil GC profiles (Fig. 2) are characteristic of heavy diesel range organics, displaying a range of *n*-alkanes centred on the C_{18}–C_{22} peaks with asymmetric tails of heavier *n*-alkane peaks up to *ca* C_{30}. The residue oil profile is similar to these, although higher *n*-alkane peaks are more prominent and there is a slight baseline rise signifying the presence of unresolved complex material (UCM) (Gough & Rowland, 1990). The UCM is the dominant feature of the waxy distillate chromatogram, which bears a close resemblance to that of typical lubricating oil profiles and includes a significant amount of high-boiling components ($> C_{30}$). For the bitumen oil and acid tar sample, GC–FID failed to resolve any saturate class components, despite lengthy and repeated sample clean-up. This is believed to be due to the extraordinarily complex and high-boiling nature of these oils. These chromatograms illustrate some of the problems encountered during GC-FID screening of high-boiling, extremely complex waste oil samples and reinforces the need for alternative techniques capable of assuaging these limitations.

Isotope ratio mass spectrometry (IRMS)

$\delta^{13}C$ values for each whole oil ($\delta^{13}C_{oil}$) and class fraction (e.g. $\delta^{13}C_{sat}$) are given in Table 1. Individual $\delta^{13}C_{oil}$ values ranged between −26.8‰ and −28.8‰ and were found to increase (i.e. become less negative) with increasing combined polar and asphaltene contents and an elevation in the upper end of oil boiling range. Thus, the acid tar ($\delta^{13}C_{oil} = -26.8‰$) bitumen (−27.4‰) and No. 6 fuel oils (−27.4‰) contained higher proportions of the ^{13}C isotope than the API separator oil (−28.5‰) ballast oil (−28.6‰) waxy distillate (−28.5‰) and residue oil (−28.8‰) Calculated values of $\delta^{13}C_{oil}$, determined from the weighted isotopic contribution of each class fraction, were in close agreement with the measured $\delta^{13}C_{oil}$ values. With such a small variation in $\delta^{13}C_{oil}$, it is essential to establish the statistical validity of the observed trend in isotope ratio. This was achieved through extensive repeat analysis of samples and a thorough statistical examination of results through analysis of variance (ANOVA) (Miller & Miller, 1988).

The variance of $\delta^{13}C_{oil}$ within each oil sample is shown in Table 2. Averaging these values produces an average within-sample variance (σ^2_1) of 0.079. The between sample variance (σ^2_2), calculated from the standard deviation of the sample means (i.e. the average $\delta^{13}C_{oil}$ values for each oil) from the overall mean $\delta^{13}C_{oil}$ value (−28.02‰) was found to be 1.77. To test whether this variance was significantly larger than the within sample variance of 0.07, a one-tailed *F*-test was employed (Miller & Miller, 1988). If the values differ significantly, the calculated value of F (σ^2_2/σ^2_1) is larger than the critical value of $F_{6,12}$ (determined with reference to the appropriate statistical table; 6 and 12 refer to the number of degrees of freedom of σ^2_1 and σ^2_2, respectively) In this case, the critical value of $F_{6,12}$ is 2.996 ($p = 0.05$). Since the calculated value was

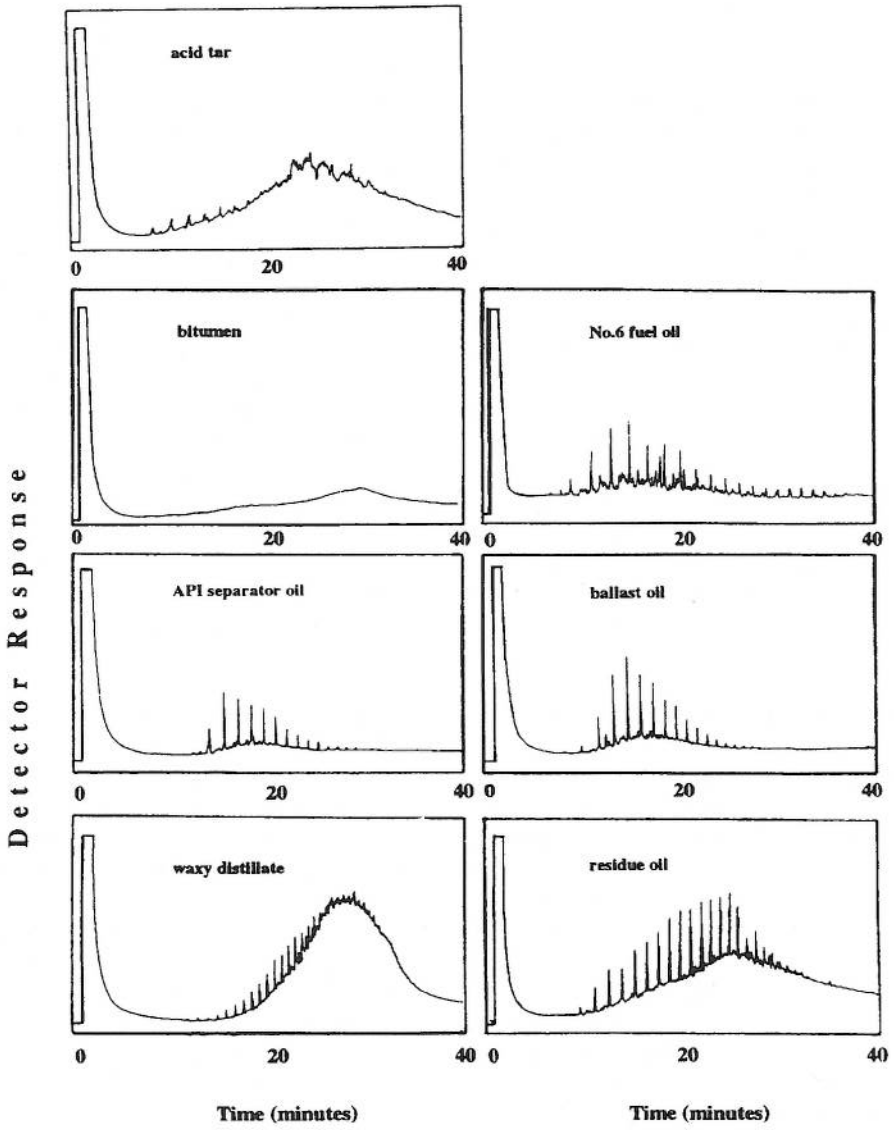


Fig. 2. GC–FID profiles of representative heavy oil saturate fractions. Peak identification was achieved using external *n*-alkane standards.

determined to be 22.41, it is concluded that the $\delta^{13}C_{oil}$ values do differ significantly between oil samples.

To identify the reason for the significant ANOVA result, the differences between $\delta^{13}C_{oil}$ values were compared with a quantity referred to as the least significant difference. This is given by

$$s\sqrt{(2/n)} \times t_{h(n-1)}$$

where s is the within sample value of σ_1 ($\sqrt{0.07}$), n is the number of replicate measurements for each oil sample ($n=3$) and $t_{h(n-1)}$ is the t-test value for the number of degrees of freedom of σ_1 ($t_{12}=2.18$) (Miller & Miller, 1988). Thus, the least significant difference here is 0.474. Comparing this value with the differences between the mean $\delta^{13}C_{oil}$ values suggests that the acid tar isotope value is significantly different from the bitumen and No. 6 fuel oil isotope values, which are in turn significantly different from the residue, waxy distillate, ballast oil and API separator oil isotope values. This strongly suggests that the observed shift in isotopic signal can be legitimately attributed to differences in oil characteristics rather than random or analytical error in repeat analyses.

A comparable range of $\delta^{13}C_{oil}$ values was noted in a previous study of isotopic variations between different petroleum distillation fractions of a single crude oil (Silverman, 1971). Although no chemical analysis of the crude oil or the respective distillation fractions was reported, $\delta^{13}C_{oil}$ values were found to be highest (*ca* −22‰) for the 115°C fraction (equivalent to a carbon number of approximately C_6), gradually decreasing to a minimum value (*ca* −24‰) in the 425–450°C range (roughly equivalent to C_{40}). Above this, $\delta^{13}C_{oil}$ increased continuously with increasing boiling temperature. A survey of previous studies involving the use of isotope ratios in the characterisation of oil samples

Table 2. Individual isotope ratio measurements and analysis of variance between $\delta^{13}C_{oil}$ values

Oil fraction	Acid tar waste	Bitumen oil	No. 6 fuel oil	API separator oil	Ballast oil	Waxy distillate	Residue oil
Whole oil	−26.89, −26.77	−27.44, −27.60, −27.21	−27.61, −27.40, −27.32	−28.46, −28.76, −28.26	−28.72, −28.53	−28.97, −28.67, −27.86	−28.96, −28.72, −28.71
Saturates	−26.85, −26.88	−27.32, −27.44, −27.48	−27.35, −27.49, −27.44	−29.15, −28.86,−28.92	−28.83, −28.87, −28.83	−28.71, −28.93, −28.60	−29.07, −28.88
Aromatics	−26.42, −26.36	−27.68, −27.15, −27.09	−27.51, −27.33, −27.07	−27.97, −27.59, −27.88	−27.75, −27.85, −27.93	−27.90, −27.89, −27.93	−28.33, −28.09, −28.11
Polars	−26.77, −27.04	−27.10, −27.13, −27.17, −27.20	−27.11, −27.14, −26.99, −27.07	−27.69, −27.76, −27.67	−27.65, −27.12, −27.82, −27.66	−28.14, −27.65, −27.78	−27.98, −27.42, −27.55
Asphaltenes	−26.63, −26.67	−27.29, −27.39	−27.70, −26.98	−26.66, −26.67	−27.14	−27.72, −27.09	−27.72
Mean $\delta^{3}C_{oil}$, S.D	−26.83, 0.08	−27.42, 0.20	−27.40, 0.15	−28.79, 0.25	−28.63, 0.14	−28.50, 0.57	−28.80, 0.14
Within sample variance	0.063	0.040	0.023	0.063	0.020	0.325	0.020

suggested that although the size and significance of isotopic variations is highly dependent upon the data set in question, the range of $\delta^{13}C_{oil}$ values found in this work, though narrow, is significant enough to allow discrimination between the various petroleum fuel samples analysed. For example, in oil migration studies, Philp and Engel (1987) reported that a change of between 1.5 and 2.6‰ in the saturate, polar and asphaltene class fractions of a crude oil with increasing oil migration distance represented a pronounced isotopic depletion within these class fractions. Similarly, Silverman (1965) reported a slight, but statistically significant, shift of 0.4‰ towards the lighter ^{12}C isotope with increased migration of a crude oil in a Venezuelan oil basin. Furthermore, biotransformation of crude oil class fractions has been documented as inducing a small but significant positive shift of 0.7‰ in the alkane fraction and a corresponding negative shift of 1.1‰ in the asphaltene fraction (Stahl, 1980).

In an isotopic correlation of crude oils and possible source rock kerogens, Stahl (1978) found that the mean difference between the $\delta^{13}C$ of asphaltene and kerogen samples assumed to be genetically associated was 0.6‰ although the standard deviation (σ) of these measurements was relatively large, at approximately 0.7‰. Accordingly, a wide $\delta^{13}C$ range of 2σ deviations (i.e. $\pm$ 1.4‰) from the mean isotopic difference was adopted to define the boundaries within which genetic association between samples was implied. In other oil–oil correlation studies, a positive correlation has been established when the differences in isotopic composition of the oil samples do not exceed 1.0‰ (Fuex, 1977). However, further examination of isotopic alterations in crude oils by Sofer (1984) demonstrated that thermal maturation effects can cause isotopic variations within a family of oils of up to 2‰, suggesting that the original figure may require some modification. Schoell (1984) provides an excellent review of the established uses of stable isotopes in petroleum research and makes clear the need for further research into the internal isotope patterns of petroleum compound classes and the information that can be extracted from them. Clearly, in the context of the present paper, to establish a role for this technique in the characterisation of heavy oil contaminants under actual conditions, where the nature and origin of the petroleum waste source term is not usually known, the identification of a wider range of $\delta^{13}C_{oil}$ values, through further analysis of common petroleum contaminants, is necessary.

In essence, the present results provide further evidence that a higher polar/asphaltene content is closely associated with a greater oil ^{13}C content and, therefore, a higher value of $\delta^{13}C_{oil}$ (Table 1). The ability to detect a high polar and asphaltene content within refractory waste streams without the need for GC-coupled analytical techniques may be welcome in the screening and selection of bioremediation technologies during remedial technology selection, where the presence of assimilable waste constituents is crucial to success. For this to be realised, however, an evaluation of the influence of soil microbial activity on established source terms and whole oil isotope ratios is required. There are indications that this latter effect may not be of major significance, although there is evidence that microbial transformation of crude oils induces certain changes in the isotopic composition of individual class fractions (Stahl, 1980). Fan *et al.* (1994) includes a brief summary of the technique in a recent review of analytical methodologies associated with the evaluation of petroleum hydrocarbons in soil. They suggest that the primary advantage of the technique lies in the analysis of samples that have undergone extensive molecular transformation, since the whole oil isotope ratio usually remains largely unaffected and can therefore still be used as a correlation parameter. This was demonstrated recently by Hostettler and Kvenvolden (1994), who used similarity in isotopic composition as further evidence of correlation between beached oils in Prince William Sound ($\delta^{13}C = -29.1$ to -29.4‰) and oil taken from the *Exxon Valdez* tanker ($\delta^{13}C = -29.2$‰).

The variation of class fraction isotope ratios within an oil is often represented by an isotope type curve. Characteristic type curves comprising whole oil and class fraction $\delta^{13}C$ values for each of the oils analysed in this study (Fig. 3) reveal a distinct difference between the heavy and light oils. For the lighter oil samples, the results are in general agreement with the conventionally observed trend, increasing in the following order: $\delta^{13}C_{sat}$ ($\approx \delta^{13}C_{oil}$) $< \delta^{13}C_{aro} < \delta^{13}C_{pol} < \delta^{13}C_{asp}$, with $\delta^{13}C_{sat}$ up to 2.5‰ more negative than $\delta^{13}C_{pol}$ and $\delta^{13}C_{asp}$. Stahl (1980) recognised a similar trend when examining the isotopic fractionation of a North Sea crude during *in vitro* microbial degradation, having previously attributed a similar effect to the differences in polarity of individual class components (Stahl, 1978). Previous workers refer to the underlying isotope-selective processes that affect the formation of the respective SAPA class fractions and, in particular, to the congregation of ^{13}C in compounds that retain stronger inter- and intramolecular linkages (Silverman & Epstein, 1958), the majority of which report in the polar and asphaltene class fractions.

The API separator oil, ballast oil, residue oil and waxy distillate type curves shown in Fig. 3 are essentially indistinguishable from one another, displaying saturate class isotope ratios that are significantly different from those of the remaining aromatic, polar and asphaltene class fractions which, particularly for the residue and waxy distillate oils, are isotopically very similar. This latter effect has been observed in previously reported type curves (e.g. Stahl, 1978) and may be due to the chemical similarity of compounds from within the three fractions and, consequently, poor column chromatographic resolution of these fractions prior to analysis. The present results also show that the bulk $\delta^{13}C_{oil}$ values do not differ significantly from the saturate class $\delta^{13}C$ values. This is not surprising, as saturate class compounds are the predominant constituents of these lighter oils.

In contrast, isotope type curves for the heavier acid tar, bitumen and No. 6 fuel oils show no conspicuous

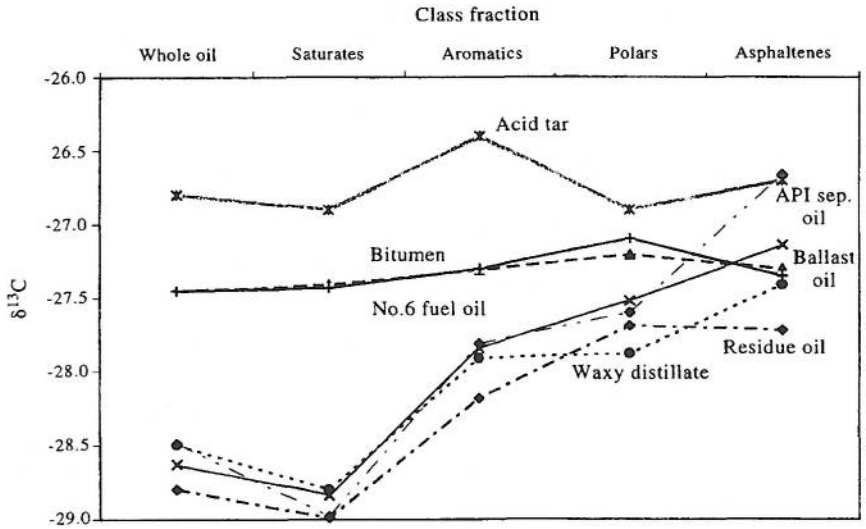


Fig. 3. Stable carbon isotopic fingerprints for selected heavy oils for use in correlation studies. The spacing along the horizontal axis is arbitrary, but it is justified on the grounds of previous applications (Stahl, 1978). Error bars have been omitted for reasons of clarity; however, standard deviations are included in Table 1.

variation in class fraction isotopic composition, resulting in zero gradient, or flat, type curves. For the acid tar sample, all class fraction $\delta^{13}C$ values lay between -26.4 and $-26.9‰$ for the bitumen and No. 6 fuel oil, the range was -27.4 to $-27.2‰$. Although a relatively high value of $\delta^{13}C$ is to be expected for the polar and asphaltene class fractions, it is surprising that the saturate fractions of these heavy oils also produce such high $\delta^{13}C_{sat}$ values. The reason for the elevated $\delta^{13}C_{sat}$ values within the bitumen, acid tar and No. 6 fuel oils has not been established. A possible explanation is that the heavier oils have been subjected to fewer of the isotope-selective refining processes required to derive petroleum fuels from the parent crude oil, and that, therefore, their constituent components have been able to retain more ^{13}C within their chemical structures. Alternatively, it may be that the acid tar, bitumen and No. 6 fuel oil saturate class fractions contain a number of very high molecular weight compounds ($> C_{40}$) that are not present in the saturate class fraction of lighter oils, that are relatively enriched in ^{13}C and that avoid detection by GC–FID. This is supported by the results of Silverman (1971), who observed a sharp increase in $\delta^{13}C$ for petroleum distillation fractions collected above 450°C, the temperature corresponding to C_{40} carbon number. Extended analysis by GC–MS may provide the information required to fully characterise the class component distribution in each of the saturate class fractions.

For unknown petroleum wastes, isotope type curves can represent useful source correlation parameters, allowing contaminants and candidate source terms to be compared more effectively than by $\delta^{13}C_{oil}$ values alone. Results presented here suggest that isotope type curves allow discrimination between heavy fuel oils, containing significant polar and asphaltenic material, and lighter fuel oils, predominantly composed of saturate class compounds. However, the diagnostic aspects of the approach appear to be severely limited in discriminating between oils of similar chemical composition. As discussed, a clearer understanding of the effects of microbial transformation on the shape of respective isotope type curves is also required. It is generally believed that, although the isotopic composition of the bulk waste term may not be significantly altered by biotransformation processes, the isotope ratios of the individual class fractions may undergo shifts that could alter the shape of contaminant isotope type curves beyond recognition from those of the fresher, possibly undegraded source term. In particular, Stahl (1980) reported that microbial degradation of crude oil class fractions produced a shift towards a more positive $\delta^{13}C$ for the saturate fraction, no shift within the aromatic fraction and a negative shift for the asphaltene fraction. This suggests that extensive biotransformation of oily wastes would ultimately result in a flattened isotope type curves similar to those obtained here for the heavier acid tar, bitumen and No. 6 fuel oil samples. In both cases, therefore, the diagnosis resulting from the type curves is the same: a flatter isotope type curve is indicative of a recalcitrant petroleum contaminant that contains a significant proportion of polar and asphaltene class components and that therefore may not be responsive to bioremedial treatment technologies. In this respect, IRMS screening of residual oil contamination may be a potentially valuable diagnostic tool.

In summary, IRMS analysis of oils appears to be a potential method for identifying a predominance of polar and asphaltenic material in heavy oils and for providing an additional source correlation parameter for undegraded oily contaminants. The technique is attractive because it does not incorporate gas chromatographic separation of oil components and facilitates analysis of the entire waste, not merely the analytically labile portions. Further work must be focussed on expanding the range of whole oil $\delta^{13}C$ values and determining the effect of microbial transformation of oil

on the isotopic composition. Based on these preliminary results, isotope type curves may be used to distinguish between petroleum fuels containing markedly different class fraction distributions and to indicate the presence of a large polar plus asphaltene content; however, discrimination between oils of similar composition was not possible. It should also be noted that the results given in the present paper are for North Sea derived oils only, and that oils derived from different genetic families of crude oil (i.e. crude oils derived from different geological facies) may have different ranges of $\delta^{13}C$ values, although the trends in $\delta^{13}C$ variation should be essentially the same. Clearly, developing an understanding of this and other analyte-specific parameters that have influence over the utility of the technique is also required, and, consequently, further interrogation of these and other oils by compound specific isotope analysis is currently underway. Having established the potential utility of this technique for source term characterisation, elucidation of the compositional and isotopic transformations occurring during the relatively shorter timespan of microbial transformations in soil is now being studied.

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A PERFORMANCE ASSESSMENT OF SOURCE CORRELATION AND WEATHERING INDICES FOR PETROLEUM HYDROCARBONS IN THE ENVIRONMENT

MARTIN WHITTAKER† and SIMON J.T. POLLARD*‡
†Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, United Kingdom
‡Aspinwall & Company, Consultants in Environmental Management, 13 Melville Street, Edinburgh, EH3 7PE, United Kingdom

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Abstract—The source of petroleum contaminants in the environment and the extent to which these contaminants have weathered following deposition can often be determined through an empirical evaluation of oil *n*-alkanes, isoprenoids (pristane and phytane), and hopane and sterane biomarkers. Common source correlation and weathering indices have been calculated for three sets of oil samples: fresh, 25% (w/w) weathered, and 50% (w/w) physically weathered diesel standards, crude oils from different sources, and a set of representative heavy oils. For the weathered diesel oils, the C_{18} : tricyclic terpanes and *n*-alkanes : tricyclic terpanes indices varied most significantly with diesel weathering. Awareness of this may be important when these indices are used to assess biotic routes of contaminant dissolution. For the crude oil samples, C_{18} : phytane demonstrated low specificity between the oils. C_{18} : 17α(*H*),21β(*H*)-Hopane and *n*-alkanes : 17α(*H*),21β(*H*)-hopane differentiated between crude oils but would be expected to vary significantly during weathering due to the microbial amenability of the alkane numerators. Pristane : phytane, phytane : 17α,21β-hopane and tricyclic terpanes : hopanes were considered to be the indices best able to distinguish between oils from different origins, based on these results. 17α(*H*),21β(*H*)-Hopane : 17α(*H*),21β(*H*)-norhopane did not adequately distinguish between the respective crude oil samples. Finally, the relationship between heavy oil composition and the index value was investigated. Here, the values of *n*-alkanes : 17α(*H*),21β(*H*)-hopane, phytane : 17α(*H*),21β(*H*)-hopane, and tricyclic terpanes : hopanes decreased as the combined total of polar and asphaltene compounds within oil samples increased. This relationship may be useful in assessing the degradation status of petroleum wastes.

Keywords—Petroleum contamination Biomarkers Weathering Refractory oils Bioremediation

INTRODUCTION

For most petroleum-contaminated sites, obtaining information on the source and composition of oily wastes is important for the informed application of risk management strategies [1,2]. Evaluating the extent of weathering undergone by the waste matrix may also be significant, because compositional changes that take place during weathering can often limit the bioremediation potential of residual soil contamination [3]. The recent emergence of "natural attenuation" as a managed approach to soil and groundwater remediation has placed fresh emphasis on the need for information on both the source and the extent of weathering of contaminants. One analytical approach that has proven successful for characterizing both the source and weathered state of spilled petroleum contaminants is measurement of the abundance and distribution of biomarker compounds within the contaminant matrix [4–9].

Chemical biomarkers, ubiquitous in crude oils and petroleum products, are compounds that can be unambiguously traced to biological precursor compounds [10]. The most commonly used biomarkers are pristane and phytane (both branched isoprenoid alkanes) and hopanes and steranes (polycyclic alkanes) (Fig. 1). Their use in oil source and weathering studies derives from two characteristics. First, biomarkers are much more resistant to oil weathering processes, such as evaporation and biotransformation, than are most oil components. This allows their use as conserved reference compounds against which the loss of less stable oil components can be quantitatively estimated (e.g., C_{18} : phytane, *n*-alkanes : 17α(*H*),21β(*H*)-hopane). These ratios, collectively referred to in this paper as "weathering indices," may be especially useful in monitoring natural attenuation or enhanced bioremediation, where confirmation of contaminant loss is essential. Examples of weathering indices being used to characterize oil degradation include monitoring depletion of spilled crude oil on beaches of Prince William Sound following a bioremedial response to the *Exxon Valdez* oil spill [4,9], evaluation of the relative degrees of biodegradation experienced by marine crude oils [11], identification of the flow patterns of dissolved hydrocarbons in ground water [12], and monitoring the transformation of oily wastes during controlled bioremedial activities [13].

The second key characteristic of oil biomarkers is that their distribution within oils represents an oil-specific fingerprint with which distinct oil samples can be correlated. This is most commonly achieved through a qualitative comparison of individual biomarker mass fragmentogram patterns (obtained by gas chromatography–mass spectrometry [GC-MS]), but can also be achieved quantitatively from a calculation of the ratio of one biomarker to another. In this study, we are concerned with the latter approach. Ratios of certain biomarkers, referred to in this paper as "oil (or source) correlation indices," are

* To whom correspondence may be addressed.
The current address of S.J.T. Pollard is Scottish Environment Protection Agency, Erskine Court, The Castle Business Park, Stirling, FK9 4TR, UK.

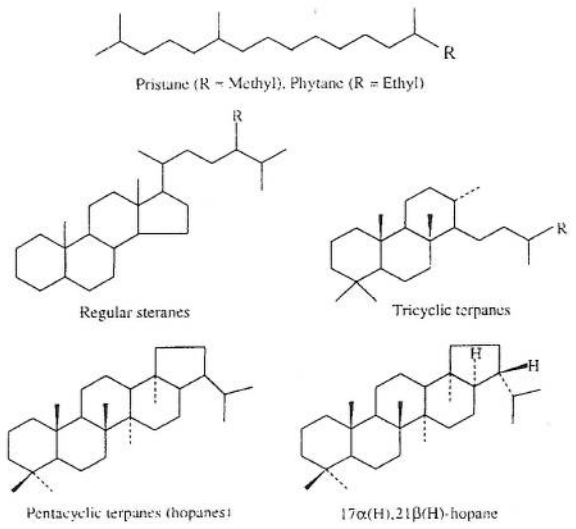


Fig. 1. Structural formulas of selected biomarker compounds.

sensitive to the geologic source of an oil, and remain consistent between related oils. Moreover, because of the environmental persistence of biomarker compounds, their values remain unaltered by weathering of oil. Recently, oil correlation indices have been used to demonstrate that certain Alaskan shoreline oil residues originated from pre-1970 industrial oil usage rather than as a result of the *Exxon Valdez* oil spill [6], to confirm the source of highly weathered no. 6 fuel oil released more than 22 years ago from the oil tanker *Arrow* [7], and to monitor chemical compositional changes and the fate of weathered crude oil residues from an Arctic beach [8].

A number of concerns exist regarding the use of biomarker indices in certain situations. Some authors have noted that in very weathered oil samples, isoprenoid biomarkers may themselves become partially biotransformed [4,7]. Research into this phenomenon has shown that both pristane and phytane are vulnerable to loss through microbial activity in appreciably weathered samples [4]. Hopane biomarkers, on the other hand, have been shown to be neither produced nor destroyed over considerable periods of oil weathering and are therefore considered to be much more reliable [9]. Concern has also been expressed over microbially facile waste components being compared with persistent biomarkers, because individual compounds have different solubilities, transport, and volatility characteristics [14]. The effects of these differences on the behavior of biomarker indices are likely to be greatest during the initial phases of a spillage, when abiotic processes (such as evaporation, leaching, and photooxidation) are most prominent. These concerns are valid because information gleaned from source and weathering indices may be used as a means of establishing environmental liabilities for petroleum contamination, or in screening risk management decisions at contaminated land sites, both of which could involve considerable financial outlay.

The derivation of oil weathering and source correlation indices is based on the established biochemical principles of petroleum microbiology [15–17] and, in particular, on the differential rates at which oil components are metabolized and transformed. In the absence of single substrate studies on numerator and denominator compounds that comprise an index, experimentally observed differences in index values can be explained with reference to the microbiology literature. In brief, microbial catabolism of *n*-alkanes proceeds via successive oxidation and cleavage of the terminal methyl groups of a hydrocarbon molecule. Branched or cyclic compounds experience slower biotransformation rates due to the presence of secondary, tertiary, and quaternary carbon atoms within the basic hydrocarbon structure that render these compounds more difficult to metabolize. Hopane and sterane biomarkers are among the most effective internal marker compounds because their linked alicyclic structures provide few pathways for biotransformation [15]. The susceptibility of compounds to microbial attack, therefore, varies widely with molecular structure and size, and tends to decrease with increasing molecular weight, molecular branching, cyclization, aromaticity, and the number of hetero-atoms incorporated into the compound [17]. Thus, in terms of oil class fractions, the open chain alkanes are generally the most labile oil components, followed by aromatic compounds, then polar resins, and finally the highly condensed asphaltenes.

In view of this, and of the wide scope of application for source correlation and weathering indices, we have conducted an empirical study of the performance of some common source and weathering indices in three well-defined areas. In the first study, our aim was to assess whether, in the immediate aftermath of an oil spill, there is potential for abiotic loss of oil components to influence source and weathering indices to such an extent that diagnosis of microbial activity or source commonality (or both) is impaired. This is most pertinent to petroleum products containing a significant low-boiling fraction or when contaminant discharge occurs under environmental conditions conducive to evaporation. To this end, we examined the effect of physical weathering on biomarker ratios by determining the values of six common source correlation and weathering indices for samples of fresh, 25% (w/w), and 50% (w/w) physically weathered diesel.

In the second study, the variation of source correlation indices between different crude oil types was examined. Source correlation indices have been used most effectively as a means of identifying marine crude oil contamination through comparison of the biomarker ratios of the waste oil with those of a suspected source. This approach relies upon the specificity of source correlation indices to individual crude oil types and their capacity to discriminate between crude oils from different backgrounds. Here, the values of seven frequently used source correlation indices are determined for an Iraqi crude oil, a Nigerian crude oil, and two North Sea crude oils, with the goal of identifying those source correlation indices best able to distinguish between the oil samples. A favorable index is one that shows a significant variation (in relation to the confidence limits of the index value, and in comparison to variations recorded in previous studies) between the three crude oil families while remaining constant for the two North Sea oil samples.

In the third section of this paper, we focus on the utility of source correlation and weathering indices in the characterization of heavier (i.e., higher boiling point) petroleum products and, in particular, on the extent to which the values of selected indices are affected by variations in oil composition. Heavy oils commonly contain a high proportion of polar and asphaltenic compounds known to resist microbial degradation and concentrate in degraded oils. Characterization of the waste–soil matrix is, therefore, particularly important when assessing the suitability of bioremediation technologies or the

Table 1. Representative heavy oil description and class fraction distribution

Oil	Source description	Approximate boiling range (°C)	Class distribution[a]			
			Saturates (% w/w)	Aromatics (% w/w)	Polars (% w/w)	Asphaltenes (% w/w)
Acid tar waste	Contaminated site	200–>700	60.2 ± 3.0	4.6 ± 0.2	8.7 ± 0.4	26.5 ± 1.3
No. 6 fuel oil	North Sea, heavy oil blend	150–600	36.7 ± 1.8	34.9 ± 1.7	12.6 ± 0.6	15.8 ± 0.8
API[b] separator oil	Refinery process run-off stream	20–400	51.3 ± 2.6	30.7 ± 1.5	14.9 ± 0.8	3.1 ± 0.2
Ballast oil	Ship discharge variety of products	20–400	75.3 ± 3.8	12.3 ± 0.6	8.1 ± 0.4	4.3 ± 0.2
Residue oil	Mixed North Sea	150–600	71.8 ± 3.6	20.7 ± 1.0	5.9 ± 0.3	1.6 ± 0.1

[a] Determined by adsorption column chromatography; ± standard deviation (based on selected triplicate determinations).
[b] API = American Petroleum Institute.

feasibility of natural attenuation, where success depends upon the depletion of assimilable waste constituents [3]. The capacity of biomarker indices to convey information on the degradation status of residual oily wastes is examined through the analysis of five heavy oils, representative of residual organic wastes at contaminated sites (Table 1).

MATERIALS AND METHODS

Sample collection

For the study of abiotic weathering, a set of progressively weathered diesel range organic (DRO) standards (Restek Corporation, Bellefontaine, PA, USA) was evaluated. These oils represent mid-range petroleum products with a carbon number range of C_{10} to C_{28}, as determined by gas chromatography with flame ionization detection (GC-FID) analysis. The DRO standards were physically weathered by the manufacturer by direct evaporation using a combination of gentle heating (water bath) and nitrogen blowdown to prevent oxidation. The percent weathering indicated with each sample (i.e., 25% [w/w], 50% [w/w]) was determined by monitoring the gravimetric weight loss from the original unweathered sample.

Examination of the reliability of oil correlation indices was carried out using four discrete crude oil samples, two North Sea-derived oils, a Nigerian export blend, and an Iraqi export crude. Analysis of crude oils by adsorption chromatography demonstrated that all were predominantly paraffinic, consisting of >85% (w/w) saturate class components.

Five heavy and middle distillate oils were used for evaluating the relationship between oil chemical composition and the value of selected source and weathering indices. Four of the oils, recovered refinery effluent oil (referred to as API [American Petroleum Institute] separator oil), oil tanker ballast oil, a crude distillation residue, and no. 6 fuel oil, were obtained as neat oils from a local oil refinery, and have been previously described [18]. The fifth material, an acid tar waste sample, was extracted from contaminated soil at a former lubricating oil recovery plant.

Adsorption chromatography

For the heavy oils (Table 1), preparative column chromatography was essential for isolating the individual saturate class fractions in which the selected target compounds biomarkers report [18]. Prior to the column fractionation, the asphaltene fraction of each oil was gravimetrically determined by an *n*-pentane precipitation method adapted from Speight et al. [19]. A Quick-Sep® (Fisher Scientific, Crawley, UK) lateral reservoir flash chromatography apparatus, with a 90 mm × 30 mm column, was packed with neutral Aldrich (Gillingham, UK) STD Grade alumina (80 mm, approx. 150 mesh, activated overnight at 130°C), followed by anhydrous Na_2SO_4 (approx. 10 mm, dehydrated by heating at 400°C for 4 h immediately prior to use). A single piston air pump (Fisons, Fisher Scientific, Crawley, UK, 50 W) was connected to the top of the column and the air pressure adjusted to produce a down-flow elution rate of approximately 20 ml/min. All solvents used were high-performance liquid chromatography (HPLC) grade. The column was preeluted with 50 ml *n*-pentane prior to the loading of the maltene (*n*-pentane-soluble) fraction of each reference oil onto the column by pipette in 2 ml of *n*-pentane. Component classes were obtained using the following elution scheme: 150 ml of *n*-pentane (for elution of saturates), 150 ml of toluene (for mono-, di-, and polyaromatics), and 150 ml of a dichloromethane : methanol mixture (50:50) (for polar compounds). Fractions were collected in preweighed, acid-washed borosilicate flasks and reduced under a forced draught to allow calculation of gravimetric recoveries.

Acid tar samples were first Soxhlet-extracted from soil subsamples (*approx.* 30 g) for 16 h using HPLC-grade dichloromethane (DCM) (BDH, Poole, UK) (150 ml). The DCM extracts were reduced overnight at ambient temperatures under forced draught.

Analyses by GC-MS

Oil saturate fractions were made up to a concentration of approximately 10 mg/ml in DCM. Analyses were conducted on an HP model 5890 gas chromatograph (Hewlett Packard, Stockport, UK) equipped with a 60-m × 0.25-mm-i.d. DB5 column and a VG Trio 1 mass spectrometer detector (Finnegan, Manchester, UK). One-microliter aliquots were injected through a 1-m × 0.53-mm deactivated fused silica retention gap using an HP model 7673A autoinjector (Hewlett Packard, Stockport, UK). A linear temperature gradient was employed, with the column temperature held at 30°C for 1 min following injection, ramped at 6°C/min to 300°C, then held at 300°C for a further 30 min. Helium carrier gas was used at a flow rate of 7.5 ml/min. The GC-MS interface was maintained at 300°C.

Electron impact ion chromatograms were obtained in selective ion monitoring mode. Two target ions were selected on the basis of previous studies [4,20]. These were *m/z* 85 (for detection of *n*- and isoprenoid alkanes) and *m/z* 191 (for tri-, tetra-, and pentacyclic terpanes). The spectrometer was tuned

daily using a heptacosafluorotributylamine standard (mol. wt. 671.1).

Source correlation and weathering indices were calculated to single decimal place precision by determining the ratio of the integrated peak areas on mass chromatograms of the compound(s) featured in the index (see Tables 2, 3, and 4). Repeat analysis of selected samples indicated a standard deviation in index values of up to 10%. Peaks corresponding to the *n*-alkanes, pristane, and phytane were determined by the use of an analytical standard comprising five *n*-alkanes (C_{15}, C_{20}, C_{25}, C_{30}, and C_{40}). Tricyclic and pentacyclic terpane (hopane) peak identification was achieved using 17β(*H*),21β(*H*)-hopane as an internal standard and by comparison of mass fragmentograms at *m/z* 191 with corresponding reference fragmentograms from the literature [7,20]. Mass fragmentograms for *m/z* 191 (tri-, tetra-, and pentacyclic terpanes) and 85 (saturated hydrocarbons) ions for the residue oil are shown in Figure 2.

RESULTS AND DISCUSSION

Rationale for formation of biomarker indices

In weathering indices, the abundance of oil components lost during weathering is compared to that of one or more conserved internal marker compounds. A decrease in the value of weathering indices over time is used as evidence of increasing oil maturity or, when used to monitor the progress of natural attenuation or enhanced bioremediation, of microbial activity.

In source correlation indices, the ratio of two environmentally persistent biomarker compounds within an oil is calculated. Because the overall distribution of biomarkers within an oil is highly dependent on the geologic background of the oil, the value of this ratio is specific to individual oil types. Moreover, providing the biomarkers are not susceptible to abiotic or biotic degradation, the value of the ratio should remain more or less constant during oil weathering. Source correlation indices, therefore, represent a convenient way of establishing commonality between two or more oils. Usually, this is done to determine the identity of anonymous oils through comparison of source index values in the waste with those of a suspected source oil. A wide number of indices have been used in the characterization of petroleum contaminants in the environment. These are listed below.

C_{17}: Pristane, and C_{18}: Phytane. Senn and Johnson [12] used the differences in rate of biotransformation of the index components to rank samples of spilled diesel oil in terms of their weathered state. C_{17}: Pristane and C_{18}: phytane decreased from 1.8 and 2.7, respectively, in oil samples considered to have been least weathered (i.e., those closest to the source of the spill), to 0.2 and 0.3, respectively, in those samples farthest from the spill source, which had been most extensively weathered. More recently, C_{17}: pristane values were used to estimate the age of diesel oil contamination. These values ranged from 2.2 for fresh oil to 0.2 for samples approximately 20 years old [21]. These ratios have also been used to illustrate weathering of crude oils spilled in the marine environment. Wang et al. [8], for example, found that extensive weathering of oily residues on an Arctic beach resulted in a decrease in the value of C_{17}: pristane from 3.5 in the unweathered oil to between 0.16 and 0.9 in the weathered residues. C_{18}: Phytane values were also found to decrease, from 1.5 to between 0.13 and 0.42.

Pristane: Phytane. This source correlation index has been recently used in studies of weathered crude oil residues in the

Table 2. Weathering and source correlation indices for physically weathered diesel range organics (DROs)

			DRO Samples					
			Unweathered		25% Weathered		50% Weathered	
Biomarker ratio[a]	*m/z* Ratio	Empirical formula and mol. wt.	Integrated peak areas	Index value[b]	Integrated peak areas	Index value[b]	Integrated peak areas	Index value[b]
Weathering indices								
C_{17}: Pristane	85:85	$C_{17}H_{36}$, (240), $C_{19}H_{40}$ (268)	1,324,320/712,924	1.9	1,639,220/868,378	1.9	1,194,220/476,244	2.5
C_{18}: Phytane	85:85	$C_{18}H_{38}$ (294), $C_{20}H_{42}$ (282)	1,092,420/528,977	2.1	1,392,010/676,104	2.1	1,081,590/778,478	1.4
C_{18}: Tricyclic terpanes	85:191	$C_{18}H_{38}$ (294), $C_{20-36}H_{16-48}$ (276–360)	1,092,420/526,813	2.1	1,392,010/947,682	1.5	1,081,590/2,060,559	0.5
n-Alkanes : tricyclic terpanes	85:191	$C_{10-22}H_{22-46}$ (142–310), $C_{20-36}H_{16-48}$ (276–360)	10,744,878/526,813	20.4	10,841,482/947,682	11.4	8,036,180/2,060,559	3.9
Source indices								
Pristane : phytane	85:85	$C_{19}H_{40}$ (268), $C_{20}H_{42}$ (282)	712,924/528,977	1.4	868,378/676,104	1.3	476,244/778,478	0.6
Pristane : tricyclic terpanes	85:191	$C_{19}H_{40}$ (268), $C_{20-36}H_{16-48}$ (276–360)	712,924/526,813	1.4	868,378/947,682	0.9	476,244/2,060,559	0.2
Phytane : tricylic terpanes	85:191	$C_{20}H_{42}$ (282), $C_{20-36}H_{16-48}$ (276–360)	528,977/526,813	1.0	676,104/947,682	0.7	778,478/2,060,559	0.4

[a] Indices are categorized according to previous usc.
[b] Confidence limits (established through triplicate analysis of selected samples) ± 10%.

Table 3. Selected indices for correlation of crude oil

Biomarker ratio	*m/z* Ratio	Nigerian crude oil: Integrated peak areas	Nigerian crude oil: Index value[a]	North Sea crude oil 1: Integrated peak areas	North Sea crude oil 1: Index value[a]	North Sea crude oil 2: Integrated peak areas	North Sea crude oil 2: Index value[a]	Iraqi crude oil: Integrated peak areas	Iraqi crude oil: Index value[a]
C_{18} : Phytane	85:85	547,718/392,658	1.4	1,080,190/470,507	2.3	1,217,090/994,841	1.2	827,991/591,110	1.4
Pristane : Phytane[b]	85:85	679,901/392,658	1.7	301,221/470,507	0.6	732,941/994,841	0.7	575,899/591,110	1.0
C_{18} : 17α(*H*),21β(*H*)-Hopane[b]	85:191	547,718/643,292	0.9	1,080,190/64,456	16.8	1,217,090/92,972	13.1	827,991/36,723	22.6
n-Alkanes : 17α(*H*),21β(*H*)-hopane[b]	85:191	6,722,148/643,292	10.4	11,902,853/64,456	184.7	15,475,568/92,972	166.5	10,189,770/36,723	277.5
Phytane : 17α(*H*),21β(*H*)-hopane[b]	85:191	392,658/643,292	0.6	470,507/64,456	7.3	994,841/92,972	10.7	591,110/36,723	16.1
Tricyclic terpanes : total hopanes[b]	191:191	416,355/2,875,231	0.2	193,585/388,602	1.0	400,842/711,858	1.3	444,433/523,083	5.6
17α(*H*),21β(*H*)-hopane : 17α(*H*), 21β(*H*)-norhopane	191:191	643,292/765,122	0.8	64,456/86,303	0.7	92,972/53,612	1.7	36,723/17,195	2.1

[a] Confidence limits (established through triplicate analysis of selected samples) ± 10%.
[b] Proposed source correlation indices.

Table 4. Selected source correlation and weathering indices for typical heavy oil samples

Biomarker ratio	*m/z* Ratio	Heavy oils: Ballast oil: Integrated peak areas	Ballast oil: Index value[a]	API separator oil: Integrated peak areas	API separator oil: Index value[a]	Residue oil: Integrated peak areas	Residue oil: Index value[a]	No. 6 fuel oil: Integrated peak areas	No. 6 fuel oil: Index value[a]	Acid tar waste oil: Integrated peak areas	Acid tar waste oil: Index value[a]
C_{18} : Phytane	85:85	370,487/228,890	1.6	956,065/597,497	1.6	626,678/483,086	1.3	817,134/379,360	2.2	848,779/557,075	1.5
Prsitane : Phytane	85:85	160,445/228,890	0.7	262,505/597,497	0.4	ND[b]		ND	ND	ND	
n-Aklanes : 17α(*H*),21β(*H*)-hopane	85:191	3,299,544/5,736	575.2	8,870,030/21,824	406.4	21,023,840/245,650	85.6	7,400,142/91,395	81.0	4,996,103/3,693,560	1.3
Phytane : 17α(*H*),21β(*H*)-hopane	85:191	228,890/5,736	39.9	597,497/21,824	27.4	483,086/245,650	2.1	379,360/91,395	4.2	557,075/3,693,560	0.2
Tricyclic terpanes : total hopanes	191:191	244,830/20,301	12.1	713,074/87,385	8.2	603,970/1,197,884	0.5	4,348,769/374,375	11.6	7,986,140/14,931,550	0.5
17α(*H*),21β(*H*)-hopane : 17α(*H*), 21β(*H*)-norhopane	191:191	5,736/5,293	1.1	21,824/20,910	1.0	245,650/144,862	1.7	91,395/82,767	1.1	3,693,560/4,784,260	0.8

[a] Confidence limits ± 10%.
[b] ND = not detected.

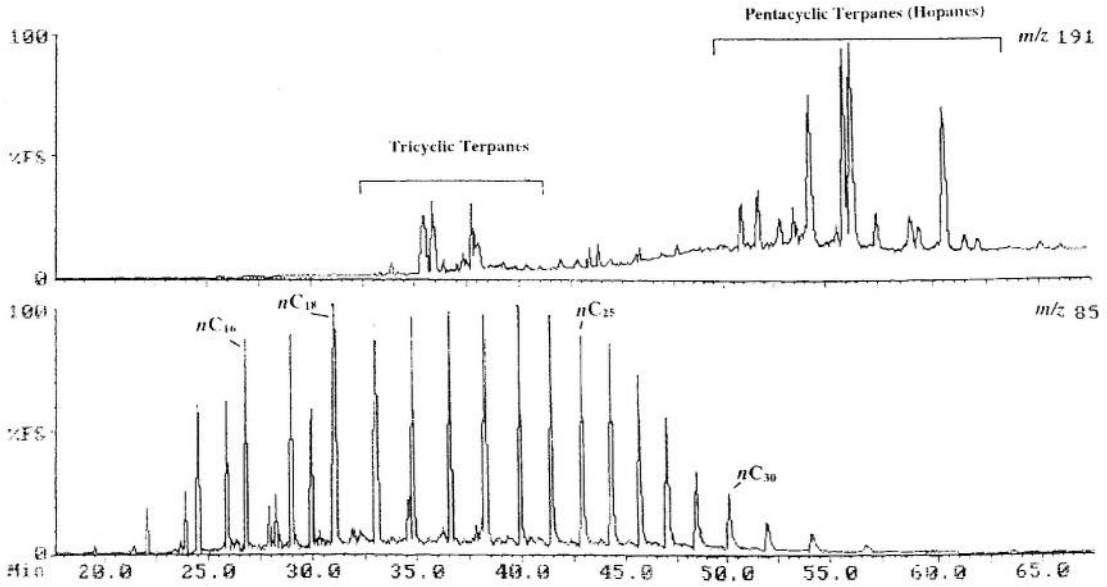


Fig. 2. Gas chromatography–mass spectrometry trace for residue oil saturate fraction, showing *m/z* 191 (tri-, tetra-, and pentacyclic terpanes) and *m/z* 85 (normal and branched alkanes) fragmentograms.

marine environment. In one study, this ratio was found to remain almost constant, at approximately 0.5, for a range of highly weathered crude oil beach residues and the original crude oil source [8]. In a related study, a slight decrease between fresh and weathered samples was observed, from 0.87 to 0.75 [7]. However, because both pristane and phytane have been shown to be susceptible to biotransformation [9], the reliability of this source correlation index is believed to be questionable in highly weathered oil samples. Evidence of this was presented by Hostettler and Kvenvolden [22], who found pristane : phytane values of between 1.2 and undetected for beach oil residues that originally were known to display a value of 1.4 for the same index.

C_{18} : 17α(H),21β(H)-Hopane, phytane : 17α(H),21β(H)-hopane, n-alkanes : 17α(H),21β(H)-hopane. These ratios have been used widely to demonstrate the loss of crude oil from beaches undergoing active bioremedial treatment [4,9], and in more general studies of oil degradation and maturity [11,13]. All three indices record the loss of oil components relative to the pentacyclic terpane found to be most resistant to oil weathering processes, 17α(*H*),21β(*H*)-hopane. Pande et al. [11] used the second of these indices to monitor biodegradation of crude oils, obtaining a spread of values from 200 for the freshest oil to 4.3 for the most degraded. Swannell et al. [23] used variation in the latter two indices to monitor the biodegradation of an Arabian crude oil. Significant shifts were recorded in the value of the ratio of total alkyl polycyclic aromatic hydrocarbons to 17α(*H*),21β(*H*)-hopane, which decreased from 43 in the freshest oil to undetected in the most degraded samples. In a similar study carried out by Croft et al. [13], the ratio of total hydrocarbons to 17α(*H*),21β(*H*)-hopane showed a small decrease, from 551 to 518, for oil samples undergoing limited biotransformation, while increasing slightly (from 551 to 663) when no biotransformation took place.

Tricyclic terpanes : Hopanes. Literature evidence suggests that lower molecular weight tricyclic terpanes degrade more rapidly than the more conserved pentacyclic terpanes (hopanes) in very weathered samples [7]. As a result, this index has been proposed as a possible means of quantifying oil weathering in highly degraded samples and for distinguishing between highly weathered oils.

17α(H),21β(H)-Hopane : 17α(H)21β(H)-norhopane. These hopane biomarkers have been shown to be both the most conserved and the most abundant biomarkers within oils [7]. This ratio is therefore the preferred source correlation parameter in many oil contaminant studies [6,8,13,22]. In general, oil samples with 17α(*H*),21β(*H*)-hopane : 17α(*H*)21β(*H*)-norhopane values within approximately 0.5 of one another have been considered to be from the same original source, although related oils often display a variation of much less than this.

The five sets of indices described above have been adapted directly from the literature in unaltered form for use in this study. In addition to these, we have identified an additional set of weathering indices with which it may be possible to characterize the weathering of diesel and other mid-distillate oil samples. These are: C_{18} : tricyclic terpanes, *n*-alkanes : tricyclic terpanes, pristane : tricyclic terpanes, phytane : tricyclic terpanes. Tricyclic terpanes are lower molecular weight analogues of hopanes that are detected in the diesel standards in sufficient amounts to be used as conserved internal marker compounds in weathering indices. Detection of these compounds may allow diesel oil weathering to be assessed more reliably than by the conventional C_{17} : pristane and C_{18} : phytane indices.

Although establishing index reliability is essential, particularly if use of indices is to be expanded within a commercial context, variations in the methods by which indices are calculated, the enormous diversity of petroleum products under study, and the influence of site-specific factors are such that a direct comparison of index values between studies should be avoided. Nevertheless, it may be possible to refer to index variations obtained in previous studies in order to gauge the significance of observed numerical variations; this is useful in attributing significance to the various indices.

Performance of weathering and source correlation indices in weathered diesel oil

Weathering indices reflect the relative rates at which selected oil components are dissipated during the combined physical, chemical, and biological processes that constitute oil weathering. In cases where the principal cause of oil component loss is biotransformation, determination of the extent to which other processes can influence weathering indices is desirable, so that any observed changes can be more confidently attributed to microbial activity. Physical weathering of spilled petroleum products is one such component of oil weathering that may cause the value of weathering indices to change in such a way as to shroud the effects caused by microbial degradation. The effect of physical weathering of oil components on the value of weathering indices is likely to be greatest in the period immediately following spillage of lighter petroleum products, such as diesel oil, into relatively impervious receiving media. To investigate this, we have evaluated four weathering indices and three source correlation indices for diesel range organics DRO samples at three stages of physical weathering; fresh, 25% (w/w) weathered, and 50% (w/w) weathered. Just as biotic losses are measured according to the relative biotransformation rates of index compounds, so physical weathering should produce variations in index values related to the difference in the volatility of the index compounds. Where this difference is large, physical weathering might be expected to induce significant variations in the value of the index. Results are shown in Table 2.

C_{18} : Phytane and C_{17} : pristane were the weathering indices found to be least sensitive to physical weathering, that is, those that varied least in value between the respective DRO samples. In oil weathering studies, both of these indices were found to decrease in value with increased oil weathering, due to preferential microbial transformation of straight chain C_{18} and C_{17} *n*-alkanes over the branched chain isoprenoid alkanes. Biotransformation of the isoprenoid alkanes proceeds more slowly than that of the *n*-alkanes because of the presence of the tertiary carbon atoms within these compounds, catabolization of which is thermodynamically more demanding. This results in the accelerated loss of the numerator *n*-alkanes relative to the denominator isoprenoid alkanes and a decrease in the value of the indices. In this study, results indicate that both C_{18} : phytane and C_{17} : pristane indices appear to be largely unaffected by light physical weathering, as both indices remained unaltered between the fresh and the 25% (w/w) weathered DRO samples, at 2.1 and 1.9, respectively. However, for the 50% (w/w) weathered DRO samples, the C_{17} : pristane index increased in value to 2.5, suggesting that the *n*-alkane was more readily conserved in the DRO samples than was the isoprenoid alkane. Conversely, C_{18} : phytane for the 50% (w/w) weathered DRO decreased to 1.4, suggesting that in this case the abundance of the C_{18} component decreased relative to that of phytane. These results cannot easily be explained with reference to the respective physical properties of the index compounds, but imply that prolonged or intense periods of physical weathering could induce significant fluctuations in the values of these indices.

As expected, physical weathering exerts the greatest influence on those indices in which the tricyclic terpanes are measured. This is presumably due to the high boiling points of these compounds relative to other diesel components. For the weathering indices in which tricyclic terpanes are used as the conserved marker species, the C_{18} : tricyclic terpanes weathering index decreased with DRO weathering from 2.1 in the fresh sample to 1.5 in the 25% (w/w) weathered sample and to 0.5 in the 50% (w/w) weathered sample. The *n*-alkanes : tricyclic terpanes ratio was found to be the most sensitive, decreasing from 20.4 in the fresh DRO sample to 11.4 in the 25% (w/w) weathered sample and to 4.0 in the 50% (w/w) weathered sample. As the molecular structures of tricyclic terpane comprise a significant cyclic component, terpanes would be expected to be much less susceptible to biotransformation than the *n*-alkanes in the index numerators. As a result, these indices would also be expected to decrease in value with microbial activity. These results indicate, therefore, that a decrease in the value of this index should not necessarily be regarded as evidence of microbial activity, and that the effect of physical weathering processes may also need to be taken into account.

The values of the three proposed source correlation indices, pristane : phytane, pristane : tricyclic terpanes, and phytane : tricyclic terpanes, for DRO samples at each stage of weathering are given in Table 2. The former index was found to remain almost unchanged between the fresh and the 25% (w/w) weathered samples, at 1.4 and 1.3. For the 50% (w/w) weathered sample, however, its value decreased to 0.6. This variation suggests that pristane was more easily lost from the DRO samples than was phytane as physical weathering proceeded. During oil weathering, the structural similarity of these two compounds and their relative resistance to biotransformation has lead to their application as source correlation indices. Their use as such depends upon the absence of any sizeable fluctuation in the value of the ratio of these two components. In this study, results indicate that this index may be unsuitable for use as a source correlation parameter for oils that have undergone significant physical weathering, due to the magnitude of the variation in index value for the most weathered DRO sample. The loss of both pristane and phytane during physical weathering is confirmed by the decrease in the values of the pristane : tricyclic terpanes and phytane : tricyclic terpanes indices with increased DRO weathering. Values of pristane : tricyclic terpanes for the fresh, 25% (w/w) weathered, and 50% (w/w) weathered DRO samples were 1.0, 0.7, and 0.4, respectively, whereas those for phytane : tricyclic terpanes changed from 1.4 to 0.9 to 0.2 with increased DRO weathering. Because of the structural differences between pristane and phytane, and the tricyclic terpanes, these indices would also be expected to decrease during oil biotransformation.

These results demonstrate that even for standard oil weathered in a controlled laboratory environment, there are difficulties to be overcome before a source correlation index capable of providing a consistent, positive correlation between weathered samples can be defined. In our study, both pristane and phytane were demonstrated to be ultimately susceptible to physical weathering and, therefore, unsuitable for use in significantly weathered samples. More generally, it would appear that for a source correlation index to maintain its integrity throughout the weathering process, it must consist of components that are truly conserved during oil weathering and that do not display significantly different physical properties. In the absence of such an index, defining source commonality between mid-distillate petroleum products such as the DRO samples analyzed here may require a more careful consideration of oil characteristics rather than a straightforward calculation of pristane : phytane or isoprenoid : tricyclic terpane

ratios, particularly for highly weathered samples. Alternative oil fingerprinting techniques were demonstrated by Baugh and Lovegreen [24], who were able to define different refined petroleum products using representative GC-FID profiles, and differentiate between crude and refined petroleum products using the C_{20} to C_{30} hydrocarbon GC peaks.

Specificity of crude oil correlation parameters

Analytical correlation of oil samples in the environment, most commonly undertaken for source identification purposes, is routinely accomplished through a comparison of the characteristic distribution fingerprints of oil components. For oils that have undergone weathering, fingerprinting is most reliably achieved using the distributions of biomarker compounds. Source correlation indices, representing the ratio of one biomarker to another, are tools with which such a meaningful comparison of two oils can be supported [6,7,25]. Although evidence of commonality produced this way should be used only in conjunction with supporting information, it is nevertheless important to review these indices with the goal of establishing a greater appreciation of their potential use.

The usefulness of source correlation indices depends upon the degree to which their values vary between discrete oil samples. Effective source indices should vary significantly in value between oil samples from different backgrounds while remaining relatively consistent between oils from the same family. Ideally, their values should remain unaltered by the effects of oil weathering. In this study, the objective was to identify those correlation indices best able to discriminate between four unweathered crude oils from three different backgrounds: a Nigerian crude oil, an Iraqi export crude oil, and two North Sea crude oils. The results, given in Table 3, show that five of the seven indices adequately discriminated between the respective crude oil types: C_{18} : 17α(*H*),21β(*H*)-hopane, *n*-alkanes : 17α(*H*),21β(*H*)-hopane, pristane : phytane, tricyclic terpanes : hopanes, and phytane : 17α(*H*),21β(*H*)-hopane. All of these indices show sufficiently discrete values for each of the oil samples to allow clear discrimination between unrelated oils and yet support a positive correlation of the two North Sea crude oils. Of these, the C_{18} : 17α(*H*),21β(*H*)-hopane index, which has a value of 0.9 for the Nigerian crude, 22.6 for the Iraqi crude, and 16.8 and 13.1 for the two North Sea crudes, and the *n*-alkanes : 17α(*H*),21β(*H*)-hopane index, which has values of 10.7, 277.5, 166.5, and 184.7 for the Nigerian, Iraqi, and North Sea crudes, respectively, would be expected to change significantly in value with oil weathering because of the degradability of *n*-alkanes and C_{18} components in relation to the recalcitrant 17α(*H*),21β(*H*)-hopane. Therefore, for fresh oils that have not been exposed to environmental weathering, such as the samples analyzed in this study, these ratios may indeed make useful oil correlation parameters. However, they may be unsuitable for correlations involving weathered oil samples.

The other indices able to discriminate between the respective crude oil samples are pristane : phytane, tricyclic hopanes : total hopanes, and phytane : 17α(*H*),21β(*H*)-hopane. The values of all these indices would be expected to remain more or less constant during light to moderate oil weathering. For highly weathered samples, however, the latter two indices may become unreliable due to the susceptibility of both pristane and phytane to prolonged microbial activity. The tricyclic hopanes : total hopanes index should not alter even in highly weathered samples, due to the environmental persistence of the cyclic alkanes, and is, therefore, proposed as the oil correlation index best able to differentiate between both fresh and weathered crude oils. Of the remaining biomarker indices, C_{18} : phytane fails to discriminate between the Nigerian and Iraqi crude oils (both exhibit values of 1.4 for this index), and 17α(*H*),21β(*H*)-hopane : 17α(*H*),21β(*H*)-norhopane fails to discriminate between the Nigerian and one of the North Sea crudes (0.8 and 0.7). The latter result is surprising, given the accepted recalcitrance of hopane and suggests that oil correlation carried out through isolated use of this index could lead to erroneous diagnosis of oil source commonality.

Relationship between heavy oil composition and selected source and weathering indices

Elucidation of the composition of residual organic wastes at hydrocarbon-contaminated sites is important when the application of bioremediation technologies that depend upon the presence of more assimilable waste constituents is under consideration. In general, saturate class compounds (*n*- and branched alkanes), which often make up a significant proportion of the overall composition of many oils, are the components most susceptible to loss during natural attenuation or enhanced bioremediation. Polar and asphaltenic compounds are generally less responsive to microbial degradation. Wastes containing a preponderance of these compounds, such as heavy oils or oils that have undergone extensive weathering (and in which polar and asphaltenic material has therefore concentrated), may not, therefore, respond to bioremediation techniques. Unfortunately, in many cases, direct analysis of the entire range of waste components by GC-coupled analytical techniques is restricted due to inadequate resolution of the complex, high molecular weight polar components [26].

To investigate whether biomarker monitoring may allow for discrimination of waste types according to their suitability to treatment by bioremedial technologies, the values of selected source and weathering indices have been determined for a suite of medium to heavy petroleum products, chosen to represent the types of wastes frequently found at sites having residual petroleum contamination. This approach may be advantageous because biomarker monitoring allows the behavior of oil components from within the saturate class fraction to be scrutinized with minimal interference from other waste constituents. Furthermore, because the saturate class fraction does not contain any highly polar components, analysis by GC-MS is relatively straightforward, with high analyte recoveries readily obtainable. In cases of particularly complex waste matrices, chromatographic isolation of the saturate class fraction prior to GC-MS analysis may improve resolution of target biomarker compounds. However, oils that are extremely heavy or highly weathered may contain a significant proportion of unresolved complex material [27], in which case even extensive sample fractionation cannot always provide a suitably refined analyte. For such samples, the application of specialized chromatographic separation and detection procedures may not be warranted, and it may be more profitable to review the waste matrix in terms of bulk component groups through application of screening techniques, such as thin-layer chromatography with flame ionization detection or isotope ratio mass spectrometry [5,26].

To forecast the bioremediation potential of heavy oils through the use of biomarker indices, a relationship between the values of the indices and the composition of the oil must exist. We have conducted a preliminary examination of this

relationship by determining the values of six selected source and weathering indices for five unweathered heavy oils of known class composition. Two of the oils, a tanker ballast oil and a refinery residue oil, are predominantly paraffinic, containing >70% (w/w) saturates and <7% (w/w) combined polars and asphaltenes. The boiling range of the residue oil is considerably higher, however, indicating that the components of this oil are generally of a higher molecular weight. Other heavy oils analyzed are a refinery waste oil (referred to as API separator oil) (54% [w/w] saturates, 15.3% [w/w] combined polars and asphaltenes), a no. 6 fuel oil (approx. 36% [w/w] saturates and approx. 22% [w/w] polars and asphaltenes), and an acid tar oil, which was the heaviest of all the samples analyzed (approx. 35% [w/w] combined polars and asphaltenes). All the oil samples analyzed were produced from North Sea crude oils. This was important, as it ensured that variations in source and weathering indices were caused by differences in oil composition and not genetic background.

Values for the six selected source and weathering indices for each oil are given in Table 4. Two indices, C_{18} : phytane and 17α(*H*),21β(*H*)-hopane : 17α(*H*),21β(*H*)-norhopane, changed very little between the oils, with both showing an overall spread in value of only 0.9. The consistency of the latter index can be explained by the recalcitrance of the 17α(*H*),21β(*H*)-hopane and 17α(*H*),21β(*H*)-norhopane biomarkers [7–9], which would not be expected to fluctuate in abundance during oil production. As all the oil samples ultimately originate from the same crude oil source, the ratio of these biomarkers would be expected to remain broadly constant, which was found to be the case in this study. The reason for the apparent lack of variation in the value of the C_{18} : phytane index is not clear. Because the physical properties of C_{18} and phytane are so similar, they possibly behave similarly during oil production and do not become depleted or enhanced relative to one another. Nonetheless, based on these results, these indices appear to be insensitive to variations in oil composition and would not, therefore, make useful indicators of oil bioremediation potential.

The remaining indices showed a marked dependence on oil composition. The indices found to be most sensitive to oil composition were *n*-alkanes : 17α(*H*),21β(*H*)-hopane and phytane : 17α(*H*),21β(*H*)-hopane. The former index showed the largest variation in value between the oils, decreasing from 575.2 in the lighter ballast oil, to 406.4 in the API separator oil, 85.6 in the residue oil, 81.0 in the no. 6 fuel oil, and as low as 1.3 in the acid tar sample. A similar, though less prodigious, change is shown by the phytane : 17α(*H*),21β(*H*)-hopane ratio, which was found to be 39.9 in the ballast oil, 27.4 in the API separator oil, 2.1 in the residue oil, 4.2 in the no. 6 fuel oil, and 0.2 in the acid tar sample. The tricyclic terpanes : total hopanes index also decreased with increasing oil boiling range, with values of 12.1 for the ballast oil, 8.2 for the API separator oil, 0.5 for the residue oil, and 0.5 for the acid tar oil. However, this index was considered to be relatively unreliable after producing an unexpectedly high value of 11.6 for the no. 6 fuel oil. These results are useful in that they associate very low values for the *n*-alkanes : 17α(*H*),21β(*H*)-hopane and phytane : 17α(*H*),21β(*H*)-hopane indices with oils containing a sizeable combined polar and asphaltene fraction and ones that may not, therefore, be suitable for treatment by bioremedial technologies. As these indices would also be expected to produce low values for oils that have undergone extensive weathering, due to the susceptibility of the *n*-alkanes and phytane to biotransformation relative to the conserved hopane biomarker, these indices may also be useful in assessing the degradation state of oily wastes. Of course, the loss of oil components during oil weathering cannot be quantified without knowledge of the initial index value for the oil, or at the very least, the value of the index prior to oil degradation. Further studies are underway to assess the relative sensitivities of the biomarker weathering and source indices presented here during biotransformation of heavy oils.

CONCLUSIONS

Volatilization of petroleum contaminants in the environment could, in certain circumstances, affect the values of biomarker source and weathering indices. If these effects are not accounted for, they could lead to mistakes in oil correlation studies and erroneous diagnosis of microbial activity. The indices most affected by physical weathering in this study were C_{18} : tricyclic terpanes, *n*-alkanes : tricyclic terpanes, pristane : tricyclic terpanes, and phytane : tricyclic terpanes.

Five biomarker indices were able to distinguish between crude oils from different geological backgrounds: C_{18} : 17α(*H*),21β(*H*)-hopane, *n*-alkanes : 17α(*H*),21β(*H*),-hopane, pristane : phytane, tricyclic terpanes : hopanes, and phytane : 17α(*H*),21β(*H*)-hopane. Of these, the C_{18} : 17α(*H*),21β(*H*)-hopane and *n*-alkanes : 17α(*H*),21β(*H*)-hopane indices would be expected to change significantly in value with oil weathering. Extensive oil weathering may influence the pristane : phytane and phytane : 17α(*H*),21β(*H*)-hopane indices. Only the tricyclic terpanes : hopanes index is likely to remain unchanged by oil weathering, and this is therefore proposed as the most favorable oil correlation index in this study.

Biomarker indices may be useful in predicting the natural attenuation or bioremediation potential of heavy oil waste matrices by providing an indication of waste composition, or degradation state. Low values for *n*-alkanes : 17α(*H*),21β(*H*)-hopane and phytane : 17α(*H*),21β(*H*)-hopane indices were indicative of oils containing high proportions of polar and asphaltene class compounds. This may be because they are innately high boiling point oils or because they are heavily weathered oils. In either case, the application of bioremedial technologies for these oils may be restricted. Future microcosm studies will assess these constraints.

The utility of these indices for contaminants in the soil environment brings particular research challenges, such as interference from soil organic matter, enhanced biotransformation kinetics in soil, multimedia partitioning, and the presence of mixed organic wastes. Current work is focusing on the application of these indices to the contaminated soil environment, in particular to the variation of biomarker indices with heavy oil biotransformation, effected through the use of soil microcosm studies.

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Direct Determination of Polycyclic Aromatic Hydrocarbons in Environmental Matrices Using Laser Desorption Laser Photoionization Time-of-flight Mass Spectrometry*

Michael J. Dale, Anita C. Jones, Simon J. T. Pollard and Patrick R. R. Langridge-Smith†

Department of Chemistry, University of Edinburgh, Kings Buildings, West Mains Road, Edinburgh, UK EH9 1JJ

A series of environmental samples contaminated with polycyclic aromatic hydrocarbons (PAHs) were analysed using laser desorption laser photoionization time-of-flight mass spectrometry (L²TOFMS). Laser desorption removes the requirement for any sample pre-treatment and selective laser photoionization results in mass spectra containing signals corresponding principally to the contaminant PAH species. The methodology is based on the spatial and temporal separation of these evaporation and ionization steps. The instrument used is able to perform rapid, selective sample screening of contaminated soils, engine oil, coal soot and coal-tar creosote. The resulting fingerprint mass spectra indicate both the presence and composition of the PAHs in the matrices with instrumental detection limits in the sub-ppm range

Keywords: Laser desorption; laser photoionization; mass spectrometry; polycyclic aromatic hydrocarbons; environmental matrices

Introduction

Early studies of polycyclic aromatic hydrocarbons (PAHs) isolated from synthetic tars led to the discovery of the first chemical carcinogen, dibenz[*a*,*h*]anthracene.[1] Subsequent work has identified many other PAHs to be potent animal carcinogens.[2,3] Although there is currently no evidence that individual PAHs cause cancer in humans, substantial evidence exists to suggest that synergistic effects among individual PAHs render them hazardous constituents of complex hydrocarbon mixtures such as pitch, coal-tar, environmental tobacco smoke, oil shales and vehicle exhaust emissions.[2,4–6] PAHs are ubiquitous in the environment, having widespread natural and anthropogenic sources.[7] Human exposure to them, at some level, is therefore unavoidable. In the light of this, PAHs have been classified as priority pollutants by the US Environmental Protection Agency (EPA).

Interest in these compounds has led to the development of a variety of analytical techniques for differentiating between PAH ring sizes and the identification of specific PAH substituents and derivatives at trace levels of detection.[8] Gas chromatography combined with mass spectrometry (GC–MS) is currently the most widespread analytical method. Recent innovative approaches to PAH analysis have included gas chromatography linked to a variety of highly selective and sensitive instruments that utilize laser excitation of the target analyte. These have included multi-photon ionization Fourier transform mass spectrometry,[9] multi-photon ionization time-of-flight (TOF) mass spectrometry (MS)[10–12] and supercritical fluid injection mass spectrometry.[13] Also, a multi-dimensional approach, utilizing a number of techniques [capillary column gas chromatography (GC), resonance-enhanced multi-photon ionization, TOFMS and laser-induced fluorescence with flame ionization detection] combined in a single instrument, has been demonstrated by Dobson *et al.*[14] for the detection of a variety of PAHs. The above techniques generally require that the PAHs are extracted from their environmental matrices prior to analysis. GC is commonly employed as it not only provides separation of the analytes prior to detection but introduces them into the detection device as gas-phase molecules. However, the analytical recovery of high molecular mass PAHs using coupled GC techniques is often impeded by their low volatility and high affinity for the stationary phase. This problem has been addressed by the use of desorption techniques such as secondary ion mass spectrometry (SIMS),[15] fast atom bombardment (FAB)[16] and laser desorption (LD).[17,18] These involve solid samples being bombarded with either atoms, ions or photons. However, these are non-selective techniques, and the mass spectral information from the analysis of complex mixtures is often obscured by matrix or fragmentation peaks.

The investigation of PAHs in environmental matrices poses further problems in terms of reliable chemical characterization because of the occurrence of contamination in more than one medium and the existence of a complex matrix of materials with a diverse range of physico-chemical properties.[19] In order to determine contaminant PAHs in environmental matrices, the techniques mentioned above require that extensive sample clean-up operations are performed. Extraction and separation procedures are expensive and time consuming and, further, can introduce problems with respect to solubility, storage, biotransformation and photodegradation. Novel techniques are currently under development that aim to enhance analyte extraction efficiencies, improve clean-up processes and permit the analysis of contaminants *in situ*. These include supercritical fluid extraction (SFE),[20] laser-excited fluorescence,[21] thermal-desorption mass spectrometry (TEMS)[22] and remote laser-induced fluorescence (RLIF).[23] Investigations concerning the separation of selected PAHs using high-performance liquid chromatography (HPLC) are well known. This technique has been used for the determination of PAHs in Welsh soils.[24]

For the purposes of assessing compliance with environmental quality criteria, the initial screening of environmental samples often requires a fast, selective fingerprinting technique that can circumvent the problems associated with complicated clean-up protocols. In this paper we describe the use of laser desorption laser photoionization time-of-flight

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† To whom correspondence should be addressed.

mass spectrometry (L²TOFMS) for the direct determination of PAH analytes in a variety of typical matrices. This two-step methodology was initially developed for mass spectrometry of involatile and/or thermally labile organic molecules.[25–30] In the first step, sample molecules are desorbed as intact neutral species using a pulsed infrared laser. In the second step, the neutral molecules are photoionized using a pulsed ultraviolet (UV) laser. At the laser wavelengths chosen for this work, ionization is *via* a two-photon excitation scheme.

L²TOFMS, as a technique for the determination of PAHs, has a number of advantageous features. First, laser desorption permits the simultaneous vaporization of the components of a complex mixture of compounds. This step (which is usually accomplished with no sample decomposition) followed by laser ionization with minimal fragmentation, results in simple, readily interpretable mass spectra consisting principally of molecular ion peaks. The temporal and spatial separation of the desorption and post-ionization steps leads to minimal matrix interference in the mass spectra. This separation also allows us to exploit the ability of resonant two-photon ionization (R2PI) to ionize selectively target molecules that have appreciable absorption cross-sections at a particular ionization laser wavelength. These attributes circumvent many conventional analytical problems, making possible the *in situ* determination of PAHs in complex matrices. The effectiveness of a similar methodology for the microscopic determination of PAHs in meteoritic acid residues has recently been demonstrated by Zare's group.[31,32]

The results presented here demonstrate the capability of L²TOFMS to screen for PAHs in a rapid, selective and sensitive manner directly in environmental samples, specifically, contaminated soils, engine oil, coal soot and coal-tar creosote. The resulting fingerprint mass spectra indicate both the presence and composition of PAHs in these environmental matrices.

Experimental

Instrumentation

A detailed description of the experimental apparatus has been given previously.[29] A schematic diagram of the instrument is shown in Fig. 1 It is composed essentially of three separate high-vacuum chambers: the desorption chamber, the ionization chamber and a third chamber housing a reflectron TOF (RETOF) mass spectrometer. In the desorption chamber, the output from a pulsed CO_2 laser (Alltec 845MS, 10.6 μm wavelength) is focused on to a stainless-steel sample probe (see inset in Fig. 1). The analyte is applied to a shallow slot in the face of the probe prior to evacuating the desorption chamber. The sample probe is translated orthogonally to the incident desorption beam, both extending the lifetime of the sample and exposing a fresh area of sample to each laser shot. The desorbed neutral molecules are entrained in the pulsed helium molecular beam and transported from the desorption chamber to the ionization chamber. Here, laser radiation at 193 nm (ArF line, Lumonics TE-861T-4 laser) or 266 nm (fourth harmonic, JK HY750 Nd:YAG laser) is used to induce two-photon ionization of the desorbed molecules. The ionization laser pulse is synchronized to coincide with the entrainment pulse at the time at which the entrained target material is present at its maximum concentration. This time is determined by measuring the ion signal intensity as a function of ionization laser firing time. Ionizing laser power densities were maintained at relatively low values to ensure that soft ionization processes dominated, thereby maximizing the intensity of molecular ions and reducing fragmentation. Power densities were maintained at approximately 1 MW cm^{-2} for the experiments at 193 nm and approximately 0.4 MW cm^{-2} for those at 266 nm.

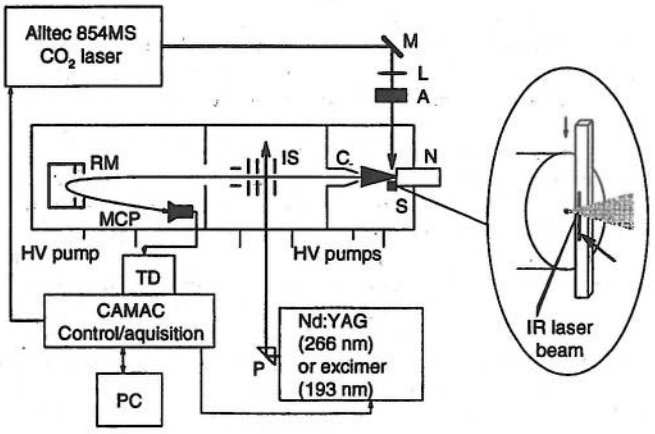


Fig. 1 Schematic diagram of the L²TOFMS instrument: A, nickel mesh attenuators; M, gold-plated mirror; P, quartz tuning prism; L, 300 mm NaCl focusing lens; N, pulsed nozzle mounted on *xyz* manipulator; S, sample probe; C, collimating skimmer; IS, ion source; RM, reflectron mirror; TD, transient digitizer; HV, high vacuum pump; MCP, microchannel plate detector; and PC, personal computer. Inset: magnification of laser desorption geometry

The resulting photo-ions are mass separated in a laboratory-built reflectron TOF mass spectrometer. The ions are detected by a tandem microchannel plate (MCP) detector and the signal is further amplified by a factor of 10. Spectra are collected using a CAMAC-based data acquisition system, employing a 200 MHz transient digitizer (Joerger TR200), interfaced to a Dell Model 325 personal computer with in-house custom software. Experiments are carried out at a repetition rate of 10 Hz. Typically, data from 200 laser shots are accumulated to enhance the signal-to-noise ratio. The complete experimental procedure, from sample presentation to data accumulation and storage, can be performed within a 10 min period.

Instrument Characterization

The TOF mass spectra were calibrated using two known species, aluminium (27 u) and coronene (300 u). The mass resolution ($m/\delta m$) is typically 500 at mass 250 u, where m is the compound mass and δm is the FWHM of the mass peak. In its present configuration, the maximum resolution achieved has been determined as 1250 for perylene at mass 252 u. The resolution of the TOF mass spectrometer is determined largely by the diameter of the ionizing laser spot and, to a lesser extent, the laser fluence. Therefore, there is a trade-off between detection sensitivity and instrument resolution, and the resolution that can be achieved in practice is influenced by the requirement for sufficient instrument sensitivity. Further, it is important to note that the resolution of the spectra recorded here is limited by the digitizer sampling speed, typically 50 MHz, and is not intrinsically limited by the instrument. To obtain the spectra shown later, the 266 nm laser beam was collimated, using a telescope, to a 4 mm diameter spot whilst the 193 nm laser beam was defined by a collimating slit as a 2 × 15 mm rectangle.

In order to assess the detection sensitivity of the instrument, the limits of detection for several PAH molecules were investigated. Successively smaller amounts of target material were doped on to the sample probe in a dichloromethane solution and the solvent was allowed to evaporate. The limit of detection was considered to be reached when the signal-to-noise ratio approached 3:1. In order to account for heterogeneous surface sample coverage, 1000 consecutive shots were accumulated. Knowing the distance the probe had

travelled during 1000 shots and the laser spot size, and assuming all the target sample is removed during the desorption stage, the limits of detection for a variety of PAHs could be obtained. Perylene, coronene and pyrene were found to have sub-picomole (10^{-12} mol) limits of detection. These limits of detection do not represent an absolute minimum. Instrument modifications should permit a sensitivity improvement of several orders of magnitude. Recent work by Zare's group[33] has demonstrated that by removing the inefficient entrainment process and optimizing the instrument transmission, zeptomole (10^{-21} mol) limits of detection for pure coronene are possible.

Samples

Four different contaminated materials were examined: contaminated soil, engine oil, coal soot and coal-tar creosote. The soil samples were obtained from a contaminated former coal gasification plant and coal-tar distillery in the UK. Samples were taken from shallow trial pits (0.5 m depth), and consisted of three grab samples taken at 120° from each other prior to being composited into approximately 5 kg total samples. These were air dried at ambient temperature in a forced draught. After the resulting aggregates had been broken up, the entire sample was passed through a 10 mesh sieve to remove rock fragments (≤2.00 mm). The fraction passing through was then homogenized by being rifled down to a 50 g sub-sample.[34] The engine oil used was Castrol GTX lubricating oil. Unused oil was examined as received and the used oil was examined following removal from a car engine after approximately 6 months of average usage. Coal soot samples were collected from the chimney of a coal-burning, open domestic fire and the coal-tar creosote (Golden Creosote) was supplied by Samuel Davies (UK).

Sample Preparation

The samples were presented directly to the instrument as received, without pre-separation or chemical treatment. To ensure good sample coverage on the desorption probe, some minimal sample preparation was required. For soils, this consisted of grinding them into a fine powder, binding the particles together with a drop of glycerol and applying the homogeneous paste to a 1.5 × 40 mm slot in the sample probe. The sample surface exposed to the desorption laser beam was then dried with a dusting of alumina type H. The oil, soot and creosote samples were treated similarly, being simply mixed into a paste with alumina and/or glycerol and then pressed directly into the sample probe slot.

Results and Discussion

Mass Spectra of Contaminated Soils

Each of the six contaminated soil samples was examined using both 266 and 193 nm laser photoionization. Typical mass spectra obtained for one of these samples, using 266 and 193 nm photoionization, are shown in Fig. 2(*a*) and (*b*), respectively. They represent the total accumulated ion signal obtained on summing 200 laser shots. It is important to note the absence of peaks corresponding to either the glycerol matrix or the soil itself. The spectra are simple and readily interpretable. These fingerprint mass spectra were obtained in consecutive experiments, and the entire preliminary screening of the six samples was completed within 90 min. Each 200 shot spectrum represented the total ion signal obtained on interrogating approximately 1 mg of the contaminated soil. Samples up to about 50 mg can be examined in one continuous scan of the probe slot. This requires the accumulation of 6000 consecutive shots but provides more consistently reproducible data concerning relative PAH concentrations.

PAH signals can be seen, in both Fig. 2(*a*) and (*b*), in the region between 100 and 400 u. Signals at masses higher than 300 u indicate the presence of PAHs with more than seven fused rings. In the low-mass region, below 100 u, the dominant signals are due to the presence of elemental cations, *e.g.*, Na^+ and K^+. The source of the signal due to Al^+ at 27 u was the alumina on the surface of the sample matrix, whereas the peak due to Fe^+ could be from either the soil sample itself or from ablation of the stainless-steel probe. The PAH signal intensity is generally lower, over all masses, in the mass spectra obtained using 266 nm laser photoionization. This means some of the less intense mass peaks may not be observed at this wavelength, as is evidenced by less intense or missing high-mass peaks (above 300 u) in the spectrum in Fig. 2(*a*). Further, the more energetic 193 nm photons are more efficient at ionizing the metal species, giving an increased ion yield for these compared with photoionization at 266 nm. At both ionizing wavelengths, the absence of signals derived from the soil matrix or glycerol binder eliminates the need for the analysis of blank samples for comparative purposes and background subtraction.

These soil samples had been previously investigated using GC–MS[34] following a Soxhlet extraction with dichloromethane and a number of specific target PAHs had been identified in the dichloromethane extract. The structures of these molecules and their molecular masses are shown in Fig. 3. It was possible to assign these previously identified species to a number of the more intense peaks in our mass spectra. For example, peaks at 178, 202, 228, 252 and 276 u correspond to phenanthrene/anthracene, fluoranthene/pyrene, chrysene/benz[*a*]anthracene, benz[*b* or *k*]fluoranthene/benzo[*a*]pyrene, and indeno[123-*cd*]pyrene/benzo[*ghi*]-perylene.

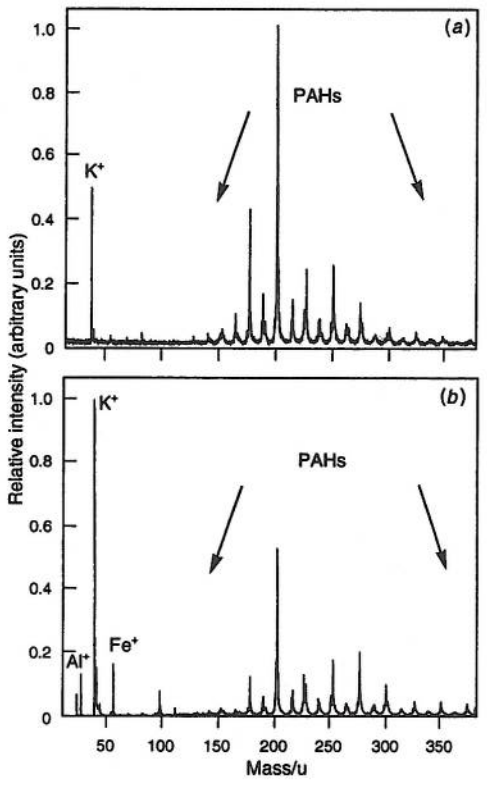


Fig. 2 L^2TOF mass spectrum of ≈1 mg of contaminated soil obtained using (*a*) 266 nm and (*b*) 193 nm laser photoionization

The peaks corresponding to these species are numbered in Fig. 4, which for clarity shows an expansion of the PAH-containing region of the mass spectrum taken using 193 nm laser photoionization. Possible assignments for all the major peaks in this spectrum, corresponding to skeleton parent PAHs, including those previously determined, are summarized in Table 1. As their identification is based only on molecular mass, only one or two representative compounds are indicated for each mass. It is worth noting that although the presence of some of these species was confirmed by GC–MS, they are not necessarily exclusively responsible for the ion signal at a particular mass; isomers cannot be differentiated directly from these photoionization mass spectra. To distinguish the component species completely would require the use of selective ionization of individual isomers or recourse to more advanced tandem (MS–MS) TOF instrumentation. The exact assignment of higher mass PAHs is further complicated by the increasing number of possible isomers that may be present. Other peaks in the spectrum can be identified that are separated by characteristic increments of 14 u. These series of peaks originate from various skeletal unsubstituted PAHs, and indicate the presence of successively alkylated species where H is successively replaced by CH_3.

The mass spectra of pure PAHs, obtained under soft ionization conditions, show that although the molecular ion dominates the mass spectra, there are other less intense peaks commonly present which correspond to $[M + 1]^+$, $[M - 1]^+$ and $[M - 2]^+$, *etc.* For example, the molecular ion region in the 266 nm photoionization mass spectrum of coronene is shown in Fig. 5. Here it can be seen that there is successive loss of hydrogen atoms down to $[M - 6]^+$. This could account for some of the intensity of the smaller mass peaks and for the presence of odd-mass peaks in the spectra.

Differences in the relative abundances of the same compound in different soil samples, from a particular contaminated site, can be estimated by comparing the signal intensities at a particular mass between two mass spectra. Relative signal intensities within a particular mass spectrum, however, do not directly reflect the relative concentrations of different species

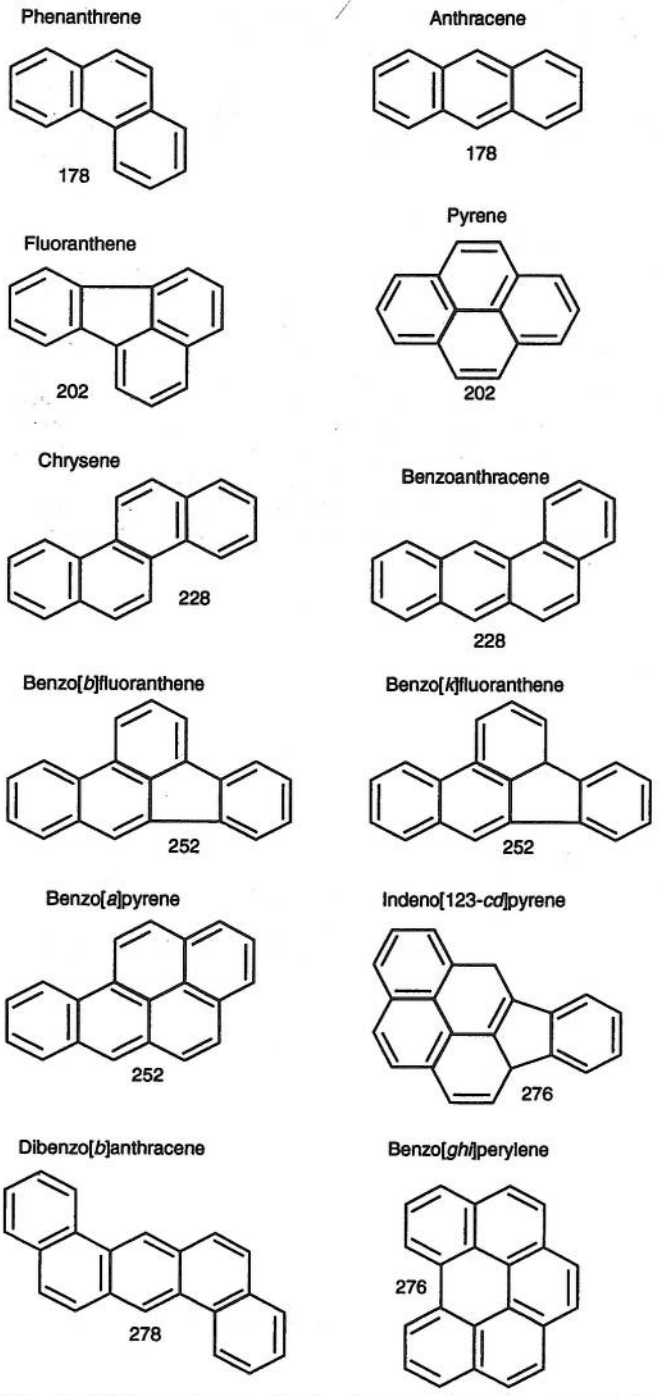


Fig. 3 PAH species previously determined to be present in contaminated soil by GC–MS following CH_2Cl_2 extraction

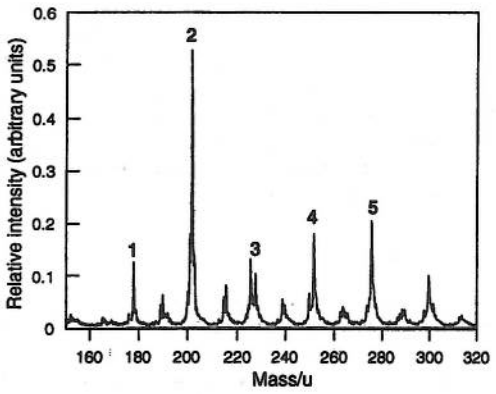


Fig. 4 Expansion of L²TOF mass spectrum of contaminated soil between 170 and 320 u to show more clearly the resolved mass spectral peaks. Confirmed mass assignments are: 1, 178, phenanthrene/anthracene; 2, 202, pyrene/fluoranthene; 3, 228, chrysene/benz[*a*]anthracene; 4, 252, benzo[*a*]fluoranthene/benzo[*a*]pyrene; 5, 276, indeno[123-*cd*]pyrene/benzo[*ghi*]perylene, from GC–MS data

Table 1 PAH assignment for the L²TOF mass spectrum of contaminated soils obtained using 193 nm laser photoionization

Mass (u)	Assignment (complete isomer set not listed)
152	Acenaphthylene
166	Fluorene
178	Phenanthrene/anthracene
190	4*H*-Cyclopenta[*def*]phenanthrene
202	Pyrene/fluoranthene
216	11*H*-Benzo[*a*]fluorene
226	Benzo[*ghi*]fluoranthene
228	Chrysene/benz[*a*]anthracene
252	Benzo[*a*]pyrene/benzo[*b* + *k*]fluoranthene
264	11*H*-Cyclopenta[*ghi*]perylene
276	Indeno[123-*cd*]pyrene/benzo[*ghi*]perylene
290	5*H*-Benzo[*b*]cyclopenta[*def*]chrysene
300	Coronene
326	Dibenzo[*a*]perylene
350	Benzo[*a*]coronene
374	Dibenzo[*a*]coronene

in the soil sample. This is because parent ion peak intensities are not only proportional to the concentration of a compound in the sample, but also depend on the ionization cross-sections for different species at any particular ionizing wavelength. Thus, for example, it is possible that the components pyrene/fluoranthene, corresponding to mass 202 u, are not the most prevalent in the sample, but are the most efficiently ionized at the laser wavelength employed.

In the earlier GC–MS work carried out on these samples, selected PAHs had been quantifiably determined as being present in concentrations between about 0.1 and several hundred ppm.[34] These concentrations are listed in Table 2 for one of the six soil samples. It is possible to determine the approximate concentrations of particular species using L²TOFMS. Quantification was achieved using a series of standard additions. Six 50 mg samples of a particular soil sample were spiked with various amounts of phenanthrene. Fig. 6 shows the 178 u:202 u signal intensity ratio *versus* the amount of phenanthrene added for the soil sample whose composition is given in Table 2. The ratio of peak heights was determined using the signal at 202 u as an internal standard, rather than the absolute signal intensity of the 178 u peak, to account for variations in the total amount of spiked sample applied to the probe. A least-squares fit of these data points was extrapolated to zero intensity to yield the concentration of phenanthrene/anthracene in an unspiked soil sample, as shown in Fig. 6. The results obtained using this approach gave values for the total anthracene/phenanthrene concentration, which are in reasonable agreement with those determined by GC–MS. For example, the value we obtain from data shown in Fig. 6 is approximately 390 ppm, compared with the combined concentration of 309.8 ppm for anthracene and phenanthrene, obtained via GC–MS (see Table 2). In comparing these two values, it is important to note that the extraction and separation processes required for sample preparation in the GC–MS study are difficult to quantify reliably and that the ionization cross-sections for anthracene and phenanthrene have been assumed to be the same in the L²TOFMS experiment.

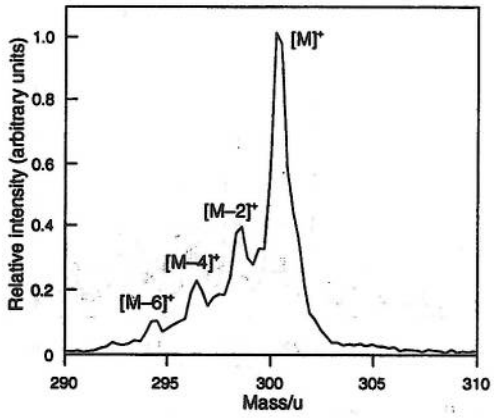


Fig. 5 L²TOF mass spectrum of coronene under soft ionization conditions showing the molecular ion region

Table 2 PAH concentrations determined for soil sample using GC–MS.[34] The combined concentration of phenanthrene and anthracene (309.8 ppm) can be compared with that obtained using L²TOFMS and the method of standard additions (see text)

PAH	Mass (u)	Concentration (ppm)
Naphthalene	128	4.3
Acenaphthene	154	175.4
Acenaphthylene	152	44.9
Fluorene	166	156.6
Phenanthrene	178	207.5
Anthracene	178	102.3
Fluoranthene	202	200.5
Pyrene	202	338.8
Chrysene	228	60.9
Benz[*a*]anthracene	228	87.2
Benzo[*b* + *k*]fluoranthene	252	124.4
Benzo[*a*]pyrene	252	118.2
Indeno[123-*cd*]pyrene	276	NF*
Dibenzo[*a*]anthracene	278	4.5
Benzo[*ghi*]perylene	276	200.3

* Not found.

Mass Spectra of Contaminated Engine Oils

The mass spectrum obtained from the interrogation of a clean, unused engine oil sample is shown in Fig. 7(*a*). This was obtained using 193 nm laser photoionization and represents the accumulation of data from 1000 laser shots. Several homologous series of peaks are immediately apparent. In the mass region between 30 and 180 u several such series can be identified. In each series the ion signals are separated by characteristic increments of 14 u. For example, the mass peaks at 91, 105, 119 and 133 u and at 117, 131, 145, 159 and 173 u constitute two such series. Similar series are observed above 250 u. Fig. 7(*b*) shows these higher homologues more clearly. No mass peaks with significant intensity are observed above 500 u. The separation between groups is again 14 u, suggesting their assignment to a homologous series in which an aromatic head group is appended with a lengthening hydrocarbon chain (or chains). The peak separation within each of these features is 2 u, which may be accounted for by the hydrogenation of unsaturated alkene bonds in the hydrocarbon side-chains. The lack of significant ion signals in the central region of the spectrum [see Fig. 7(*a*), and at lower masses, suggests that photofragmentation is minimal under the soft ionization conditions employed and that the peaks correspond to the presence of individual molecular ions, not fragmentation products.

The mass region between about 170 and 300 u is where signals corresponding to PAH components would be expected to occur. In the case of the 'clean' oil sample these species are not observed. They are, therefore, either not present or are present in concentrations below the limit of detection of the instrument (sub-ppm). However, the presence of PAHs as combustion products in used engine oils is well known and consequently the disposal of such materials is of considerable environmental concern. The mass spectra we obtain, under conditions identical with those stated above, for a similar

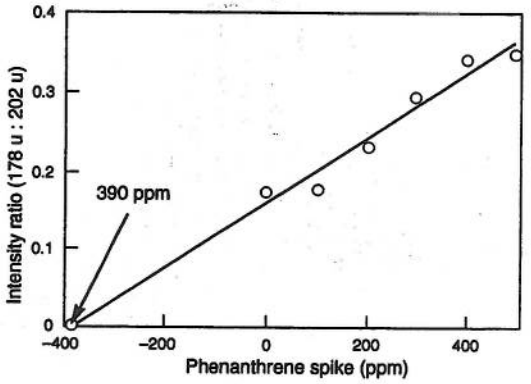


Fig. 6 Plot of 178 u:202 u signal intensity ratio *versus* spiked concentration of phenanthrene for a contaminated soil sample. Extrapolation yields an approximate concentration of phenanthrene/anthracene contamination of 390 ppm (R = 0.9756)

sample of used engine oil are shown in Fig. 8(*a*) and (*b*). There is an important difference between these spectra and those of the clean oil [Fig. 7(*a*) and (*b*)]. The central region of the mass spectrum corresponding to the used oil is now dense with new features, as shown in Fig. 8(*b*). These new peaks can be tentatively identified as belonging to several series of successively alkylated parent PAHs where H is replaced with CH_3. For example, a series of alkylated phenanthrenes is indicated by the arrows on the mass spectrum in Fig. 8(*b*). In Table 3 the most prominent series of ion peaks that can be identified in the mass spectrum are summarized together with an assignment of the parent PAHs.

It is clear that these fingerprint mass spectra yield analytically useful data, allowing rapid screening of lubricating oils for contaminant PAHs. Despite the presence of background signals from the base oil, these contaminant species are observable, without requiring recourse to any extraction and separation procedures. Because these species are by-products formed during the active employment of lubricating oils, such a rapid screening technique may have application in the on-line monitoring of their development. In addition, the concentrations of these contaminants that are present may be obtained using the sample spiking methodology described in the previous section.

Mass Spectra of Coal Soot

The L²TOF mass spectrum for a sample of coal soot is shown in Fig. 9. This spectrum represents the accumulation of 500 shots. Again, a number of peaks are observable that correspond in mass to the presence of unsubstituted PAHs. Such species have been observed previously in rice straw soot using a similar methodology.[35] The dominant signals found in the spectra obtained from rice straw soot were at 178, 202, 228 and 252 u. These mass peaks correspond to three-, four- and five-ring PAHs. The distribution of PAHs in oil shale soot particles has been the subject of a previous study using laser microprobe mass analysis (LAMMA) spectrometry.[18] The positive ion LAMMA spectra contained features corresponding to both inorganic and organic components, rendering the

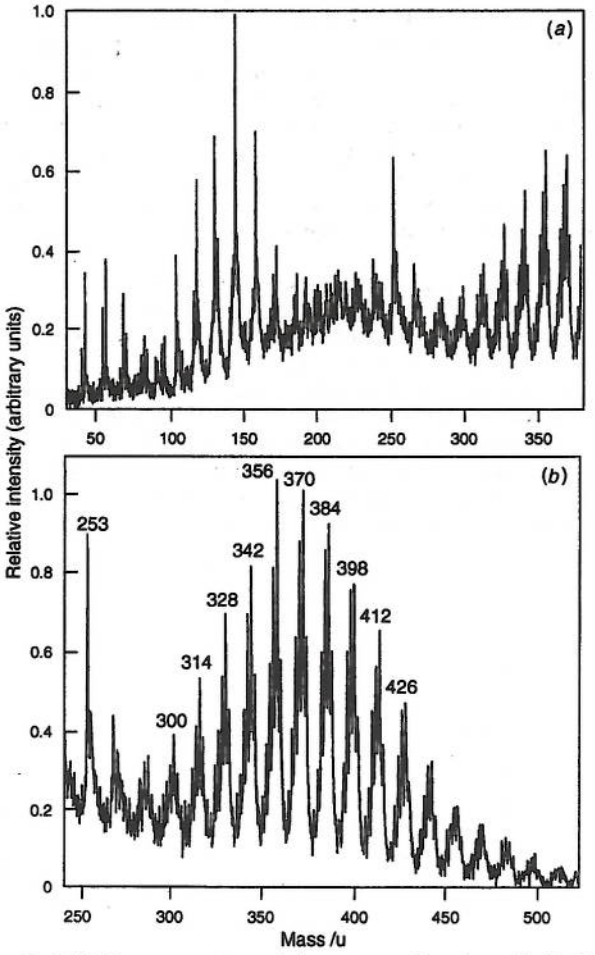


Fig. 7 L²TOF mass spectra of clean, unused engine oil obtained using 193 nm laser photoionization; spectrum (*a*) shows the entire mass range up to 380 u and spectrum (*b*) an expansion of the region between 240 u and 520 u

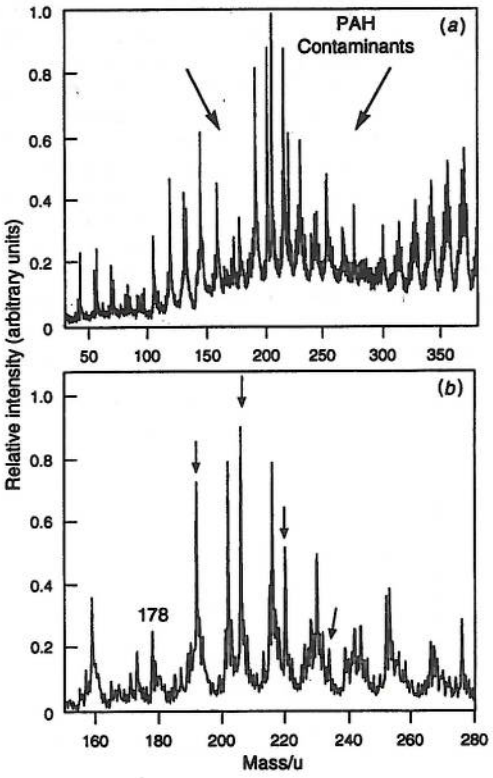


Fig. 8 L²TOF mass spectra of contaminated, used engine oil obtained using 193 nm photoionization. In spectrum (*a*) a series of contaminants in the mass 'window' between 170 u and 300 u in the previous mass spectrum [Fig. 7(*a*)] can be clearly identified. These are shown more clearly in the expanded spectrum (*b*). The assignment of some of these peaks to a series of alkylated PAHs is indicated (see text)

Table 3 Peak assignments for L²TOF mass spectrum of contaminated engine oil obtained using 193 nm laser photoionization

Mass (u)	Assignment*	Molecular formula
178	Phenanthrene/anthracene	$C_{14}H_{10}$
192	C_1-phenanthrene	$C_{15}H_{12}$
206	C_2-phenanthrene	$C_{16}H_{14}$
220	C_3-phenanthrene	$C_{17}H_{16}$
234	C_4-phenanthrene	$C_{18}H_{18}$
248	C_5-phenanthrene	$C_{19}H_{20}$
202	Pyrene/fluoranthene	$C_{16}H_{10}$
216	C_1-pyrene	$C_{17}H_{12}$
230	C_2-pyrene	$C_{18}H_{14}$
244	C_3-pyrene	$C_{19}H_{16}$
258	C_5-pyrene	$C_{20}H_{18}$
252	Benzo[*a*]pyrene/perylene	$C_{20}H_{12}$
266	C_1-benzopyrene	$C_{21}H_{14}$
276	Benzo[*ghi*]perylene	$C_{22}H_{12}$

* Complete isomer set not listed.

assignment of some peaks ambiguous. However, here again a series of mass peaks were observed corresponding to parent PAHs. In these oil shale soot particles, predominantly high-mass components, corresponding to five-ring PAHs and above, were found. It is possible to assign parent isomer groups to the mass peaks observed in the mass spectrum shown in Fig. 9. The peaks labelled in the mass spectrum at 178, 202, 228, 252 u correspond to phenanthrene, pyrene, chrysene, benzo[*a*]pyrene and benzo[*ghi*]perylene, respectively, or their isomers. The production of high-mass PAHs is favoured by the high temperatures found in combustion processes.[36] This is confirmed by the relatively strong signals corresponding to the higher molecular mass PAHs, although signals corresponding to PAHs with more than five rings are not observed. The contribution from odd-mass peaks is very small in Fig. 9, suggesting that nitrogen heterocycles are either not present or are present only at low concentrations in the soot matrix.

Mass Spectra of Coal-tar Creosote

Fig. 10 shows a characteristic fingerprint mass spectrum of a coal-tar creosote sample. Creosote is derived from either coal or coal-tar distillation, the creosote fraction being the material that distills over between 210 and 280 °C.[37] Acute toxicity and carcinogenicity associated with this material have obvious ramifications for human health.[38] Table 4 lists the predominant PAHs found in coal-tar creosote.[39] This list is incomplete as creosote contains many phenolic (~10%) and heterocylic compounds (~5%) in addition to the PAHs.[39–41] However, this simplified list highlights the correlation between expected and observed polyaromatic species. The mass spectrum shown in Fig. 10 is dominated by the signals at mass 178 and 202 u, corresponding to three- and four-ring PAHs, respectively. However, the spectrum also contains peaks corresponding to the masses of most of the species listed in Table 4. The only species not accounted for are those of low mass, such as naphthalene and the methylnaphthalenes. These species are considerably more volatile than the higher mass PAHs and were probably lost from the sample during the pump-down of the desorption vacuum chamber. The persistence of naphthalenes in solid environmental samples is known to be relatively low because of their volatility and facility to undergo biotransformations (most of the naphthalene in the environment is associated with the vapour phase[42]). This probably accounts for the absence of these well known contaminants from all the mass spectra shown so far. There are also other mass peaks present in Fig. 10 that correspond to PAHs not listed in Table 4. The most intense of these are at 190, 218, 230 and 243 u. These can be tentatively assigned to 4*H*-cyclopenta[*def*]phenanthrene, dimethyl-4*H*-cylopenta(*def*]phenanthrenes, methylbenzofluorenes and methylchrysenes, respectively, or their isomers. A further group of neutral components known to be present are the alkanes. However, these are not ionized at the UV laser wavelengths used in this study and therefore do not appear in the mass spectra.

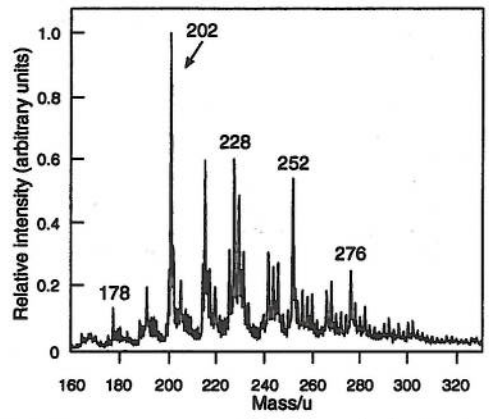


Fig. 9 L²TOF mass spectrum of coal soot obtained using 193 nm photoionization

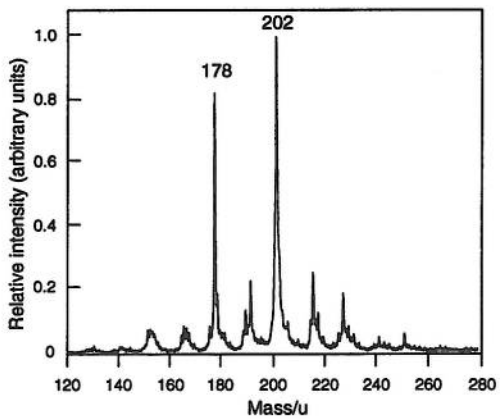


Fig. 10 L²TOF mass spectrum of coal-tar creosote obtained using 193 nm photoionization

L²TOFMS as a Screening Tool

The results presented above demonstrate the utility of L²TOFMS for the rapid qualitative analysis of PAH mass groups by the direct interrogation of their host environmental matrices. This approach to sample screening is both robust and flexible, featuring low limits of detection for PAHs. The minimal sample preparation that is required reduces sample extraction and handling difficulties. Further, the instrument is capable of handling a large throughput of real, dirty sample systems. This rapid screening capability is complemented by the ability to perform semi-quantitative analysis on individual components or isomer groups.

The technique of L²TOFMS should therefore prove to be a valuable addition to existing environmental screening methodologies.[43] The ability to provide fingerprint mass spectra of high molecular mass PAHs, five-ring PAHs and above, extends its range beyond that of GC–MS. In addition, as a tool for the examination of environmental contaminants themselves, *e.g.*, oil, the mass spectra provide rapid information

Table 4 Predominant PAHs in coal-tar creosote

PAH	Relative concentration (% m/m)	Mass (u)
Naphthalene	13	128
2-Methylnaphthalene	13	142
Phenanthrene	13	178
Anthracene	13	178
1-Methylnaphthalene	8	142
Biphenyl	8	154
Fluorene	8	166
2,3-Dimethylnaphthalene	4	156
2,6-Dimethylnaphthalene	4	156
Acenaphthene	4	154
Fluoranthene	4	202
Chrysene	2	228
Pyrene	2	202
Anthraquinone	1	208
2-Methylanthracene	1	192
2,3-Benzo[*b*]fluorene	1	216
Benzo[*a*]pyrene	1	252

concerning the generation of PAHs in such materials. Increasing concern about human exposure to PAHs means that future target matrices are likely to include foodstuffs, aerosol condensates, food additives and roadside particulates.

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Application of Two-Step Laser Mass Spectrometry to the Analysis of Polynuclear Aromatic Hydrocarbons in Contaminated Soils

Michael J. Dale, Anita C. Jones, Simon J. T. Pollard, and Patrick R. R. Langridge-Smith*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, U.K.

Alan G. Rowley

218 Dinerth Road, Rhos-on-Sea, Colwyn Bay, Clwyd, LL28 4UH, U.K.

Introduction

Contaminated site remediation is a multistage process that commences with an initial indication of contamination and is concluded with the long-term monitoring of remedial measures (*1–3*). Critical to the successful completion of the process is the informative nature of the site assessment data. This information ultimately determines the level of confidence with which risks to human health and the environment can be adequately assessed and managed (*4–6*).

Hydrocarbon-contaminated soils, such as those found at former manufactured gas plant sites, creosote wood-preserving plants, and petroleum refineries pose specific problems for reliable chemical characterization because of the presence of multimedia contamination, the existence of a complex matrix of individual contaminants exhibiting a diverse range of physiochemical properties, and the expensive analytical procedures often required (*4, 7*). Such sites have generated growing concern throughout industrialized countries because the chemical contaminants identified on-site almost invariably include the polynuclear aromatic hydrocarbons (PAHs), several high molecular weight analogues of which pose a toxicological hazard due to their documented carcinogenic activity (*8*).

Analytical techniques such as conventional gas chromatography-mass spectrometry (GC-MS) for hydrocarbon-contaminated soils require lengthy and involved sample cleanup procedures which can render them cost-prohibitive for extensive contaminated site assessment. Delay times between sampling in the field and the receipt of analytical data can result in sampling protocols being less focused than they would be if even a semiquantitative estimate of the extent of contamination were readily available. In acknowledgement of these difficulties, considerable effort has recently been focused at developing and validating field techniques capable of analyzing contaminants on-site without the need for sample cleanup. On-site screening and field techniques allow the rapid feedback of information to field personnel during the sampling procedure (*9*). Under certain sampling protocols, the screening of large numbers of samples prior to indicator compound(s) analysis will result in significant cost savings throughout the risk assessment and risk management process. Among the analytical methods currently under evaluation for on-site analysis are thermal desorption-gas chromatography-mass spectrometry (TE-GC-MS), ultraviolet fluorescence, and remote laser-induced fluorescence (RLIF) techniques (*9–15*).

In this paper, we describe initial investigations into the use of laser desorption laser photoionization time-of-flight mass spectrometry (L^2TOFMS) for the direct determination of PAH analytes in solid waste matrices. This relatively new technique has potential as an on-site field screening tool, offering the ability to determine a wide variety of organics contained in a wide variety of matrices. It involves a two-step process in which the first laser desorbs primarily intact neutral molecules from the sample and the second laser causes "soft ionization" of selected classes of compounds which are identified by time-of-flight (TOF) mass spectrometry (*16–18*). This method of mass analysis, with its advantages of rapid, multiplexed data aquisition is ideally interfaced to the pulsed lasers used for sample desorption and photoionization. Previous work performed using this two-stage methodology has demonstrated its ability to determine analytically important organic compounds. These have included peptides (*19*), porphyrins (*20*), commercial dyestuffs (*21*), PAHs (*22*), and polymers (*23*). More recently, Kovalenko et al. have used a similar methodology to investigate the PAH components of selected meteorites (*24*). As a novel approach to sample screening, this circumvents many problems associated with more conventional analytical techniques, allowing determination of semivolatile, involatile, and thermally labile species without the need for extensive extraction and separation procedures. The results presented here demonstrate the capability of L^2TOFMS to analyze PAHs in a rapid, highly selective, and sensitive manner directly from the contaminated soil matrix.

Experimental Section

Soils. The six soil samples used in this study were obtained from a contaminated former coal gasification plant and coal-tar distillery in the UK. Samples were taken from shallow trial pits (0.5 m depth) and consisted of three grab samples taken at 120° from each other prior to being composited into approximately 5-kg total samples. Samples were air-dried at ambient temperatures in a forced draught. After the resulting aggregates were broken up, the entire sample was passed through a 10-mesh sieve (≤2.00 mm), the fraction passing through was then homogenized by being riffled down to a 50-g subsample (*25*). Previous gas chromatography-mass spectrometry has determined the concentration of individual PAHs in these samples to range from 1 and 400 ppm.

Sample preparation for the L^2TOFMS technique consisted of grinding the soils further into a fine powder, binding the particles together with a drop of glycerol, and applying the homogeneous paste to a 1.5 × 40 mm^2 slot in the sample probe. The sample surface open to the desorption laser beam was then dried with a dusting of alumina-type H.

Instrumentation. A detailed account of the experimental apparatus has previously been reported (*21*). The instrument is composed essentially of three separate high vacuum chambers: the desorption chamber, ionization chamber, and a TOF mass spectrometer.

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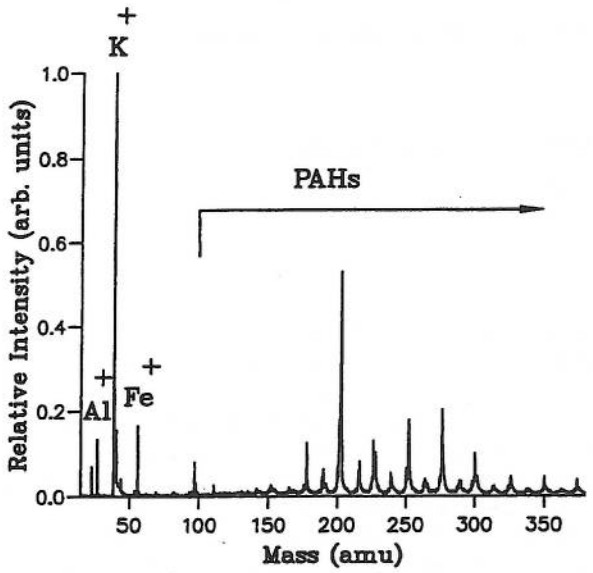


Figure 1. L²TOFMS spectrum of ca. 1 mg of contaminated soil produced by 193-nm photoionization.

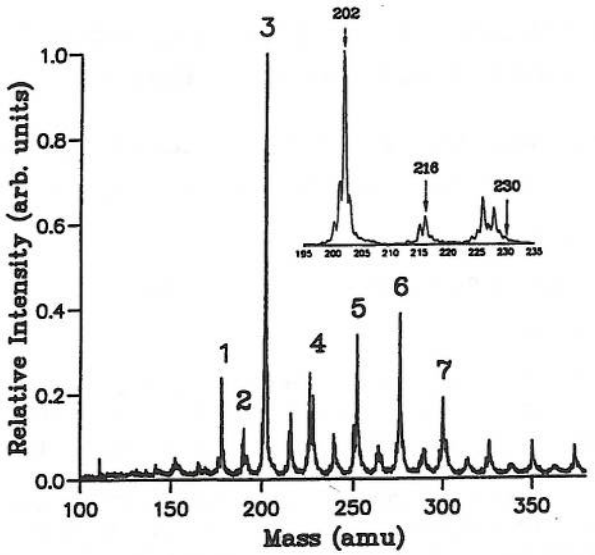


Figure 2. L²TOFMS mass spectrum of contaminated soil expanded to clearly show the resolved mass spectral peaks in the region containing the PAHs. Mass identifications are 1, 178, phenanthrene/anthracene; 2, 190, 4*H*-cyclopentaphenanthrene; 3, 202, fluoranthene/pyrene; 4, 228, chrysene/benzo[*a*]anthracene; 5, 252, benzo[*a*]fluoranthene/benzo[*a*]pyrene; 6, 276, indeno[1,2,3-*cd*]pyrene/benzo[*ghi*]perylene; 7, 300, coronene. Insert: expansion of 195–235 amu region showing a series of alkylated pyrene/fluoranthene species.

In the desorption chamber, the output from a pulsed CO_2 laser (Alltec 854MS, 10.6 μm wavelength) is focused, using a NaCl lens, onto a stainless steel sample probe. The sample probe is translated orthogonally to the incident desorption beam, both extending the lifetime of the sample and exposing a fresh area of sample to each laser shot. The neutral molecules thus desorbed are entrained in a pulsed supersonic helium molecular beam and transported from the desorption chamber into the ionization chamber. Here, 193-nm photons (ArF line, Lumonics TE-860T laser) or 266-nm photons (fourth harmonic, JK HY750, Nd:YAG laser) are used to induce the multiphoton ionization (MPI) of the desorbed molecules. These ionizing wavelengths provide selective ionization of aromatic species over aliphatic components in a mixture of organic materials. Judicious control of the ionizing laser fluence, typically of the order ca. $2–5 \times 10^5$ W cm^{-2}, provides "soft ionization" conditions so that the parent ions of the polynuclear aromatic compounds almost exclusively dominate the mass spectra (*17*, *18*).

The laser-generated photoions are mass separated in a home-built reflectron TOF mass spectrometer (resolution typically ca. 500) and detected by a dual chevron-type microchannel plate (MCP) detector. Experimental control and data aquisition are performed using a CAMAC-based system and interfaced to a Dell system 325 personal computer with in-house custom software. The entire experiment is performed at a repetition rate of 10 Hz. Typically, data from 200 laser shots were accumulated to enhance the overall signal to noise ratio. Using the present experimental configuration, the entire procedure, from subsample preparation to obtaining a mass spectrum, can be performed within a 10-min period.

Results and Discussion

Each of the six contaminated soil samples were examined using both 266-nm and 193-nm laser photoionization. The mass spectrum of one of the soil samples produced using 193-nm photoionization is shown in Figure 1, and an expansion of the region containing the PAH peaks is shown in Figure 2. Similar spectra were obtained for all the soil samples investigated. Figure 1 represents the total accumulated ion signal on summing of 200 laser shots. These fingerprint mass spectra were obtained in consecutive experiments; the entire preliminary screening of the samples was completed within 90 min. Under the prevailing experimental conditions, a 200-shot spectrum represented the total ion signal obtained on interrogating ca. 1 mg of soil. Samples of up to 50 mg can be interrogated in one continuous scan of the present sample probe. Examination of 50-mg quantities of material provides a better average PAH concentration and reduces subsampling errors.

The PAH signals are observed in the region between 100 and 400 amu. Signals at masses higher than 300 amu indicate the presence of PAHs with more than seven fused rings. Peaks at masses less than 100 amu are generally the result of ionization of elemental species, e.g., Na and K, or attributed to fragmentation of higher molecular weight species. This low mass region of the mass spectrum is dominated by a peak at 39 amu, corresponding to the atomic mass of potassium.

From Figure 2 it is possible to clearly identify strong ion signals which correspond to the masses of parent PAH skeletons. The dominant masses of 178, 202, 228, 252, and 276 amu correspond to phenanthrene/anthracene, fluoranthene/pyrene, chrysene/benz[*a*]anthracene, benz[*a*]fluoranthene/benzo[*a*]pyrene, and indeno[1,2,3-*cd*]pyrene/benzo[*ghi*]perylene. Other peaks of significant intensity correspond to further PAH compounds, e.g., 4*H*-cyclopentaphenanthrene at 190 amu and coronene at 300 amu. It is also possible to identify a series of peaks with mass separations of 14 amu, characteristic of a homologous series of successively alkylated PAHs, e.g., for pyrene/fluoranthene at 216 and 230 amu. This is shown more clearly in the insert in Figure 2. The absence of significant soil matrix peaks is striking. This eliminates the need for the analysis of blank samples. The use of ultraviolet (UV) radiation for ionization of the desorbed species means that photoionization mass spectra will only contain peaks from

organic species which contain a UV chromophore. There is further selectivity of detection in the specific choice of the wavelength of the ionizing radiation. Photoionization at 266 nm is well known to enhance the detection of PAHs over other organic analytes such as porphyrins (*24*). The choice of 193-nm photons, which are of higher energy, leads to the ionization of higher mass species not observed in the spectra obtained at 266 nm.

Differences in the relative abundances of the same compound in different soil samples can be directly estimated from the peak intensity. We have also determined the concentrations of particular PAHs in the soils using a series of standard additions, in a procedure similar to that used by Hahn et al. (*26*). The results obtained by this methodology were consistent with previously determined concentrations obtained using gas chromatography-mass spectrometry. The results show clearly that the technique is able to detect PAHs contained in the soil matrices at the ppm level. Preliminary instrument characterization, using pure PAHs as analytes, showed minimum detection limits for a number of these species using 193-nm photoionization were in the subpicomole region. It is important to note that the parent ion peak intensities are not only proportional to the concentration of the compound in the samples but also depend on the overall ionization efficiency, which is largely determined by the absorption cross-sections for that compound at the laser wavelength employed. Furthermore, the different PAHs may have different desorption efficiencies. Therefore, the relative peak intensities do not necessarily directly reflect the relative concentrations of the different PAHs in the matrix.

These results demonstrate that L^2TOFMS is a fast, effective, and sensitive analytical tool for the direct determination of PAHs in complex solid environmental matrices. Furthermore, as a quantitative analytical tool for the prediction of PAH distributions in soils, L^2TOFMS could provide an effective alternative to more conventional approaches. Investigations are presently underway to determine the efficacy of the technique for the analysis of PAHs in a variety of different environmental media and to explore its potential as a rapid, on-site screening tool.

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Natural and anthropogenic components in soil: an examination of recent applications and future data requirements

Simon J T Pollard[1], Jeff P Obbard[1] & John G Farmer[2]

[1]Aspinwall & Company, 13 Melville Street, Edinburgh EH3 7PE
[2]Environmental Chemistry Unit, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

The recent research focus on the environmental fate and transport of chemical species in soil has prompted a re-evaluation of background and anthropogenic contributions, along with an analysis of the implications for environmental health. The collection and critical appraisal of chemical data on soils now forms a routine component of contaminated site investigations, environmental impact assessments and health risk assessments, but are such projects taking full account of the historical data and spatial variations in component distributions? Here, we present an overview of current issues in soil contamination from the perspective of the environmental consulting industry, together with an evaluation of existing practice, potential problems and future research needs. We present a case for an open exchange of data between the research and commercial communities such that environmental risks associated with exposures to soil components can be effectively characterized, managed and communicated.

Baseline environmental data are integral to the assessment of whether pollution has occurred, irrespective of the environmental medium under study. Only with this information at hand can we (i) establish whether or not contamination, defined here as any substance present but not causing harm, or pollution, meaning harmful effects apparent, is present; (ii) conduct an evaluation of the extent and magnitude of the problem; (iii) present a contextual interpretation of environmental risk; and (iv) effectively prioritise remedial activity that tackles the worst situations first.

As environmental quality criteria have successively been developed for water, food, air and most recently, soils, a need has arisen to place them in the context of existing background values, usually those that relate to 'uncontaminated media'. Rapid developments in analytical science, however, over the last 25 years have demonstrated that few media are truly pristine. As analytical detection limits are lowered increasingly towards the the single molecule, the absolute limit of chemical detection, often with environmental quality criteria tailing closely behind, we find that all media are apparently 'contaminated' and that the natural world, previously held as benign, contributes its own pollution and toxicity to the total environment. Examples of natural 'contamination' include the elevated occurrences of arsenic in soils of the south-west of England (Mitchell & Barr, 1995), radon gas in indoor air (NRCP, 1987), cyanobacterial toxins in drinking water supplies from algal blooms (Lambert *et al*, 1994) and natural toxins in common plant foods (Ames *et al*, 1987). Much of the current debate centres on the extent to which this natural contamination actually represents environmental pollution.

Such revelations have had far reaching consequences for the research and lay communities. From an academic stance, there has been substantial research activity in the transport and ultimate fate of environmental contaminants in air, water, soil and biota. Regulators and business have had to recognize that pollution effects can be interrelated across the different media and that an integrated pollution control approach is appropriate and necessary in order to effect control. At the other end of the spectrum, the general public has acquired greater awareness of environmental issues, but the complexity of the multiple sources of environmental hazard, their interrelationships, the apportionment of environmental risk and responsibility for remedial action can easily cause confusion (Douglas, 1994). Part of the solution to the problem of effectively communicating risk lies in interpretation of hazard, exposure and receptor sensitivity, in the local context. For the soil environment, this inevitably requires reflection on what's already in the ground, whether 'natural' or 'anthropogenic'.

Natural and anthropogenic additions

There is a plethora of trace metal data for soils in the scientific literature which, arguably, has a limited representativeness in global terms. Much of the data has been acquired in the industrialized world and is centred on geochemically anomalous or polluted areas, where data relating to normal background concentrations in soils are less readily accessible. Furthermore, the rapid evolution and persistent discrepancy in the sampling and analysis of soils has resulted in limitations on the use of baseline data for both scientific and regulatory purposes.

High concentrations of some metals may be found naturally in soils and are frequently related to the presence of geochemical 'hot-spots' normally associated with metalliferous ore deposits. In the UK for example, elevated soil concentrations of lead, zinc cadmium and copper occur in metalliferous areas although in many instances these concentrations have been increased by mining activities which extend back to pre-Roman times. More recent anthropogenic activity which has resulted in localized contamination of soils with trace metals includes the agricultural use of fertilizers and pesticides, the application of sewage sludge to land, urban and traffic sources, fall out associated with metal smelters and incinerators, leakages and spillages from industrial uses and the landfilling of wastes.

It is now acknowledged that anthropogenic releases of trace metals (Table 1) dominate the mobilization of metals via global weathering processes, and that atmospheric transport and deposition is resulting in extensive transfer of metals from contaminant sources (Nriagu 1990). The implication of this is that all soils in the UK are likely to be contaminated with trace metals above their true natural or 'historical' background concentration (Haygarth & Jones, 1992) with consequences for plant-uptake and foodchain transfer. It is now also increasingly evident that heavy metal contamination of soils can result in impacts on soil ecology and nutrient cycling with long term implications for soil fertility. For example, the application of heavy metal contaminated sewage sludge on agricultural land can result in impacts on biological nitrogen fixation and carbon mineralization (Obbard *et al*, 1993; Obbard & Jones, 1993). Research in this area has forced a re-appraisal of European limits and hence a more enlightened approach to the assessment of soil toxicity compared with criteria based on total metal concentrations and plant uptake alone.

Source	Trace Elements (x 1000 tonnes/annum)					
	Zn	Cu	Ni	Cr	Pb	Cd
Agricultural & animal wastes	[illegible]	67	[illegible]	82	[illegible]	2.2
Logging & wood wastes	[illegible]	28	[illegible]	10	[illegible]	1.1
Urban refuse	[illegible]	26	[illegible]	20	[illegible]	4.2
Municipal sewage & organic waste	[illegible]	13	[illegible]	6.5	[illegible]	0.18
Solid wastes from metal fabrication	[illegible]	4.3	[illegible]	1.5	[illegible]	0.04
Coal ashes	[illegible]	214	[illegible]	298	[illegible]	7.2
Fertilisers & peat	[illegible]	1.4	[illegible]	0.32	[illegible]	0.20
Discarded manufactured products	[illegible]	592	[illegible]	458	[illegible]	1.2
Atmospheric fallout	[illegible]	25	[illegible]	22	[illegible]	5..3
Total input	[illegible]	971	[illegible]	898	[illegible]	22

Table 1 Worldwide inputs and sources of trace elements into soils (after Nriagu, 1990)

Widespread anthropogenic contamination of soils with trace organic compounds is also evident. Natural combustion processes (*eg*, forest fires) result in releases of polyaromatic hydrocarbon (PAH) compounds to atmosphere and subsequent deposition to soil surface. However, atmospheric deposition of PAHs that are associated with large-scale burning of fossil fuels has resulted in elevated soil concentrations in the UK (Jones 1994). Generally, soils have a capacity to store contaminants by sorption and act as a long term sink for trace organics, and historical contamination patterns for PAHs demonstrate that many compounds are related to changing patterns of fossil fuel consumption over time. Similarly, concentration trends for polychlorinated biphenyls (PCBs) are related to knowledge of the production and use of these compounds in the UK (Alcock *et al*, 1993). The concentration of trace organics in soils over the longer term is dependent on the chemical properties of the compound itself and natural processes including biotic and abiotic degradation, leaching and vegetation uptake.

It is evident that spatial and temporal variability of organic and trace metal contaminants in soils demands a rigorous approach to environmental assessment, where the mobility of a contaminant is not only dependent on its chemical characteristics, but also on the properties of the soil. Therefore, the absolute concentration of a contaminant may not be an accurate indicator of its environmental risk and careful evaluation is required to assess the significance of contamination in the context of natural background levels, documented chemical fate and behaviour, and historical contamination.

Historical lessons and current research directions

The recent past provides sufficient examples of well-published environmental scares concerning natural 'hot-spots' of potentially harmful metals to convince us of the need for caution in both the interpretation of scientific data and the communication of our findings to the media and the community. Perhaps the most obvious example is that of the village of Shipham in Somerset, where, after an initial blaze of publicity, the high levels of cadmium found in soil, partly as a consequence of past mining of the local ores, were found ultimately to have caused no adverse health effects in the residents, some of whom, in fact, were extremely healthy octogenarians who had thrived on home-grown produce for many years (Morgan & Sims, 1988). Similarly, the greatly elevated levels of lead in, for example, the soils of Derbyshire and of southern Scotland (Leadhills, Wanlockhead) mining areas, and of arsenic in Cornish soils have, in general, not been reflected in either the biological fluids (blood, urine) or in observable changes in the health status of the local populations (Cotter-Howells & Thornton, 1991; Moffat, 1989; Johnson & Farmer, 1989). This does not, however, serve to justify any complacency in the face of 'hot-spots' in the trace element data produced by the British Geological Survey in its stream sediment-based regional geochemical atlases of Great Britain, but rather re-emphasizes the need for a measured and transparently honest approach in explaining to the public the rationale, design and implications of any subsequent follow-up studies.

In this respect, there are similarities with the problems of anthropogenically contaminated land in urban areas, where the nature of soil-plant-human interactions and uptake of potentially harmful heavy metals is again of obvious importance, whether remediation or human health effects be the issue at stake. While traditional skills, based on the analytical chemistry approach of selective extraction and measurement, will continue to be essential in assessing the chemical speciation and bioavailability to plants of metals in soils (*eg*, Ure, 1995), it seems likely that the latter will increasingly be addressed via a range of ecologically relevant bioassays, which can also assess environmental toxicity (Paton *et al*, 1995). In addition, solutions to difficult questions, such as the relative magnitude of different sources contributing to the direct uptake by children of lead in soils and dust (Wixson & Davies, 1994), should also benefit from the wider application of more sophisticated analytical techniques (Delves & Campbell, 1993; Farmer *et al*, 1994). Research effort will likely continue to be driven by legislative pressures on polluters to address the problems of contaminated land.

Contaminated land in the urban environment: current themes

Within the urban environment, contaminated land issues have retained prominence with the continued development of 'brownfield' sites, the controversy in the early 1990's over S143 registers (of land subject to potentially contaminative use) and the provisions recently made in the Environment Act (1995). Whilst the philosophy of the 'polluter pays' is embodied in the provision for remediation notices under the Act, where the polluter cannot be found, residual liability rests with the owner/occupier, and where the occupier refuses consent to remedial works, the 'then-owner' or occupier of the land may be liable. The Act also places a requirement on local authorities to assess the potential for contaminated sites either to cause 'significant harm' or possess a 'significant possibility of causing such harm'. An essential component of this assessment process will be the issue of Department of the Environment guidance values on soil concentrations of key pollutants to replace the existing Interdepartmental Committee on the Redevelopment of Contaminated Land threshold and action trigger values. However, and importantly, application of these guidance values alone without reference to a risk-based rationale is unlikely to receive wide support.

With the continuation of a development-led, 'suitable-for-use' approach, the need to assess soil quality in natural and made ground will be retained as a key feature of site investigations and risk and liability appraisals for contaminated sites. A review of existing

Component	Concentration range in natural soils (mg/kg)	ICRCL threshold (2) (mg/kg)	DUTCH target (3) (mg/kg)	DUTCH intervention (4) (mg/kg)	CCME assessment (6) (mg/kg)	DUTCH human toxic (5) (mg/kg)
As	[illegible]	[illegible]	29	[illegible]	5	[illegible]
Cd	[illegible]	[illegible]	0.6	[illegible]	0.5	[illegible]
Cr	[illegible]	[illegible]	100	[illegible]	20	[illegible]
Cu	[illegible]	[illegible]	36	[illegible]	30	[illegible]
Hg	[illegible]	[illegible]	0.3	[illegible]	0.1	[illegible]
Pb	[illegible]	[illegible]	85	[illegible]	25	[illegible]
Zn	[illegible]	[illegible]	140	[illegible]	60	[illegible]
Ni	[illegible]	[illegible]	35	[illegible]	20	[illegible]
PAH (total)	[illegible]	[illegible]	1	[illegible]	0.9	[illegible]
Phenol	[illegible]	[illegible]	0.05	[illegible]	0.1	[illegible]
Mineral oil	[illegible]	[illegible]	50	[illegible]		[illegible]

Table 2 Selected soil criteria in context.

international soil quality criteria and a comparison of the normal range of individual species in soils (Table 2) demonstrates that existing assessment and soil remediation criteria for individual species regularly fall within the concentration ranges of 'natural 'soils. This presents clear difficulties for site owners, developers, financiers and occupants along with their professional advisers when assessing the risks asscociated with contaminated land.

A recent change in philosophy towards the assessment of contaminated land now places a greater emphasis on the application of risk assessment techniques in determining (i) whether or not land is contaminated; and (ii) the meaning of 'significant harm' on a site-specific basis (DoE, 1995). In its rudimentary form, the risk assessment approach considers the potential connectivity between a hazard source, an exposure pathway and the receptor and allows a qualitative judgement to be made over the magnitude of risk, contingent on the sensitivity of the receptor, the direct or indirect nature of the exposure pathway and the toxicity of the hazard. Identification of 'high', 'medium', 'low' and 'very low' categories of risk at a screening stage can assist in the design of detailed site investigations aimed at refining the assessment, and providing a more site-specific assessment of risk (Pollard *et al*, 1995).

Recent assessment criteria issued by the Dutch Government (Table 2) have embodied the philosophy of risk assessment for human and ecological receptors by defining soil concentrations, exposure above which can potentially result in the exceedance of a maximum tolerable risk level, defined with reference to World Health Organisation tolerable daily intakes (TDI) or a tolerable excess lifetime cancer risk of 1 in 10 000. The so-called 'toxicological humans intervention values' are reported for selected chemical species in Table 2 and represent order of magnitude differences above the assessment criteria currently being used which are based on background concentrations in natural soils. Significantly, the compounds that are likely to provoke continued attention are those where the discrepancy between natural values and the TDI is least, notably arsenic, cadmium, lead and the polynuclear aromatic hydrocarbons (PAH). These soil components have historically driven quantified risk assessments due to their carcinogenic activity (As, PAH) phytoaccumulation potential (Cd) and apparent (or assumed) non-threshold toxicological behaviour (Pb, As, PAH). Much of this assumed behaviour, however, results from studies conducted at elevated concentrations and there remains a need for research studies to report on these effects at the much lower concentrations of environmental exposure.

Future research needs

Professional environmental consultants engaged in the assessment and remediation of contaminated land are acutely aware of the gaps in the current literature with respect to certain aspects of the science that underpins much of their work. Selected examples of these research needs (Hrudey & Pollard, 1993) are summarized below. This list indicates the breadth of disciplines represented.

(i) **Statistical sampling protocols**: a need to optimize methods for the cost-effective sampling of contaminated soils both spatially and through depth across contaminated sites;

(ii) **Statistical treatment of data**: no accepted methodology currently exists for the statistical treatment of 'hot-spot' data within quantified risk assessments;

(iii) **Analytical methods**: there remains a need to develop and refine analytical methods and sample clean-up methodologies that can tackle the authentic components of the waste-soil matrix rather than standard lists of priority pollutants (Pollard *et al*, 1994). This is particularly the case for organic contaminants. Chemical data should ideally be coupled with bioassay information so as to relate chemical presence to soil-bound toxicity;

(iv) **Bioavailability**: quantified risk assessments rarely extend beyond estimates of risk based on a received dose. In reality, effective doses achieve their desired effect at the target organ *in vivo* and require consideration of component bioavailability, and ideally, pharmacokinetic behaviour. Such considerations are now being made for lead exposure;

(v) **Uncertainty analysis**: risk assessments inevitably involve considerable uncertainty because extensive study on a site-specific basis is rarely affordable. Therefore, extrapolation from the general to the specific becomes the norm, with the input of default parameters in the absence of site-specific data. An analysis of the costs and merits of obtaining quality critical data (*eg* low-dose toxicological information, soil-type bioavailabilities, compound-specific partition coefficients) and the anticipated improvements in risk assessment output expected to result is urgently required;

(vi) **Soil bound toxicity**: an assessment of the synergistic/antagonistic toxicological effects of contaminants on the microflora/fauna in the soil matrix is important with respect to the ecological impact of soil pollution, largely ignored to date;

(vii) **Environmental fate and transport studies**: many of the partitioning studies conducted to date rely heavily on model

situations with single components on well-defined soils. These need to be extended to account for the authenticity of contaminated soil matrices, multicomponent mixtures (and co-solvent effects) and non-equilibrium conditions; and

(viii) **Risk communication**: there are very real and complex problems associated with the communication of environmental risk to individuals, tenant groups and communities affected by soil contamination. Further research into the sociological construct of perceived environmental risk is needed if we are to address the concerns of all those involved in the purchase and transaction of land.

Conclusions

(i) Analytical discrepancy and widespread anthropogenic contamination of soils has resulted in limitations on the representativeness of baseline data for scientific and regulatory purposes;

(ii) Spatial and temporal variability of organic and trace metal contaminants demands an enlightened approach to environmental assessment, where total metal concentrations are not indicative of chemical behaviour and potential impact;

(iii) Measured ecotoxicological effects of soil contaminants on essential microbiological processes related to soil fertility is resulting in re-appraisal of acceptable pollution limits;

(iv) There is an apparent gulf between researchers and practitioners in the field of contaminated land; researchers correctly press for rigorous data collection and treatment whilst the best practice employed by consultants engaged in the assessment of contaminated land is increasingly constrained by decreasing financial provision; and

(v) We are seeing the increasing prominence of risk assessment as a means of interpreting the problems of contaminated land in the local context.

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A PERFORMANCE ASSESSMENT OF SOURCE CORRELATION AND WEATHERING INDICES FOR PETROLEUM HYDROCARBONS IN THE ENVIRONMENT

MARTIN WHITTAKER† and SIMON J.T. POLLARD*‡
†Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, United Kingdom
‡Aspinwall & Company, Consultants in Environmental Management, 13 Melville Street, Edinburgh, EH3 7PE, United Kingdom

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Abstract—The source of petroleum contaminants in the environment and the extent to which these contaminants have weathered following deposition can often be determined through an empirical evaluation of oil *n*-alkanes, isoprenoids (pristane and phytane), and hopane and sterane biomarkers. Common source correlation and weathering indices have been calculated for three sets of oil samples: fresh, 25% (w/w) weathered, and 50% (w/w) physically weathered diesel standards, crude oils from different sources, and a set of representative heavy oils. For the weathered diesel oils, the C_{18} : tricyclic terpanes and *n*-alkanes : tricyclic terpanes indices varied most significantly with diesel weathering. Awareness of this may be important when these indices are used to assess biotic routes of contaminant dissolution. For the crude oil samples, C_{18} : phytane demonstrated low specificity between the oils. C_{18} : 17α(*H*),21β(*H*)-Hopane and *n*-alkanes : 17α(*H*),21β(*H*)-hopane differentiated between crude oils but would be expected to vary significantly during weathering due to the microbial amenability of the alkane numerators. Pristane : phytane, phytane : 17α,21β-hopane and tricyclic terpanes : hopanes were considered to be the indices best able to distinguish between oils from different origins, based on these results. 17α(*H*),21β(*H*)-Hopane : 17α(*H*),21β(*H*)-norhopane did not adequately distinguish between the respective crude oil samples. Finally, the relationship between heavy oil composition and the index value was investigated. Here, the values of *n*-alkanes : 17α(*H*),21β(*H*)-hopane, phytane : 17α(*H*),21β(*H*)-hopane, and tricyclic terpanes : hopanes decreased as the combined total of polar and asphaltene compounds within oil samples increased. This relationship may be useful in assessing the degradation status of petroleum wastes.

Keywords—Petroleum contamination Biomarkers Weathering Refractory oils Bioremediation

INTRODUCTION

For most petroleum-contaminated sites, obtaining information on the source and composition of oily wastes is important for the informed application of risk management strategies [1,2]. Evaluating the extent of weathering undergone by the waste matrix may also be significant, because compositional changes that take place during weathering can often limit the bioremediation potential of residual soil contamination [3]. The recent emergence of "natural attenuation" as a managed approach to soil and groundwater remediation has placed fresh emphasis on the need for information on both the source and the extent of weathering of contaminants. One analytical approach that has proven successful for characterizing both the source and weathered state of spilled petroleum contaminants is measurement of the abundance and distribution of biomarker compounds within the contaminant matrix [4–9].

Chemical biomarkers, ubiquitous in crude oils and petroleum products, are compounds that can be unambiguously traced to biological precursor compounds [10]. The most commonly used biomarkers are pristane and phytane (both branched isoprenoid alkanes) and hopanes and steranes (polycyclic alkanes) (Fig. 1). Their use in oil source and weathering studies derives from two characteristics. First, biomarkers are much more resistant to oil weathering processes, such as evaporation and biotransformation, than are most oil components. This allows their use as conserved reference compounds against which the loss of less stable oil components can be quantitatively estimated (e.g., C_{18} : phytane, *n*-alkanes : 17α(*H*),21β(*H*)-hopane). These ratios, collectively referred to in this paper as "weathering indices," may be especially useful in monitoring natural attenuation or enhanced bioremediation, where confirmation of contaminant loss is essential. Examples of weathering indices being used to characterize oil degradation include monitoring depletion of spilled crude oil on beaches of Prince William Sound following a bioremedial response to the *Exxon Valdez* oil spill [4,9], evaluation of the relative degrees of biodegradation experienced by marine crude oils [11], identification of the flow patterns of dissolved hydrocarbons in ground water [12], and monitoring the transformation of oily wastes during controlled bioremedial activities [13].

The second key characteristic of oil biomarkers is that their distribution within oils represents an oil-specific fingerprint with which distinct oil samples can be correlated. This is most commonly achieved through a qualitative comparison of individual biomarker mass fragmentogram patterns (obtained by gas chromatography–mass spectrometry [GC-MS]), but can also be achieved quantitatively from a calculation of the ratio of one biomarker to another. In this study, we are concerned with the latter approach. Ratios of certain biomarkers, referred to in this paper as "oil (or source) correlation indices," are

* To whom correspondence may be addressed.
The current address of S.J.T. Pollard is Scottish Environment Protection Agency, Erskine Court, The Castle Business Park, Stirling, FK9 4TR, UK.

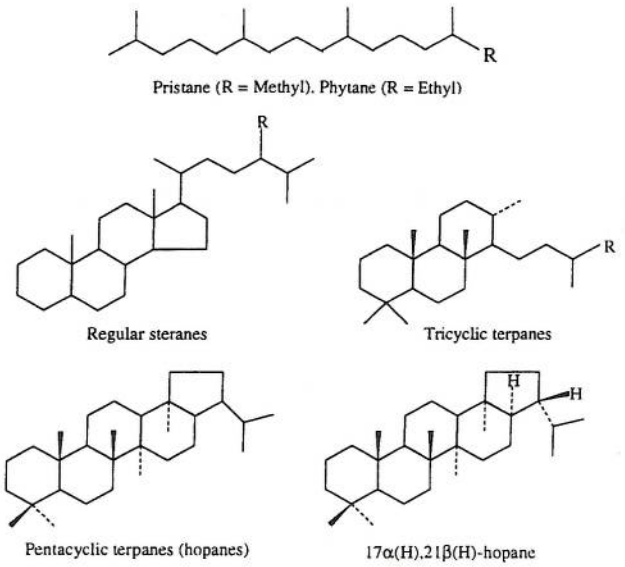


Fig. 1. Structural formulas of selected biomarker compounds.

sensitive to the geologic source of an oil, and remain consistent between related oils. Moreover, because of the environmental persistence of biomarker compounds, their values remain unaltered by weathering of oil. Recently, oil correlation indices have been used to demonstrate that certain Alaskan shoreline oil residues originated from pre-1970 industrial oil usage rather than as a result of the *Exxon Valdez* oil spill [6], to confirm the source of highly weathered no. 6 fuel oil released more than 22 years ago from the oil tanker *Arrow* [7], and to monitor chemical compositional changes and the fate of weathered crude oil residues from an Arctic beach [8].

A number of concerns exist regarding the use of biomarker indices in certain situations. Some authors have noted that in very weathered oil samples, isoprenoid biomarkers may themselves become partially biotransformed [4,7]. Research into this phenomenon has shown that both pristane and phytane are vulnerable to loss through microbial activity in appreciably weathered samples [4]. Hopane biomarkers, on the other hand, have been shown to be neither produced nor destroyed over considerable periods of oil weathering and are therefore considered to be much more reliable [9]. Concern has also been expressed over microbially facile waste components being compared with persistent biomarkers, because individual compounds have different solubilities, transport, and volatility characteristics [14]. The effects of these differences on the behavior of biomarker indices are likely to be greatest during the initial phases of a spillage, when abiotic processes (such as evaporation, leaching, and photooxidation) are most prominent. These concerns are valid because information gleaned from source and weathering indices may be used as a means of establishing environmental liabilities for petroleum contamination, or in screening risk management decisions at contaminated land sites, both of which could involve considerable financial outlay.

The derivation of oil weathering and source correlation indices is based on the established biochemical principles of petroleum microbiology [15–17] and, in particular, on the differential rates at which oil components are metabolized and transformed. In the absence of single substrate studies on numerator and denominator compounds that comprise an index, experimentally observed differences in index values can be explained with reference to the microbiology literature. In brief, microbial catabolism of *n*-alkanes proceeds via successive oxidation and cleavage of the terminal methyl groups of a hydrocarbon molecule. Branched or cyclic compounds experience slower biotransformation rates due to the presence of secondary, tertiary, and quaternary carbon atoms within the basic hydrocarbon structure that render these compounds more difficult to metabolize. Hopane and sterane biomarkers are among the most effective internal marker compounds because their linked alicyclic structures provide few pathways for biotransformation [15]. The susceptibility of compounds to microbial attack, therefore, varies widely with molecular structure and size, and tends to decrease with increasing molecular weight, molecular branching, cyclization, aromaticity, and the number of hetero-atoms incorporated into the compound [17]. Thus, in terms of oil class fractions, the open chain alkanes are generally the most labile oil components, followed by aromatic compounds, then polar resins, and finally the highly condensed asphaltenes.

In view of this, and of the wide scope of application for source correlation and weathering indices, we have conducted an empirical study of the performance of some common source and weathering indices in three well-defined areas. In the first study, our aim was to assess whether, in the immediate aftermath of an oil spill, there is potential for abiotic loss of oil components to influence source and weathering indices to such an extent that diagnosis of microbial activity or source commonality (or both) is impaired. This is most pertinent to petroleum products containing a significant low-boiling fraction or when contaminant discharge occurs under environmental conditions conducive to evaporation. To this end, we examined the effect of physical weathering on biomarker ratios by determining the values of six common source correlation and weathering indices for samples of fresh, 25% (w/w), and 50% (w/w) physically weathered diesel.

In the second study, the variation of source correlation indices between different crude oil types was examined. Source correlation indices have been used most effectively as a means of identifying marine crude oil contamination through comparison of the biomarker ratios of the waste oil with those of a suspected source. This approach relies upon the specificity of source correlation indices to individual crude oil types and their capacity to discriminate between crude oils from different backgrounds. Here, the values of seven frequently used source correlation indices are determined for an Iraqi crude oil, a Nigerian crude oil, and two North Sea crude oils, with the goal of identifying those source correlation indices best able to distinguish between the oil samples. A favorable index is one that shows a significant variation (in relation to the confidence limits of the index value, and in comparison to variations recorded in previous studies) between the three crude oil families while remaining constant for the two North Sea oil samples.

In the third section of this paper, we focus on the utility of source correlation and weathering indices in the characterization of heavier (i.e., higher boiling point) petroleum products and, in particular, on the extent to which the values of selected indices are affected by variations in oil composition. Heavy oils commonly contain a high proportion of polar and asphaltenic compounds known to resist microbial degradation and concentrate in degraded oils. Characterization of the waste–soil matrix is, therefore, particularly important when assessing the suitability of bioremediation technologies or the

Table 1. Representative heavy oil description and class fraction distribution

Oil	Source description	Approximate boiling range (°C)	Class distribution[a] Saturates (% w/w)	Aromatics (% w/w)	Polars (% w/w)	Asphaltenes (% w/w)
Acid tar waste	Contaminated site	200–>700	60.2 ± 3.0	4.6 ± 0.2	8.7 ± 0.4	26.5 ± 1.3
No. 6 fuel oil	North Sea, heavy oil blend	150–600	36.7 ± 1.8	34.9 ± 1.7	12.6 ± 0.6	15.8 ± 0.8
API[b] separator oil	Refinery process run-off stream	20–400	51.3 ± 2.6	30.7 ± 1.5	14.9 ± 0.8	3.1 ± 0.2
Ballast oil	Ship discharge variety of products	20–400	75.3 ± 3.8	12.3 ± 0.6	8.1 ± 0.4	4.3 ± 0.2
Residue oil	Mixed North Sea	150–600	71.8 ± 3.6	20.7 ± 1.0	5.9 ± 0.3	1.6 ± 0.1

[a] Determined by adsorption column chromatography; ± standard deviation (based on selected triplicate determinations).
[b] API = American Petroleum Institute.

feasibility of natural attenuation, where success depends upon the depletion of assimilable waste constituents [3]. The capacity of biomarker indices to convey information on the degradation status of residual oily wastes is examined through the analysis of five heavy oils, representative of residual organic wastes at contaminated sites (Table 1).

MATERIALS AND METHODS

Sample collection

For the study of abiotic weathering, a set of progressively weathered diesel range organic (DRO) standards (Restek Corporation, Bellefontaine, PA, USA) was evaluated. These oils represent mid-range petroleum products with a carbon number range of C_{10} to C_{28}, as determined by gas chromatography with flame ionization detection (GC-FID) analysis. The DRO standards were physically weathered by the manufacturer by direct evaporation using a combination of gentle heating (water bath) and nitrogen blowdown to prevent oxidation. The percent weathering indicated with each sample (i.e., 25% [w/w], 50% [w/w]) was determined by monitoring the gravimetric weight loss from the original unweathered sample.

Examination of the reliability of oil correlation indices was carried out using four discrete crude oil samples, two North Sea-derived oils, a Nigerian export blend, and an Iraqi export crude. Analysis of crude oils by adsorption chromatography demonstrated that all were predominantly paraffinic, consisting of >85% (w/w) saturate class components.

Five heavy and middle distillate oils were used for evaluating the relationship between oil chemical composition and the value of selected source and weathering indices. Four of the oils, recovered refinery effluent oil (referred to as API [American Petroleum Institute] separator oil), oil tanker ballast oil, a crude distillation residue, and no. 6 fuel oil, were obtained as neat oils from a local oil refinery, and have been previously described [18]. The fifth material, an acid tar waste sample, was extracted from contaminated soil at a former lubricating oil recovery plant.

Adsorption chromatography

For the heavy oils (Table 1), preparative column chromatography was essential for isolating the individual saturate class fractions in which the selected target compounds biomarkers report [18]. Prior to the column fractionation, the asphaltene fraction of each oil was gravimetrically determined by an *n*-pentane precipitation method adapted from Speight et al. [19]. A Quick-Sep™ (Fisher Scientific, Crawley, UK) lateral reservoir flash chromatography apparatus, with a 90 mm × 30 mm column, was packed with neutral Aldrich (Gillingham, UK) STD Grade alumina (80 mm, approx. 150 mesh, activated overnight at 130°C), followed by anhydrous Na_2SO_4 (approx. 10 mm, dehydrated by heating at 400°C for 4 h immediately prior to use). A single piston air pump (Fisons, Fisher Scientific, Crawley, UK, 50 W) was connected to the top of the column and the air pressure adjusted to produce a down-flow elution rate of approximately 20 ml/min. All solvents used were high-performance liquid chromatography (HPLC) grade. The column was preeluted with 50 ml *n*-pentane prior to the loading of the maltene (*n*-pentane-soluble) fraction of each reference oil onto the column by pipette in 2 ml of *n*-pentane. Component classes were obtained using the following elution scheme: 150 ml of *n*-pentane (for elution of saturates), 150 ml of toluene (for mono-, di-, and polyaromatics), and 150 ml of a dichloromethane : methanol mixture (50:50) (for polar compounds). Fractions were collected in preweighed, acid-washed borosilicate flasks and reduced under a forced draught to allow calculation of gravimetric recoveries.

Acid tar samples were first Soxhlet-extracted from soil subsamples (*approx.* 30 g) for 16 h using HPLC-grade dichloromethane (DCM) (BDH, Poole, UK) (150 ml). The DCM extracts were reduced overnight at ambient temperatures under forced draught.

Analyses by GC-MS

Oil saturate fractions were made up to a concentration of approximately 10 mg/ml in DCM. Analyses were conducted on an HP model 5890 gas chromatograph (Hewlett Packard, Stockport, UK) equipped with a 60-m × 0.25-mm-i.d. DB5 column and a VG Trio 1 mass spectrometer detector (Finnegan, Manchester, UK). One-microliter aliquots were injected through a 1-m × 0.53-mm deactivated fused silica retention gap using an HP model 7673A autoinjector (Hewlett Packard, Stockport, UK). A linear temperature gradient was employed, with the column temperature held at 30°C for 1 min following injection, ramped at 6°C/min to 300°C, then held at 300°C for a further 30 min. Helium carrier gas was used at a flow rate of 7.5 ml/min. The GC-MS interface was maintained at 300°C.

Electron impact ion chromatograms were obtained in selective ion monitoring mode. Two target ions were selected on the basis of previous studies [4,20]. These were *m/z* 85 (for detection of *n*- and isoprenoid alkanes) and *m/z* 191 (for tri-, tetra-, and pentacyclic terpanes). The spectrometer was tuned

daily using a heptacosafluorotributylamine standard (mol. wt. 671.1).

Source correlation and weathering indices were calculated to single decimal place precision by determining the ratio of the integrated peak areas on mass chromatograms of the compound(s) featured in the index (see Tables 2, 3, and 4). Repeat analysis of selected samples indicated a standard deviation in index values of up to 10%. Peaks corresponding to the *n*-alkanes, pristane, and phytane were determined by the use of an analytical standard comprising five *n*-alkanes (C_{15}, C_{20}, C_{25}, C_{30}, and C_{40}). Tricyclic and pentacyclic terpane (hopane) peak identification was achieved using 17β(*H*),21β(*H*)-hopane as an internal standard and by comparison of mass fragmentograms at *m/z* 191 with corresponding reference fragmentograms from the literature [7,20]. Mass fragmentograms for *m/z* 191 (tri-, tetra-, and pentacyclic terpanes) and 85 (saturated hydrocarbons) ions for the residue oil are shown in Figure 2.

RESULTS AND DISCUSSION

Rationale for formation of biomarker indices

In weathering indices, the abundance of oil components lost during weathering is compared to that of one or more conserved internal marker compounds. A decrease in the value of weathering indices over time is used as evidence of increasing oil maturity or, when used to monitor the progress of natural attenuation or enhanced bioremediation, of microbial activity.

In source correlation indices, the ratio of two environmentally persistent biomarker compounds within an oil is calculated. Because the overall distribution of biomarkers within an oil is highly dependent on the geologic background of the oil, the value of this ratio is specific to individual oil types. Moreover, providing the biomarkers are not susceptible to abiotic or biotic degradation, the value of the ratio should remain more or less constant during oil weathering. Source correlation indices, therefore, represent a convenient way of establishing commonality between two or more oils. Usually, this is done to determine the identity of anonymous oils through comparison of source index values in the waste with those of a suspected source oil. A wide number of indices have been used in the characterization of petroleum contaminants in the environment. These are listed below.

C_{17} : Pristane, and C_{18} : Phytane. Senn and Johnson [12] used the differences in rate of biotransformation of the index components to rank samples of spilled diesel oil in terms of their weathered state. C_{17} : Pristane and C_{18} : phytane decreased from 1.8 and 2.7, respectively, in oil samples considered to have been least weathered (i.e., those closest to the source of the spill), to 0.2 and 0.3, respectively, in those samples farthest from the spill source, which had been most extensively weathered. More recently, C_{17} : pristane values were used to estimate the age of diesel oil contamination. These values ranged from 2.2 for fresh oil to 0.2 for samples approximately 20 years old [21]. These ratios have also been used to illustrate weathering of crude oils spilled in the marine environment. Wang et al. [8], for example, found that extensive weathering of oily residues on an Arctic beach resulted in a decrease in the value of C_{17} : pristane from 3.5 in the unweathered oil to between 0.16 and 0.9 in the weathered residues. C_{18} : Phytane values were also found to decrease, from 1.5 to between 0.13 and 0.42.

Pristane : Phytane. This source correlation index has been recently used in studies of weathered crude oil residues in the

Table 2. Weathering and source correlation indices for physically weathered diesel range organics (DROs)

Biomarker ratio[a]	*m/z* Ratio	Empirical formula and mol. wt.	DRO Samples					
			Unweathered		25% Weathered		50% Weathered	
			Integrated peak areas	Index value[b]	Integrated peak areas	Index value[b]	Integrated peak areas	Index value[b]
Weathering indices								
C_{17} : Pristane	85:85	$C_{17}H_{36}$ (240), $C_{19}H_{40}$ (268)	1,324,320/712,924	1.9	1,639,220/868,378	1.9	1,194,220/476,244	2.5
C_{18} : Phytane	85:85	$C_{18}H_{38}$ (294), $C_{20}H_{42}$ (282)	1,092,420/528,977	2.1	1,392,010/676,104	2.1	1,081,590/778,478	1.4
C_{18} : Tricyclic terpanes	85:191	$C_{18}H_{38}$ (294), $C_{20-26}H_{36-48}$ (276–360)	1,092,420/526,813	2.1	1,392,010/947,682	1.5	1,081,590/2,060,559	0.5
n-Alkanes : tricyclic terpanes	85:191	$C_{10-22}H_{22-46}$ (142–310), $C_{20-26}H_{36-48}$ (276–360)	10,744,878/526,813	20.4	10,841,482/947,682	11.4	8,036,180/2,060,559	3.9
Source indices								
Pristane : phytane	85:85	$C_{19}H_{40}$ (268), $C_{20}H_{42}$ (282)	712,924/528,977	1.4	868,378/676,104	1.3	476,244/778,478	0.6
Pristane : tricyclic terpanes	85:191	$C_{19}H_{40}$ (268), $C_{20-26}H_{36-48}$ (276–360)	712,924/526,813	1.4	868,378/947,682	0.9	476,244/2,060,559	0.2
Phytane : tricylic terpanes	85:191	$C_{20}H_{42}$ (282), $C_{20-26}H_{36-48}$ (276–360)	528,977/526,813	1.0	676,104/947,682	0.7	778,478/2,060,559	0.4

[a] Indices are categorized according to previous use.
[b] Confidence limits (established through triplicate analysis of selected samples) ± 10%.

Table 3. Selected indices for correlation of crude oil

Biomarker ratio	*m/z* Ratio	Nigerian crude oil: Integrated peak areas	Nigerian crude oil: Index value[a]	North Sea crude oil 1: Integrated peak areas	North Sea crude oil 1: Index value[a]	North Sea crude oil 2: Integrated peak areas	North Sea crude oil 2: Index value[a]	Iraqi crude oil: Integrated peak areas	Iraqi crude oil: Index value[a]
C_{18} : Phytane	85:85	547,718/392,658	1.4	1,080,190/470,507	2.3	1,217,090/994,841	1.2	827,991/591,110	1.4
Pristane : Phytane[b]	85:85	679,901/392,658	1.7	301,221/470,507	0.6	732,941/994,841	0.7	575,899/591,110	1.0
C_{18} : 17α(*H*),21β(*H*)-Hopane[b]	85:191	547,718/643,292	0.9	1,080,190/64,456	16.8	1,217,090/92,972	13.1	827,991/36,723	22.6
n-Alkanes : 17α(*H*),21β(*H*)-hopane[b]	85:191	6,722,148/643,292	10.4	11,902,853/64,456	184.7	15,475,568/92,972	166.5	10,189,770/36,723	277.5
Phytane : 17α(*H*),21β(*H*)-hopane[b]	85:191	392,658/643,292	0.6	470,507/64,456	7.3	994,841/92,972	10.7	591,110/36,723	16.1
Tricyclic terpanes : total hopanes[b]	191:191	416,355/2,875,231	0.2	193,585/388,602	1.0	400,842/711,858	1.3	444,433/523,083	5.6
17α(*H*),21β(*H*)-hopane : 17α(*H*), 21β(*H*)-norhopane	191:191	643,292/765,122	0.8	64,456/86,303	0.7	92,972/53,612	1.7	36,723/17,195	2.1

[a] Confidence limits (established through triplicate analysis of selected samples) ± 10%.
[b] Proposed source correlation indices.

Table 4. Selected source correlation and weathering indices for typical heavy oil samples

Biomarker ratio	*m/z* Ratio	Heavy oils: Ballast oil: Integrated peak areas	Ballast oil: Index value[a]	API separator oil: Integrated peak areas	API separator oil: Index value[a]	Residue oil: Integrated peak areas	Residue oil: Index value[a]	No. 6 fuel oil: Integrated peak areas	No. 6 fuel oil: Index value[a]	Acid tar waste oil: Integrated peak areas	Acid tar waste oil: Index value[a]
C_{18} : Phytane	85:85	370,487/228,890	1.6	956,065/597,497	1.6	626,678/483,086	1.3	817,134/379,360	2.2	848,779/557,075	1.5
Prsitane : Phytane	85:85	160,445/228,890	0.7	262,505/597,497	0.4	ND[b]		ND	ND	ND	
n-Aklanes : 17α(*H*),21β(*H*)-hopane	85:191	3,299,544/5,736	575.2	8,870,030/21,824	406.4	21,023,840/245,650	85.6	7,400,142/91,395	81.0	4,996,103/3,693,560	1.3
Phytane : 17α(*H*),21β(*H*)-hopane	85:191	228,890/5,736	39.9	597,497/21,824	27.4	483,086/245,650	2.1	379,360/91,395	4.2	557,075/3,693,560	0.2
Tricyclic terpanes : total hopanes	191:191	244,830/20,301	12.1	713,074/87,385	8.2	603,970/1,197,884	0.5	4,348,769/374,375	11.6	7,986,140/14,931,550	0.5
17α(*H*),21β(*H*)-hopane : 17α(*H*), 21β(*H*)-norhopane	191:191	5,736/5,293	1.1	21,824/20,910	1.0	245,650/144,862	1.7	91,395/82,767	1.1	3,693,560/4,784,260	0.8

[a] Confidence limits ± 10%.
[b] ND = not detected.

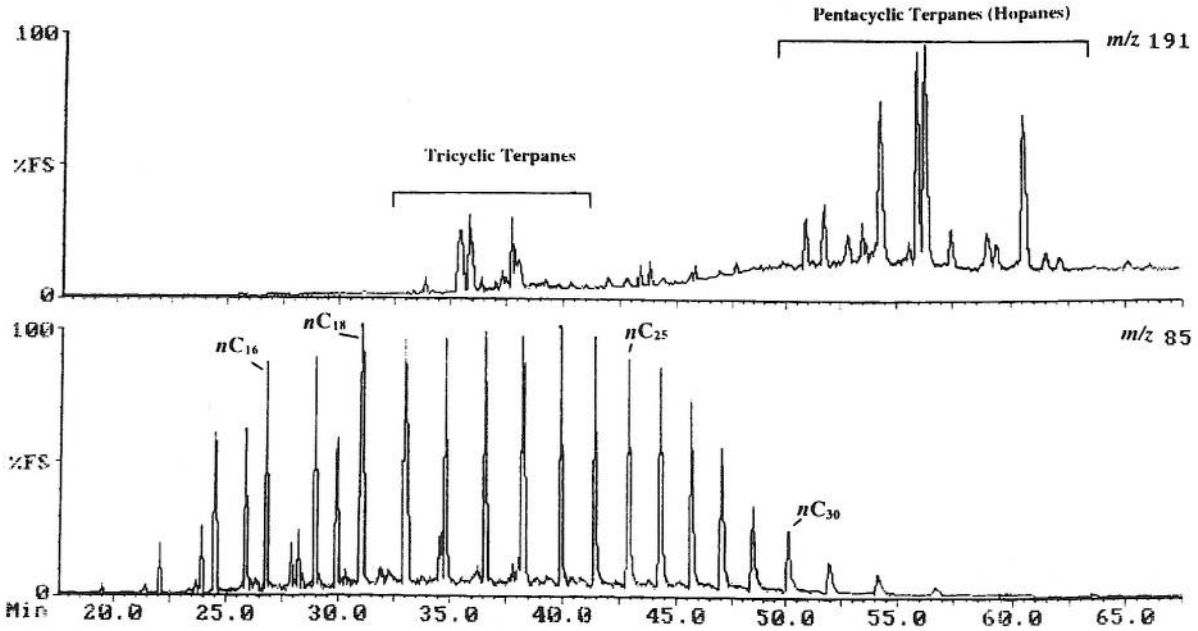


Fig. 2. Gas chromatography–mass spectrometry trace for residue oil saturate fraction, showing *m/z* 191 (tri-, tetra-, and pentacyclic terpanes) and *m/z* 85 (normal and branched alkanes) fragmentograms.

marine environment. In one study, this ratio was found to remain almost constant, at approximately 0.5, for a range of highly weathered crude oil beach residues and the original crude oil source [8]. In a related study, a slight decrease between fresh and weathered samples was observed, from 0.87 to 0.75 [7]. However, because both pristane and phytane have been shown to be susceptible to biotransformation [9], the reliability of this source correlation index is believed to be questionable in highly weathered oil samples. Evidence of this was presented by Hostettler and Kvenvolden [22], who found pristane : phytane values of between 1.2 and undetected for beach oil residues that originally were known to display a value of 1.4 for the same index.

C_{18} : 17α(H),21β(H)-Hopane, phytane : 17α(H),21β(H)-hopane, n-*alkanes : 17α(H),21β(H)-hopane.* These ratios have been used widely to demonstrate the loss of crude oil from beaches undergoing active bioremedial treatment [4,9], and in more general studies of oil degradation and maturity [11,13]. All three indices record the loss of oil components relative to the pentacyclic terpane found to be most resistant to oil weathering processes, 17α(*H*),21β(*H*)-hopane. Pande et al. [11] used the second of these indices to monitor biodegradation of crude oils, obtaining a spread of values from 200 for the freshest oil to 4.3 for the most degraded. Swannell et al. [23] used variation in the latter two indices to monitor the biodegradation of an Arabian crude oil. Significant shifts were recorded in the value of the ratio of total alkyl polycyclic aromatic hydrocarbons to 17α(*H*),21β(*H*)-hopane, which decreased from 43 in the freshest oil to undetected in the most degraded samples. In a similar study carried out by Croft et al. [13], the ratio of total hydrocarbons to 17α(*H*),21β(*H*)-hopane showed a small decrease, from 551 to 518, for oil samples undergoing limited biotransformation, while increasing slightly (from 551 to 663) when no biotransformation took place.

Tricyclic terpanes : Hopanes. Literature evidence suggests that lower molecular weight tricyclic terpanes degrade more rapidly than the more conserved pentacyclic terpanes (hopanes) in very weathered samples [7]. As a result, this index has been proposed as a possible means of quantifying oil weathering in highly degraded samples and for distinguishing between highly weathered oils.

17α(H),21β(H)-Hopane : 17α(H)21β(H)-norhopane. These hopane biomarkers have been shown to be both the most conserved and the most abundant biomarkers within oils [7]. This ratio is therefore the preferred source correlation parameter in many oil contaminant studies [6,8,13,22]. In general, oil samples with 17α(*H*),21β(*H*)-hopane : 17α(*H*)21β(*H*)-norhopane values within approximately 0.5 of one another have been considered to be from the same original source, although related oils often display a variation of much less than this.

The five sets of indices described above have been adapted directly from the literature in unaltered form for use in this study. In addition to these, we have identified an additional set of weathering indices with which it may be possible to characterize the weathering of diesel and other mid-distillate oil samples. These are: C_{18} : tricyclic terpanes, *n*-alkanes : tricyclic terpanes, pristane : tricyclic terpanes, phytane : tricyclic terpanes. Tricyclic terpanes are lower molecular weight analogues of hopanes that are detected in the diesel standards in sufficient amounts to be used as conserved internal marker compounds in weathering indices. Detection of these compounds may allow diesel oil weathering to be assessed more reliably than by the conventional C_{17} : pristane and C_{18} : phytane indices.

Although establishing index reliability is essential, particularly if use of indices is to be expanded within a commercial context, variations in the methods by which indices are calculated, the enormous diversity of petroleum products under study, and the influence of site-specific factors are such that a direct comparison of index values between studies should be avoided. Nevertheless, it may be possible to refer to index variations obtained in previous studies in order to gauge the significance of observed numerical variations; this is useful in attributing significance to the various indices.

Performance of weathering and source correlation indices in weathered diesel oil

Weathering indices reflect the relative rates at which selected oil components are dissipated during the combined physical, chemical, and biological processes that constitute oil weathering. In cases where the principal cause of oil component loss is biotransformation, determination of the extent to which other processes can influence weathering indices is desirable, so that any observed changes can be more confidently attributed to microbial activity. Physical weathering of spilled petroleum products is one such component of oil weathering that may cause the value of weathering indices to change in such a way as to shroud the effects caused by microbial degradation. The effect of physical weathering of oil components on the value of weathering indices is likely to be greatest in the period immediately following spillage of lighter petroleum products, such as diesel oil, into relatively impervious receiving media. To investigate this, we have evaluated four weathering indices and three source correlation indices for diesel range organics DRO samples at three stages of physical weathering; fresh, 25% (w/w) weathered, and 50% (w/w) weathered. Just as biotic losses are measured according to the relative biotransformation rates of index compounds, so physical weathering should produce variations in index values related to the difference in the volatility of the index compounds. Where this difference is large, physical weathering might be expected to induce significant variations in the value of the index. Results are shown in Table 2.

C_{18} : Phytane and C_{17} : pristane were the weathering indices found to be least sensitive to physical weathering, that is, those that varied least in value between the respective DRO samples. In oil weathering studies, both of these indices were found to decrease in value with increased oil weathering, due to preferential microbial transformation of straight chain C_{18} and C_{17} *n*-alkanes over the branched chain isoprenoid alkanes. Biotransformation of the isoprenoid alkanes proceeds more slowly than that of the *n*-alkanes because of the presence of the tertiary carbon atoms within these compounds, catabolization of which is thermodynamically more demanding. This results in the accelerated loss of the numerator *n*-alkanes relative to the denominator isoprenoid alkanes and a decrease in the value of the indices. In this study, results indicate that both C_{18} : phytane and C_{17} : pristane indices appear to be largely unaffected by light physical weathering, as both indices remained unaltered between the fresh and the 25% (w/w) weathered DRO samples, at 2.1 and 1.9, respectively. However, for the 50% (w/w) weathered DRO samples, the C_{17} : pristane index increased in value to 2.5, suggesting that the *n*-alkane was more readily conserved in the DRO samples than was the isoprenoid alkane. Conversely, C_{18} : phytane for the 50% (w/w) weathered DRO decreased to 1.4, suggesting that in this case the abundance of the C_{18} component decreased relative to that of phytane. These results cannot easily be explained with reference to the respective physical properties of the index compounds, but imply that prolonged or intense periods of physical weathering could induce significant fluctuations in the values of these indices.

As expected, physical weathering exerts the greatest influence on those indices in which the tricyclic terpanes are measured. This is presumably due to the high boiling points of these compounds relative to other diesel components. For the weathering indices in which tricyclic terpanes are used as the conserved marker species, the C_{18} : tricyclic terpanes weathering index decreased with DRO weathering from 2.1 in the fresh sample to 1.5 in the 25% (w/w) weathered sample and to 0.5 in the 50% (w/w) weathered sample. The *n*-alkanes : tricyclic terpanes ratio was found to be the most sensitive, decreasing from 20.4 in the fresh DRO sample to 11.4 in the 25% (w/w) weathered sample and to 4.0 in the 50% (w/w) weathered sample. As the molecular structures of tricyclic terpane comprise a significant cyclic component, terpanes would be expected to be much less susceptible to biotransformation than the *n*-alkanes in the index numerators. As a result, these indices would also be expected to decrease in value with microbial activity. These results indicate, therefore, that a decrease in the value of this index should not necessarily be regarded as evidence of microbial activity, and that the effect of physical weathering processes may also need to be taken into account.

The values of the three proposed source correlation indices, pristane : phytane, pristane : tricyclic terpanes, and phytane : tricyclic terpanes, for DRO samples at each stage of weathering are given in Table 2. The former index was found to remain almost unchanged between the fresh and the 25% (w/w) weathered samples, at 1.4 and 1.3. For the 50% (w/w) weathered sample, however, its value decreased to 0.6. This variation suggests that pristane was more easily lost from the DRO samples than was phytane as physical weathering proceeded. During oil weathering, the structural similarity of these two compounds and their relative resistance to biotransformation has lead to their application as source correlation indices. Their use as such depends upon the absence of any sizeable fluctuation in the value of the ratio of these two components. In this study, results indicate that this index may be unsuitable for use as a source correlation parameter for oils that have undergone significant physical weathering, due to the magnitude of the variation in index value for the most weathered DRO sample. The loss of both pristane and phytane during physical weathering is confirmed by the decrease in the values of the pristane : tricyclic terpanes and phytane : tricyclic terpanes indices with increased DRO weathering. Values of pristane : tricyclic terpanes for the fresh, 25% (w/w) weathered, and 50% (w/w) weathered DRO samples were 1.0, 0.7, and 0.4, respectively, whereas those for phytane : tricyclic terpanes changed from 1.4 to 0.9 to 0.2 with increased DRO weathering. Because of the structural differences between pristane and phytane, and the tricyclic terpanes, these indices would also be expected to decrease during oil biotransformation.

These results demonstrate that even for standard oil weathered in a controlled laboratory environment, there are difficulties to be overcome before a source correlation index capable of providing a consistent, positive correlation between weathered samples can be defined. In our study, both pristane and phytane were demonstrated to be ultimately susceptible to physical weathering and, therefore, unsuitable for use in significantly weathered samples. More generally, it would appear that for a source correlation index to maintain its integrity throughout the weathering process, it must consist of components that are truly conserved during oil weathering and that do not display significantly different physical properties. In the absence of such an index, defining source commonality between mid-distillate petroleum products such as the DRO samples analyzed here may require a more careful consideration of oil characteristics rather than a straightforward calculation of pristane : phytane or isoprenoid : tricyclic terpane

ratios, particularly for highly weathered samples. Alternative oil fingerprinting techniques were demonstrated by Baugh and Lovegreen [24], who were able to define different refined petroleum products using representative GC-FID profiles, and differentiate between crude and refined petroleum products using the C_{20} to C_{30} hydrocarbon GC peaks.

Specificity of crude oil correlation parameters

Analytical correlation of oil samples in the environment, most commonly undertaken for source identification purposes, is routinely accomplished through a comparison of the characteristic distribution fingerprints of oil components. For oils that have undergone weathering, fingerprinting is most reliably achieved using the distributions of biomarker compounds. Source correlation indices, representing the ratio of one biomarker to another, are tools with which such a meaningful comparison of two oils can be supported [6,7,25]. Although evidence of commonality produced this way should be used only in conjunction with supporting information, it is nevertheless important to review these indices with the goal of establishing a greater appreciation of their potential use.

The usefulness of source correlation indices depends upon the degree to which their values vary between discrete oil samples. Effective source indices should vary significantly in value between oil samples from different backgrounds while remaining relatively consistent between oils from the same family. Ideally, their values should remain unaltered by the effects of oil weathering. In this study, the objective was to identify those correlation indices best able to discriminate between four unweathered crude oils from three different backgrounds; a Nigerian crude oil, an Iraqi export crude oil, and two North Sea crude oils. The results, given in Table 3, show that five of the seven indices adequately discriminated between the respective crude oil types: C_{18} : 17α(*H*),21β(*H*)-hopane, *n*-alkanes : 17α(*H*),21β(*H*)-hopane, pristane : phytane, tricyclic terpanes : hopanes, and phytane : 17α(*H*),21β(*H*)-hopane. All of these indices show sufficiently discrete values for each of the oil samples to allow clear discrimination between unrelated oils and yet support a positive correlation of the two North Sea crude oils. Of these, the C_{18} : 17α(*H*),21β(*H*)-hopane index, which has a value of 0.9 for the Nigerian crude, 22.6 for the Iraqi crude, and 16.8 and 13.1 for the two North Sea crudes, and the *n*-alkanes : 17α(*H*),21β(*H*)-hopane index, which has values of 10.7, 277.5, 166.5, and 184.7 for the Nigerian, Iraqi, and North Sea crudes, respectively, would be expected to change significantly in value with oil weathering because of the degradability of *n*-alkanes and C_{18} components in relation to the recalcitrant 17α(*H*),21β(*H*)-hopane. Therefore, for fresh oils that have not been exposed to environmental weathering, such as the samples analyzed in this study, these ratios may indeed make useful oil correlation parameters. However, they may be unsuitable for correlations involving weathered oil samples.

The other indices able to discriminate between the respective crude oil samples are pristane : phytane, tricyclic hopanes : total hopanes, and phytane : 17α(*H*),21β(*H*)-hopane. The values of all these indices would be expected to remain more or less constant during light to moderate oil weathering. For highly weathered samples, however, the latter two indices may become unreliable due to the susceptibility of both pristane and phytane to prolonged microbial activity. The tricyclic hopanes : total hopanes index should not alter even in highly weathered samples, due to the environmental persistence of the cyclic alkanes, and is, therefore, proposed as the oil correlation index best able to differentiate between both fresh and weathered crude oils. Of the remaining biomarker indices, C_{18} : phytane fails to discriminate between the Nigerian and Iraqi crude oils (both exhibit values of 1.4 for this index), and 17α(*H*),21β(*H*)-hopane : 17α(*H*),21β(*H*)-norhopane fails to discriminate between the Nigerian and one of the North Sea crudes (0.8 and 0.7). The latter result is surprising, given the accepted recalcitrance of hopane and suggests that oil correlation carried out through isolated use of this index could lead to erroneous diagnosis of oil source commonality.

Relationship between heavy oil composition and selected source and weathering indices

Elucidation of the composition of residual organic wastes at hydrocarbon-contaminated sites is important when the application of bioremediation technologies that depend upon the presence of more assimilable waste constituents is under consideration. In general, saturate class compounds (*n*- and branched alkanes), which often make up a significant proportion of the overall composition of many oils, are the components most susceptible to loss during natural attenuation or enhanced bioremediation. Polar and asphaltenic compounds are generally less responsive to microbial degradation. Wastes containing a preponderance of these compounds, such as heavy oils or oils that have undergone extensive weathering (and in which polar and asphaltenic material has therefore concentrated), may not, therefore, respond to bioremediation techniques. Unfortunately, in many cases, direct analysis of the entire range of waste components by GC-coupled analytical techniques is restricted due to inadequate resolution of the complex, high molecular weight polar components [26].

To investigate whether biomarker monitoring may allow for discrimination of waste types according to their suitability to treatment by bioremedial technologies, the values of selected source and weathering indices have been determined for a suite of medium to heavy petroleum products, chosen to represent the types of wastes frequently found at sites having residual petroleum contamination. This approach may be advantageous because biomarker monitoring allows the behavior of oil components from within the saturate class fraction to be scrutinized with minimal interference from other waste constituents. Furthermore, because the saturate class fraction does not contain any highly polar components, analysis by GC-MS is relatively straightforward, with high analyte recoveries readily obtainable. In cases of particularly complex waste matrices, chromatographic isolation of the saturate class fraction prior to GC-MS analysis may improve resolution of target biomarker compounds. However, oils that are extremely heavy or highly weathered may contain a significant proportion of unresolved complex material [27], in which case even extensive sample fractionation cannot always provide a suitably refined analyte. For such samples, the application of specialized chromatographic separation and detection procedures may not be warranted, and it may be more profitable to review the waste matrix in terms of bulk component groups through application of screening techniques, such as thin-layer chromatography with flame ionization detection or isotope ratio mass spectrometry [5,26].

To forecast the bioremediation potential of heavy oils through the use of biomarker indices, a relationship between the values of the indices and the composition of the oil must exist. We have conducted a preliminary examination of this

relationship by determining the values of six selected source and weathering indices for five unweathered heavy oils of known class composition. Two of the oils, a tanker ballast oil and a refinery residue oil, are predominantly paraffinic, containing >70% (w/w) saturates and <7% (w/w) combined polars and asphaltenes. The boiling range of the residue oil is considerably higher, however, indicating that the components of this oil are generally of a higher molecular weight. Other heavy oils analyzed are a refinery waste oil (referred to as API separator oil) (54% [w/w] saturates, 15.3% [w/w] combined polars and asphaltenes), a no. 6 fuel oil (approx. 36% [w/w] saturates and approx. 22% [w/w] polars and asphaltenes), and an acid tar oil, which was the heaviest of all the samples analyzed (approx. 35% [w/w] combined polars and asphaltenes). All the oil samples analyzed were produced from North Sea crude oils. This was important, as it ensured that variations in source and weathering indices were caused by differences in oil composition and not genetic background.

Values for the six selected source and weathering indices for each oil are given in Table 4. Two indices, C_{18} : phytane and 17α(*H*),21β(*H*)-hopane : 17α(*H*),21β(*H*)-norhopane, changed very little between the oils, with both showing an overall spread in value of only 0.9. The consistency of the latter index can be explained by the recalcitrance of the 17α(*H*),21β(*H*)-hopane and 17α(*H*),21β(*H*)-norhopane biomarkers [7–9], which would not be expected to fluctuate in abundance during oil production. As all the oil samples ultimately originate from the same crude oil source, the ratio of these biomarkers would be expected to remain broadly constant, which was found to be the case in this study. The reason for the apparent lack of variation in the value of the C_{18} : phytane index is not clear. Because the physical properties of C_{18} and phytane are so similar, they possibly behave similarly during oil production and do not become depleted or enhanced relative to one another. Nonetheless, based on these results, these indices appear to be insensitive to variations in oil composition and would not, therefore, make useful indicators of oil bioremediation potential.

The remaining indices showed a marked dependence on oil composition. The indices found to be most sensitive to oil composition were *n*-alkanes : 17α(*H*),21β(*H*)-hopane and phytane : 17α(*H*),21β(*H*)-hopane. The former index showed the largest variation in value between the oils, decreasing from 575.2 in the lighter ballast oil, to 406.4 in the API separator oil, 85.6 in the residue oil, 81.0 in the no. 6 fuel oil, and as low as 1.3 in the acid tar sample. A similar, though less prodigious, change is shown by the phytane : 17α(*H*),21β(*H*)-hopane ratio, which was found to be 39.9 in the ballast oil, 27.4 in the API separator oil, 2.1 in the residue oil, 4.2 in the no. 6 fuel oil, and 0.2 in the acid tar sample. The tricyclic terpanes : total hopanes index also decreased with increasing oil boiling range, with values of 12.1 for the ballast oil, 8.2 for the API separator oil, 0.5 for the residue oil, and 0.5 for the acid tar oil. However, this index was considered to be relatively unreliable after producing an unexpectedly high value of 11.6 for the no. 6 fuel oil. These results are useful in that they associate very low values for the *n*-alkanes : 17α(*H*),21β(*H*)-hopane and phytane : 17α(*H*),21β(*H*)-hopane indices with oils containing a sizeable combined polar and asphaltene fraction and ones that may not, therefore, be suitable for treatment by bioremedial technologies. As these indices would also be expected to produce low values for oils that have undergone extensive weathering, due to the susceptibility of the *n*-alkanes and phytane to biotransformation relative to the conserved hopane biomarker, these indices may also be useful in assessing the degradation state of oily wastes. Of course, the loss of oil components during oil weathering cannot be quantified without knowledge of the initial index value for the oil, or at the very least, the value of the index prior to oil degradation. Further studies are underway to assess the relative sensitivities of the biomarker weathering and source indices presented here during biotransformation of heavy oils.

CONCLUSIONS

Volatilization of petroleum contaminants in the environment could, in certain circumstances, affect the values of biomarker source and weathering indices. If these effects are not accounted for, they could lead to mistakes in oil correlation studies and erroneous diagnosis of microbial activity. The indices most affected by physical weathering in this study were C_{18} : tricyclic terpanes, *n*-alkanes : tricyclic terpanes, pristane : tricyclic terpanes, and phytane : tricyclic terpanes.

Five biomarker indices were able to distinguish between crude oils from different geological backgrounds: C_{18} : 17α(*H*),21β(*H*)-hopane, *n*-alkanes : 17α(*H*),21β(*H*),-hopane, pristane : phytane, tricyclic terpanes : hopanes, and phytane : 17α(*H*),21β(*H*)-hopane. Of these, the C_{18} : 17α(*H*),21β(*H*)-hopane and *n*-alkanes : 17α(*H*),21β(*H*)-hopane indices would be expected to change significantly in value with oil weathering. Extensive oil weathering may influence the pristane : phytane and phytane : 17α(*H*),21β(*H*)-hopane indices. Only the tricyclic terpanes : hopanes index is likely to remain unchanged by oil weathering, and this is therefore proposed as the most favorable oil correlation index in this study.

Biomarker indices may be useful in predicting the natural attenuation or bioremediation potential of heavy oil waste matrices by providing an indication of waste composition, or degradation state. Low values for *n*-alkanes : 17α(*H*),21β(*H*)-hopane and phytane : 17α(*H*),21β(*H*)-hopane indices were indicative of oils containing high proportions of polar and asphaltene class compounds. This may be because they are innately high boiling point oils or because they are heavily weathered oils. In either case, the application of bioremedial technologies for these oils may be restricted. Future microcosm studies will assess these constraints.

The utility of these indices for contaminants in the soil environment brings particular research challenges, such as interference from soil organic matter, enhanced biotransformation kinetics in soil, multimedia partitioning, and the presence of mixed organic wastes. Current work is focusing on the application of these indices to the contaminated soil environment, in particular to the variation of biomarker indices with heavy oil biotransformation, effected through the use of soil microcosm studies.

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Matrix effects in applying mono- and polyclonal ELISA systems to the analysis of weathered oils in contaminated soil

S.J.T. Pollard[a,*], J.G. Farmer[b], D.M. Knight[b], P.J. Young[c]

[a]*Environment Agency, National Centre for Risk Analysis and Options Appraisal, Steel House, 11 Tothill Street, London SW1H 9NF, UK*
[b]*Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[c]*Enviros Aspinwall, Walford Manor, Baschurch, Shrewsbury SY4 2HH, UK*

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"Capsule": *Highly weathered oils in contaminated soil samples can compromise ELISA performance.*

Abstract

Commercial mono- and polyclonal enzyme-linked immunosorbent assay (ELISA) systems were applied to the on-site analysis of weathered hydrocarbon-contaminated soils at a former integrated steelworks. Comparisons were made between concentrations of solvent extractable matter (SEM) determined gravimetrically by Soxhlet (dichloromethane) extraction and those estimated immunologically by ELISA determination over a concentration range of 2000–330 000 mg SEM /kg soil dry weight. Both ELISA systems under-reported for the more weathered soil samples. Results suggest this is due to matrix effects in the sample rather than any inherent bias in the ELISA systems and it is concluded that, for weathered hydrocarbons typical of steelworks and coke production sites, the use of ELISA requires careful consideration as a field technique. Consideration of the target analyte relative to the composition of the hydrocarbon waste encountered appears critical. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Contaminated soils; Complex hydrocarbons; Monitoring; On-site screening

1. Introduction

Enzyme-linked immunosorbent assay (ELISA) test kits offer a rapid, on-site method of screening contaminated soil samples (Van Emon and Gerlach, 1995). Configured for a range of target analytes (e.g. polychlorinated biphenyls, pentachlorophenol, benzene, toluene, ethylbenzene, xylene, total petroleum hydrocarbons, polynuclear aromatic hydrocarbons, pesticides), these systems have undergone regulatory scrutiny and gained a qualified acceptance for a range of environmental pollutants in soils (Green and Mackenzie, 1994; Waters, et al., 1997; Barceló et al., 1998; USEPA, 1998a,b). They function through the interaction between a target analyte and an antibody, usually immobilised on a test tube surface. Following exposure of the analyte in the sample to the immobilised antibody, the amount of enzyme-tagged analyte is determined analytically by photometry. Monoclonal antibody systems generally offer more analyte specificity than polyclonal systems, but the latter are regarded as more sensitive and capable of responding better to classes of analytes, on the basis of a functional group or a structural region characteristic of the compound class.

Whilst commercial ELISA test kits for on-site screening have been available for over 12 years, few assessments of their performance exist for the complex weathered hydrocarbon wastes at contaminated sites. These sources of contamination pose well-recognised analytical challenges (Pollard et al., 1992; Whittaker et al., 1995). The verification of ELISA test kits for hydrocarbons has concentrated instead on narrow range gasoline, diesel and jet fuel distillates (Carter and McInereney, 1993; Knight, 1995; Knopp et al., 2000). Anecdotal evidence has suggested, however, that these systems may be routinely subject to the separate interference mechanisms of cross-reactivity between analytes and false negative (under) reporting for heavier oils (McDonald, 1993; USEPA, 2000). Wishing to test this assertion for a range of weathered oil types, we conducted a performance assessment of two commercial ELISA systems on a

* Corresponding author. Tel.: +44-207-664-6832; fax: +44-207-664-6836.
E-mail address: simon.pollard@environment-agency.gov.uk (S.J.T. Pollard).

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range of contaminated soils representative of historic contamination at integrated steelworks and coke production sites.

2. Methods

2.1. Soil samples

Contaminated soils (0.5–1.0 kg) were sampled from five discrete areas (A–E) of a former steelworks: (A) the coking by-products tar storage area; (B) the effluent treatment lagoons; (C) the coking by-products benzole plant; (D) below the gas seal pot areas; and (E) the oil catchment ponds. Soils in these areas contained weathered oils of substantial chemical complexity and were derived from various fractions of condensate produced from the coke plant off-gas. Using detailed site investigation studies to identify suitable sampling points, three soil samples were taken from each area, representing: 'high' (> 2000 mg SEM/kg soil, dry weight throughout), 'medium' (ca. 2000 mg SEM/kg soil) and 'low' (< 2000 mg SEM/kg soil) levels of oil contamination. Soil sub-samples (ca. 40 g) were air-dried overnight, Soxhlet-extracted (Martin et al., 1990) with 200 ml HPLC grade dichloromethane (DCM) for 16–18 h and SEM reported gravimetrically using a verified procedure with a typical RSD of < 5% w/w (Pollard et al., 1999).

2.2. ELISA test kit protocol

We employed the EnSys™ polynuclear aromatic hydrocarbon (PAH) PAH RIS^C and the Millipore Enviroguard™ PAH ELISA systems that incorporate antibodies raised against phenanthrene and pyrene, respectively. Both systems were established as sufficiently sensitive for PAH to act as a surrogate for the concentration of 'oil' in the hydrocarbon-contaminated soils (Knight, 1995). In order to enhance the analytical response, each ELISA kit was optimised and calibrated against standard dilutions of a methanolic stock solution (5000 mg/kg) of 'wash oil' from the coking by-products plant (Area C; total 16 USEPA PAH content of ca. 3% w/w), a common source term. By calibration, the ELISA-determined 'oil' concentration was then presented as 'mg oil/kg soil'; that is, as 'wash oil equivalents'.

The performance of each ELISA test kit was assessed at three different levels of contamination (A1, A2, A3, etc.) for each source area. For the monoclonal Ensys™ system, methanol extracts were tested at three discrete detection levels corresponding to the equivalent of 400, 2000 and 10 000 mg oil/kg soil. For the polyclonal Enviroguard system, extracts were tested at the equivalent of 400, 1000 and 2000 mg oil/kg soil. Triplicate analysis was undertaken for one sample in three from each area to assess system reproducibility (Pollard et al., 2000).

Accurately pre-weighed sub-samples (5–10 ± 0.1 g) of soil were extracted in methanol using the manufacturer's instructions and filtered. Aliquots (typically 10–75 μl), diluted as appropriate, were pipetted into the relevant antibody test vials and the immunoassay completed. Photometric measurement of optical density (OD) allowed an estimation of the concentration of PAH in the diluted sample. Calibration of each system allowed the 'oil' concentration range in the methanolic filtrate to be back calculated and the 'oil' concentration range in the soil to be estimated.

3. Results and discussion

3.1. Comparison of extractable material and oil load in soils

Soxhlet extraction and ELISA results are presented in Figs. 1 and 2. Samples representing each of the three levels of contamination were not found for areas A–E. However, the overall range of Soxhlet-extracted SEM encountered was 2000–330 000 mg SEM/kg dry soil. ELISA results are presented by reference to the predefined detection levels noted above. For example, for sample A1, the Ensys system reports a 'wash oil equivalent' concentration above (>) 2000 mg oil/kg and > 10 000 mg oil/kg. Enviroguard™ also offers a quantitation facility (Enviroquant™), from which an individual sample concentration can be inferred and a 'response factor' (RF) relative to the SEM concentration derived and we have reported on this capability separately (Pollard et al., 2000).

Within the practical context of this study, the following idealised assumptions were required in comparing SEM concentrations with ELISA 'oil' determinations (Knight, 1995): (1) DCM Soxhlet and methanol field extractions are broadly equivalent in removing SEM and bulk 'oil' load and achieve 100% extraction recovery, despite different extraction times, physical processes, solvating power and sample water content; (2) SEM and methanol extracts are compositionally equivalent; and (3) ELISA filtrates are analysed by dilution in the linear portion of the ELISA calibration curve.

3.2. Performance of ELISA systems for complex hydrocarbons

The results provide a variable picture of the performance of these ELISA systems for the complex hydrocarbon-contaminated soils studied. Examination of the results highlights a number of factors critical to the practical use of ELISA test kits for on-site monitoring and these have been discussed elsewhere (Pollard et al., 2000). We were especially concerned with the observation of apparent matrix effects in the study and the

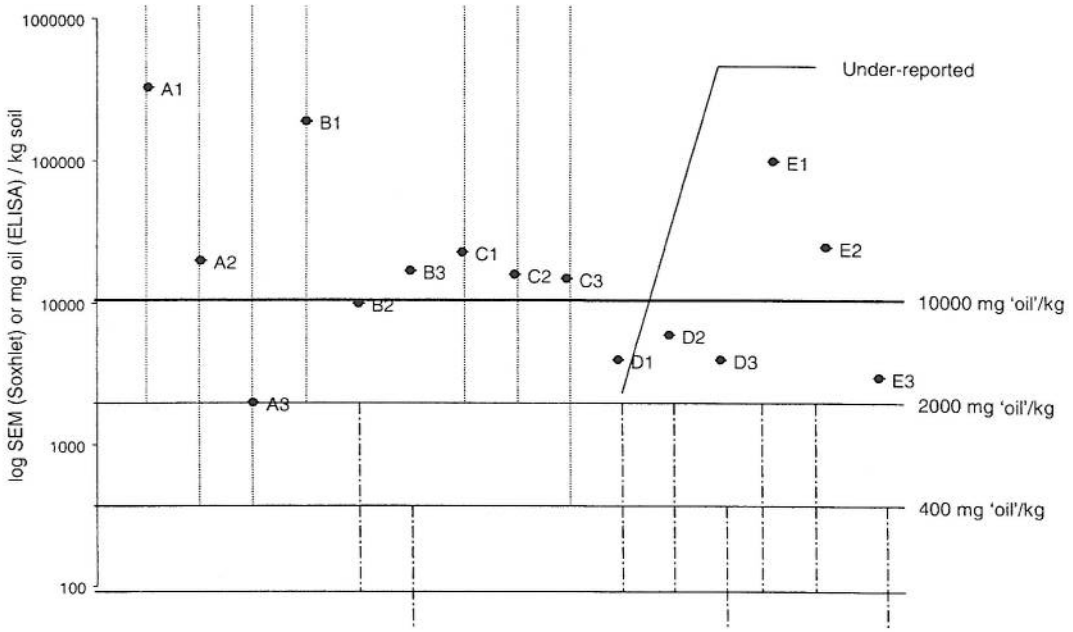


Fig. 1. Individual solvent (DCM) — extractable matter concentrations (●) and monoclonal ELISA (EnSys™ PAH RIS^{C}) concentration ranges (as lines) reported for contaminated soils in site areas A–E. Broken dot-dash lines indicate under-reporting.

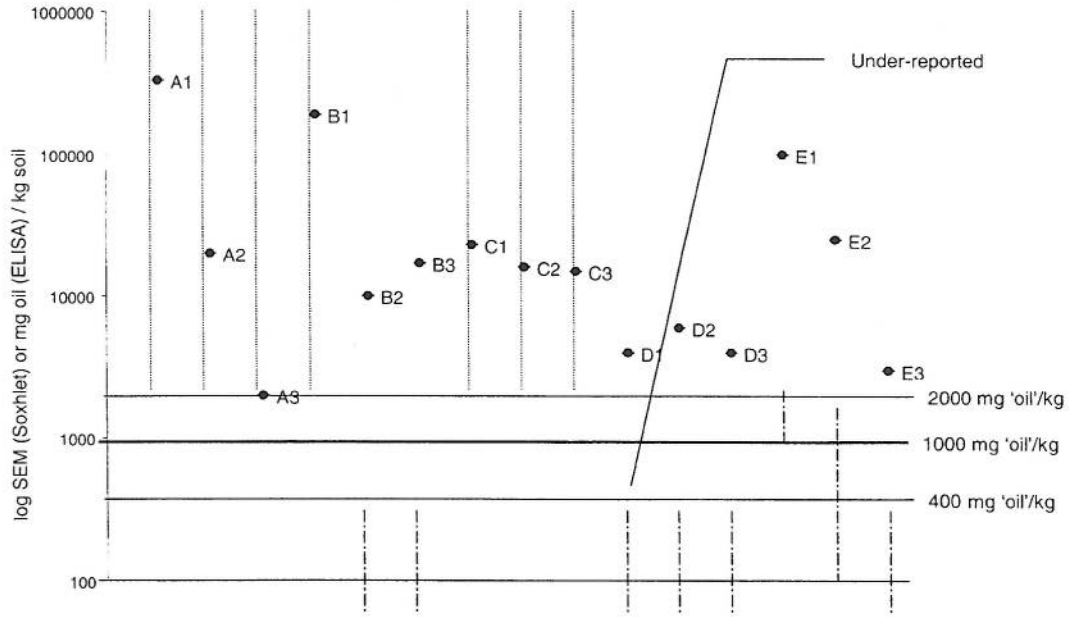


Fig. 2. Individual solvent (DCM) — extractable matter concentrations (●) and polyclonal ELISA (Enviroguard™) concentration ranges (as lines) reported for contaminated soils in site areas A–E. Broken dot-dash lines indicate under-reporting.

implications for the on-site use of ELISA systems by field practitioners.

Reviewing Figs. 1 and 2, consistent results between the gravimetric and ELISA methods are reported for soils originating from areas A and C, the oils most similar to the 'wash oil' against which both systems were optimised. Importantly, however, the ELISA analysis revealed 8/15 misreported ELISA determinations (broken dot-dash lines) compared with the SEM data, these eight determinations consistently under-reporting in both systems. This included samples with SEM concentrations around the 2000 mg SEM/kg soil target concentration (D1, D2, D3, E3), expected to be well within the linear range of each technique.

Given the documented reproducibility and sensitivity of these systems (Van Emon and Gerlach, 1995), the

consistent under-reporting in identical samples suggests that the performance of mono- and polyclonal ELISA systems for the contaminated soils examined is subject to matrix effects. Without optimisation, the level of under-reporting would arguably have been greater. Access to the PAH target analyte in 'oil' extracts may be compromised by masking within the unresolved complex mixture of hydrocarbons typical of these wastes (Whittaker et al., 1995), or poor recoveries during methanol extraction, restricted by the often asphaltic characteristics of weathered oils (Pollard et al., 1994). Other potential matrix effects include the differential water content between samples which has a marked influence on extractability, cross-reactivity between analytes (Knight, 1995) and interferences from humic substances (Knopp et al., 2000).

4. Conclusions

Where ELISA test kits are being considered for a range of on-site uses, it is clearly necessary to consider the complexity of the source of contamination in deciding whether or not to use them. ELISA systems perform well for refined fuel distillates and contamination high in PAH [e.g. creosote-contaminated soils (Millipore, 1995)], but for complex, weathered source terms, the ability of these systems to infer total 'oil' load appears compromised across a range of weathered oil types. Our conclusions need to be viewed in the context in which the results were obtained; i.e. comparisons made here are between SEM in dichloromethane against methanol-extracted PAH calibrated against 'wash oil'. Nevertheless, this comparison does represent an assessment of the capabilities of these systems to reflect 'oil' concentrations in soils contaminated with complex hydrocarbons as opposed to single compounds. Further study might usefully focus on eliminating the differences between sample preparations and elucidating the influence of weathering in isolation of other matrix/analytical effects.

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Bioaerosol releases from compost facilities: Evaluating passive and active source terms at a green waste facility for improved risk assessments

M.P.M. Taha, G.H. Drew, P.J. Longhurst, R. Smith, S.J.T Pollard*

Integrated Waste Management Centre, Sustainable Systems Department, School of Industrial and Manufacturing Science, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK

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Abstract

The passive and active release of bioaerosols during green waste composting, measured at source is reported for a commercial composting facility in South East (SE) England as part of a research programme focused on improving risk assessments at composting facilities. *Aspergillus fumigatus* and actinomycetes concentrations of $9.8–36.8 \times 10^6$ and $18.9–36.0 \times 10^6$ cfu m^{-3}, respectively, measured during the active turning of green waste compost, were typically 3-log higher than previously reported concentrations from static compost windrows. Source depletion curves constructed for *A. fumigatus* during compost turning and modelled using SCREEN3 suggest that bioaerosol concentrations could reduce to background concentrations of 10^3 cfu m^{-3} within 100 m of this site. Authentic source term data produced from this study will help to refine the risk assessment methodologies that support improved permitting of compost facilities.
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Keywords: Bioaerosols; Compost; Actinomycetes; *Aspergillus fumigatus*; Risk; Assessment

1. Introduction

1.1. Background

A steady growth in composting in the UK is one response to the need to divert municipal solid waste (MSW) away from landfill under the devolved waste strategies of the UK and the European Waste Framework and Landfill Directives. The growth requires local authority and environmental regulators to permit the sitting and operation of new compost facilities (Composting Association, 2001). Operating a composting facility should be a low hazard activity. However, composting does have the potential to cause pollution, harm to health and nuisance through odours, leachate, fires, dust, vermin and potentially harmful bioaerosols, if not operated properly (Fig. 1). As a result of public health concerns and the need for operators to demonstrate the safe and responsible operation of their facilities, environmental regulators have been requesting regulatory risk assessments prior to licensing the composting plants (Wheeler et al., 2001; Pollard et al., 2005). Regulatory risk assessments allow operators to demonstrate they understand the hazards associated with their processes

*Corresponding author. Tel.: +44 1234 754101; fax: +44 1234 751671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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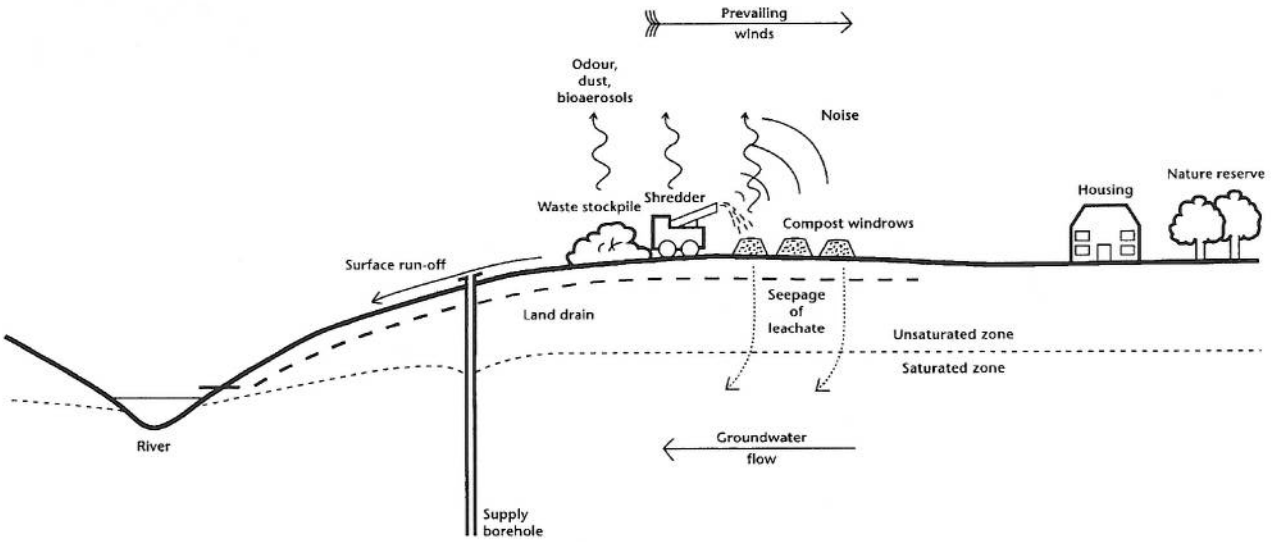


Fig. 1. Typical layout of open windrow composting facilities with sources, pathways and receptors for risk assessment.

and can design and implement technical and management procedures to minimise unacceptable risks. Regulators use risk assessments to inform environmental permitting and the drafting of conditions within the operator's licences or permits to operate (Environment Agency, 2002).

Concerns about the impact of compost operations on public health and amenity (dust, odour, traffic movements, and chemical and pathogen release) are frequently voiced when proposals are made for larger facilities in, or adjacent to built-up areas (National Audit Office, 2002). Increasingly, public health concerns about composting focus on the potential release of, and exposure to, bioaerosols. The risk assessments undertaken to date have largely relied on air dispersion modelling to estimate downwind concentrations of bioaerosols at distance from facilities and to allow comparisons with measured data upwind or at background locations.

In practice, the quality of the risk assessments is highly dependant on the availability and quality of the bioaerosol source term data they employ (Pollard et al., 2005). This data is frequently unavailable or limited, in part because of the practical difficulties of microbiological analyses and also the cost constraints. Our own research (Taha et al., 2004, 2005) focuses on improving the quality of regulatory risk assessments for composting facilities by providing authentic source term data at the point of release, as compared to 50, 100 or 200 m downwind, where data uncertainties abound. This is critical because bioaerosols deplete rapidly with distance from their source, and measurements at distance (say >50 m and beyond) are far more difficult to authenticate as being from a specific operation as opposed to other, non-compost sources.

In practice, most waste management operations generate episodic or periodic releases due to factors such as their operational cycles (composting), the fluctuations in diurnal temperature that alter the characteristics of emissions (e.g. odour profiles), or the fluctuations in atmospheric pressure that dictate the initial releases of pollutants (e.g. landfill gas). Furthermore, with the integration of multiple waste processing technologies on single sites, there are often a number of sources contributing to a facility's 'source term'. In this paper, we seek to understand the key contributing sources of bioaerosols released at a green waste composting facility and, using rudimentary air dispersion analysis, to characterise the depletion curves under static and active conditions in order to inform risk assessments. These data are of value to regulatory agencies guiding operators on the requirements of regulatory risk assessment, to operators themselves and to their professional advisors, as well as the publics living in the vicinity of such facilities.

1.2. *Bioaerosols and composting*

Bioaerosol is a general term used for microorganisms suspended in air. Bioaerosols include allergens

such as fungi, bacteria, actinomycetes, arthropods, and protozoa, as well as microbial products such as mycotoxins, endotoxins and glucans (Millner et al., 1994). Bioaerosols are generally $<10\,\mu m$ in size and are not filtered out by the hairs and specialised cells that line the nose. They can penetrate deep into the lungs, causing both respiratory and gastro-intestinal symptoms (Fattal et al., 1983; Sigsgaard et al., 1994; Thorn et al., 1998; Ivens et al., 1999; Douwes et al., 2003) and, where prolonged (usually occupational) exposure occurs, potentially result in allergic lung diseases such as Farmers Lung Disease and Mushroom Workers Lung Disease (Flannigan et al., 1991). Although the link between bioaerosols and these symptoms and diseases has been shown, clear dose-response relationships have not been defined (Douwes et al., 2003), and this remains a principal constraint to characterising the significance of the risks to public, as opposed to occupational, health from these agents.

1.3. Prior art

Composting provides a favourable environment for the proliferation of bioaerosols in substantial amounts as the degradation of biodegradable organic matter progresses (Fischer et al., 1999). In particular actinomycetes species, a heterogeneous group of filamentous bacteria that superficially resemble fungi, can produce thousands of very small spores (1–3 μm) that easily become airborne when highly colonised material such as compost is disturbed. Also commonly present (Millner et al., 1977) is *Aspergillus fumigatus*, a known opportunistic human fungal pathogen which, under prolonged exposure conditions, may cause invasive aspergilliosis, particularly among immunocompromised individuals (Shen et al., 2004). During conventional compost processing, agitation activities, such as screening, shredding and the turning of waste and compost, result in episodic bioaerosol releases to air (Millner et al., 1980). The agitation of green compost windrows may result in airborne fungi and bacteria levels averaging 10^4–$10^7\,cfu\,m^{-3}$ (Lacey, 1997; Wheeler et al., 2001; Recer et al., 2001). In contrast, static compost windrows typically emit bioaerosols at rates of $10^3\,cfu\,m^{-3}$ for actinomycetes and *A. fumigatus* (Taha et al., 2005).

Bioaerosol emission rate and dispersal is influenced by a number of factors, including (Swan et al., 2002) (i) the materials being composted; (ii) the on-site processes involved; (iii) the associated vehicle movements; (iv) the process equipment used; (v) individual bioaerosol properties; and (vi) the geographical, topographical and meteorological conditions on- and off-site.

In previous studies (Taha et al., 2005), and in order to determine the most appropriate mode of dispersal during agitation, we have treated bioaerosols as a fugitive, continuous large point source for which both area and volume type release modes have been considered. Both sets of assumptions are acknowledged gross simplifications of the reported behaviour of bioaerosols, characterised by total protein and culturable microorganisms (Borodulin et al., 2005). We have yet to encapsulate the characteristic aggregation (so-called 'clumping') behaviour of bioaerosols emitted at composting facilities or account for microbial inactivation within the air column following release. However, we are investigating this in current studies.

1.4. Study rationale

In this paper, we present results from measuring the dispersal of bioaerosols from the agitation of a compost pile at a green waste composting facility in SE England. Results are compared to the fugitive emission flux of bioaerosols off a static windrow (Taha et al., 2005). In order to measure the emission rate of compost agitation activities, bioaerosol concentrations were sampled as close as feasibly practical to the pile upon which agitation was performed. The two microorganisms chosen, actinomycetes and *A. fumigatus*, are known to be the most dominant culturable bioaerosols in green waste compost (Ryckeboer et al., 2003; Lacey, 1997) and are used to represent viable bioaerosols within this study.

Air dispersion modelling was employed to estimate their dispersal using the SCREEN3 model (USEPA, 1995a), an air quality model frequently applied to coarse, 'screening-level' air quality modelling analyses for new air pollution sources. It adopts steady-state Gaussian plume algorithms and meteorological scenarios to estimate worst-case dispersal. The objective was to understand, using rudimentary dispersion modelling, the impact of compost processing on downwind bioaerosol concentrations and to evaluate the source term as it depleted downwind of the site. More advanced air dispersion models such as ISC-AERMOD (USEPA, 1995b; Cimorelli et al., 1998), ADMS (Carruthers et al., 1994; CERC, 2003) and CALPUFF (Scire

et al., 2000), which take into account multiple and varied rates of sources, are now being considered in subsequent studies.

2. Material and methods

2.1. Process activities at the study site

The study site was a 320 tonne capacity, conventional commercial green waste facility in SE England, situated adjacent to a landfill site. At the site, agitation and turning of compost were performed using a front-end loader fitted with a $3\,m^3$ bucket Green waste was shredded mechanically and continuously prior to composting, stored in compost windrows and the matured compost was screened before, in this case, being transported from the facility for use as landfill cover. Bioaerosol sampling during active compost processing and passive compost storage in compost windrows was undertaken.

2.2. Bioaerosol sampling of static compost windrows (passive sampling)

Sampling of bioaerosols from static compost windrows was undertaken coincident with the active processing described below. A portable wind tunnel (Jiang and Kaye, 2001; Taha et al., 2005) was positioned on the static compost windrows to allow measurement of the bioaerosol flux. Incoming air, filtered through activated carbon is blown into the inlet duct using a fan. Bioaerosols are mixed into the bulk of the carrier air and vented from the hood to the sampling device (see below). Control, ambient (i.e. on-site background) bioaerosol concentrations were measured at a height of 1.8 m, at positions up- and downwind (5–10 m) of the compost windrows.

2.3. Bioaerosol sampling during process activity (active sampling)

For safety and practical reasons, it was not possible to use the portable wind tunnel used for sampling the static windrows during compost processing activities. Instead, bioaerosols were sampled (11th and 15th March 2004) at the closest safe and practical distance (10 m) downwind of various process activities. Mean wind speed (max and mean) and temperature (K) during sampling were recorded using a thermal anemometer (Testo 425). Three successive samples were taken over a 45 min sampling interval during turning. Samples were taken during the screening, turning ($\times 3$) and loading ($\times 2$) operations.

2.4. Sample collection and preservation

There are two principal methods of sampling bioaerosols: culture or non-culture based. Culture-based techniques include filtration and direct impact, either on Petri dishes or within all-glass impingers (AGI) (Eduard and Heederik, 1998). Non-culture-based methods involve the direct counting of cells through a microscope. Here, a culture-based filtration method (Wheeler et al., 2001; Herr et al., 2003) was selected because of its applicability to high concentrations at source. In both the active and passive cases above, bioaerosols were sampled using a medium flow, personal aerosol filter sampler (SKC Universal dust and vapour sampling pump). Turning samples were collected on 11 March 2004. The maximum recoded wind speed maximum was $3.92\,m\,s^{-1}$ (mean of $0.06\,m\,s^{-1}$). The average temperature was 11 °C and the sampling time 15 ± 1 min. Screening and loading samples were obtained on 14 March 2004. The maximum wind speed was $0.56\,m\,s^{-1}$ (mean of $0.56\,m\,s^{-1}$) during the screening sampling and $1.59\,m\,s^{-1}$ (mean $0.54\,m\,s^{-1}$) during loading. The temperature measured during screening was 16.3 °C and during loading (late pm) 19.3 °C with sampling times of 12 min (screening) and 7 min (loading; the time taken to load mature, screened compost onto a truck).

The pump was operated at $2.0\pm0.1\,l\,min^{-1}$ and fitted with SKC dust sampling Institute of Occupational Medicine (IOM) heads (25 mm) (Wheeler et al., 2001), loaded with mixed cellulose ester filters (25 mm × 0.8 μm pore size). Microorganisms were quantified using the CAMNEA-method (Collection of Airborne Microorganisms on Nuclepore filters, Estimation and Analysis) (Palmgren et al., 1986). The cellulose ester filters were placed inside a 30 ml vial containing 10 ml 0.05%v/v Tween-80 mixed with 0.1%w/w NaCl to prevent cell osmosis and stored within a cold box at <4 °C. On return to the laboratory, bioaerosols were re-suspended by agitating the filter, the filter casing and the amended Tween-80 solution together in the vial for about 2 min. The solution was then diluted in a common logarithm order and inoculated within 48 h on nutrient plates.

2.5. Bioaerosol enumeration

A. fumigatus and actinomycetes sampled during active processing operations and from static compost windrows were enumerated by visual inspection. Media preparation, inoculation, dilution and sterilisation were performed in accordance with BS 5763: Part 0:1996. For actinomycetes, two media were used and developed simultaneously:

(i) half strength nutrient agar (Oxoid); and
(ii) soil compost agar (a supernatant of 10%w/w of loam-based compost John Innes No. 1 compost in agar).

After preparation, both media were autoclaved (105 °C, 15 min), left to cool to below 47 °C and then treated with 1%v/v antifungal cycloheximide, dissolved in less than 2 ml of ethanol. For *A. fumigatus*, malt extract agar (Merck) was mixed with 0.01% w/w antibacterial chloramphenicol (Sigma, UK). Nutrient agar plates and soil compost agar plates were incubated at 44 °C. Malt extract agar plates were incubated at 37 °C, the optimum temperature for *A. fumigatus* (Swan et al., 2002). Colonies growing on both media were enumerated visually after 3–14 days. The 95% confidence interval of microorganisms dispersed in a solution was estimated using guidelines provided in the BS 5763 standard.

2.6. Constructing bioaerosol depletion curves

Estimating the depletion of bioaerosols with distance downwind of a facility requires prior air dispersion analysis of a bioaerosol flux. An estimation of the bioaerosol emission flux and construction of a depletion curve for static compost windrows is provided in Taha et al. (2005). We were interested in the role that compost pile geometry and compost load may have on passive source depletion, and therefore constructed depletion curves for typical facility sizes using the emission flux parameters reported in Taha et al. (2005). For illustrative purposes, an *A. fumigatus* emission flux from the top surface of the pile of 8.8×10^3 cfu $m^{-2} s^{-1}$ was employed (Taha et al., 2004), with the data generated by SCREEN3 representing the maximum concentration based on full meteorology conditions (all stabilities and wind speeds). The height of the windrow is critical in determining bioaerosol depletion at 1.8 m (representing a typical human receptor height). Areas were modelled as plan views of width and length according to a trapezoidal compost pile geometry (Fig. 2). Depletion curves were constructed for compost windrows of 2 tonnes (1.5 m height), 5 tonnes (1.5 m height), 10 tonnes (2 m height), 100 tonnes (2 m height) and 200 tonnes (2 m height). For the 2 m high pile of 100 and 200 tonnes , pile lengths were adjusted to 24 from 16 m to maintain the same volume.

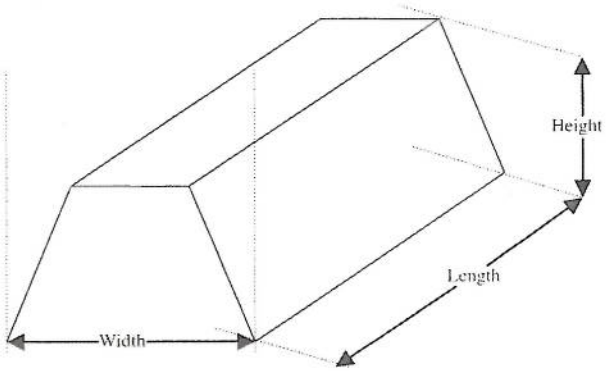


Fig. 2. Trapezoidal geometries of compost windrows for construction of passive source depletion curves.

From the active source term study, compost turning proved to be the principal contributor to bioaerosol generation (Fig. 3). Agitation was therefore selected as the on-site process for which depletion curves (× 3) were to be constructed. Here, the approach of Dowd et al. (2000) was adopted, in which field analysis data was first used to back-calculate a flux rate at source using an airborne transport model (there is no safe method of measuring the rate of release during agitation directly at 0 m). Candidate emission rates were then tested as inputs to SCREEN3 together with the measured mean temperature (284.16 K), wind speed and height of sampling. The candidate emission rates were subsequently plotted (Fig. 3) against bioaerosol concentrations generated by the model at 10 m. Emission rates at source for actinomycetes and *A. fumigatus* were then interpolated for volume and point source assumptions from the bioaerosol concentrations determined in this study (Fig. 3). Comparisons revealed that a higher emission rate was required by a volume—compared to a point source for an identical concentration. Dowd et al. (2000) previous employed a point source as a more appropriate type of source for this type of study and this was adopted here using a release rate in cfu s^{-1}.

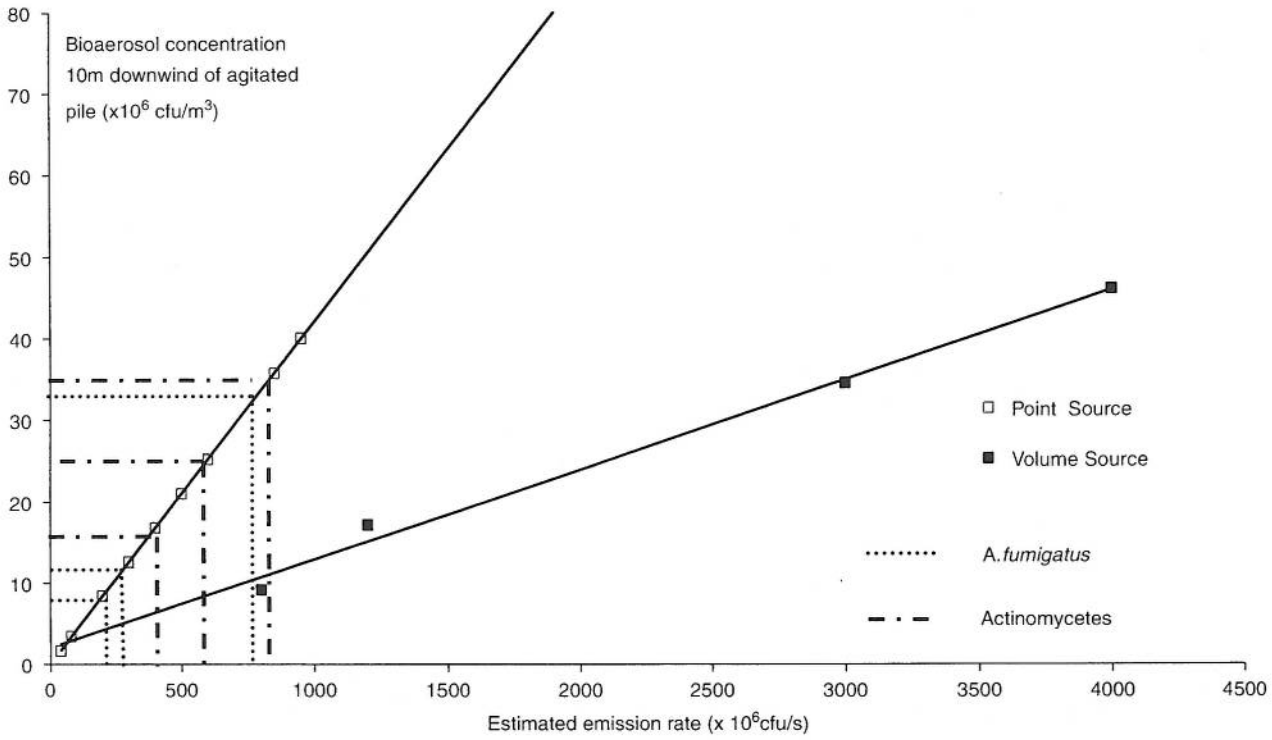


Fig. 3. Back-extrapolation of emission rates for agitation activities for two type of emission mode.

Having made these sets of assumptions for the passive and active studies, depletion curves were then constructed for compost turning (× 3) and for static compost windrows of different geometries and compost load. For air dispersion analysis, SCREEN3 (USEPA, 1995a) was employed. The dispersion model requires parameterisation for the dimensions of the emission source and the emission velocity or rate. In order to determine these, the size of the bioaerosol release created by agitation was observed and the dimensions estimated. The 'internal stack' diameter for the point source was assumed to be 3 m and the dimensions for the volume source were 3 m × 3 m × 3 m. As the material was disturbed from the base of the compost pile during turning, the release height was set to 0 m (Dowd et al., 2000).

Several simplifying and limiting assumptions are made in performing the modelling: (a) the particles displayed a Gaussian distribution in both lateral (crosswind) and vertical directions; (b) no gravitational deposition is assumed; (c) the source was assumed to be continuous; (d) the wind velocity and direction were constant over the modelled time and distance; (e) the modelled surface was relatively flat; (f) the gravitational settling of particles was assumed to be negligible; (g) the particle and wind velocity were assumed to be the same; and (h) microbial inactivation was not considered. The results must be viewed in the light of these substantial simplifications and methodological constraints.

3. Results and discussion

Bioaerosol concentrations measured 10 m downwind from various processing activities are presented in Fig. 4 with error limits. For source depletion, passive source depletion curves for compost windrows of varying load and geometry are presented in Fig. 5. Back-extrapolation of field data (Fig. 3) provided emission rates for *A. Fumigatus* and actinomycetes during agitation (Table 1), from which depletion curves (× 3) were constructed (Fig. 6). To our knowledge, these are the first 'at source' estimates of this kind for compost process operations, though we recognise these figures are conservative and artificially elevated on account of the modelling assumptions discussed above.

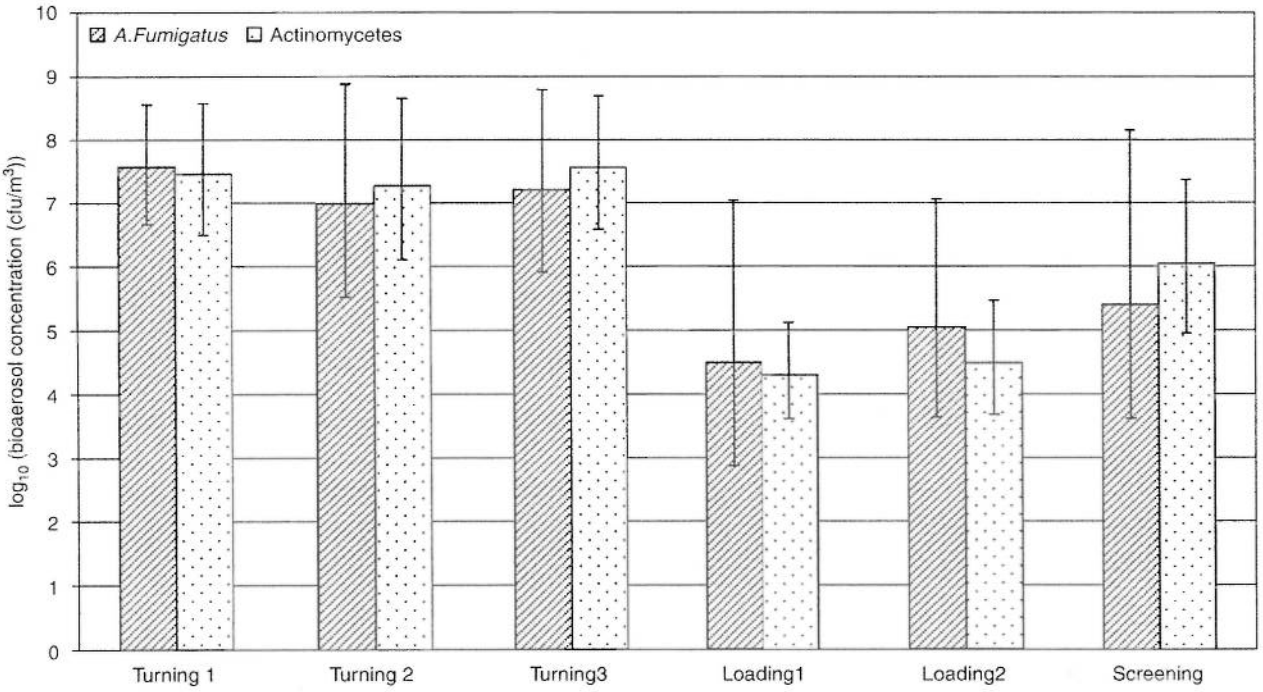


Fig. 4. Histogram of *A. fumigatus* and actinomycetes bioaerosol concentrations measured at 10 m distance from various compost processing activities.

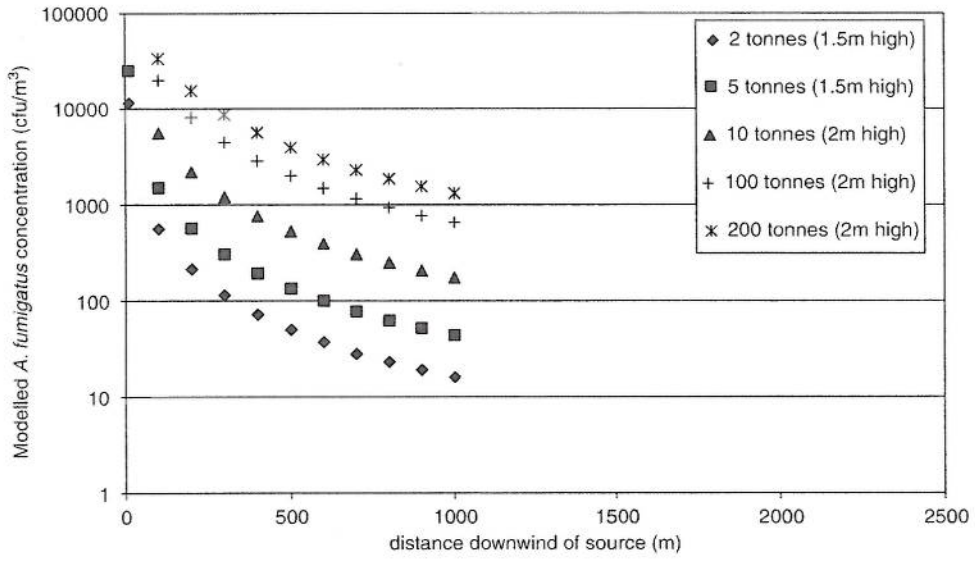


Fig. 5. Modelled source depletion curves for static compost windrows of varying geometry and load.

3.1. Bioaerosol concentrations

We have reported net *A. fumigatus* concentrations in air (passive) sourced directly from static compost windrows of 19 and 28×10^3 cfu m^{-3} and modelled concentrations 10 m from compost windrows of 61 and 102×10^3 cfu m^{-3} (Taha et al., 2005). The increase of bioaerosols levels immediately downwind of an actively agitated compost pile is reported elsewhere and known to dissipate to background

Table 1
Estimated emission rate extrapolated from Fig. 2 for agitated compost windrows

Sample	*A. Fumigatus*		Actinomycetes	
	Concn. at 10 m ($\times 10^6$ cfu m^{-3})	Emission rate at source ($\times 10^6$ cfu s^{-1})	Concn. at 10 m ($\times 10^6$ cfu m^{-3})	Emission rate at source ($\times 10^6$ cfu s^{-1})
Upwind (control)	0.01	—	0.02	—
Downwind (control)	0.02	—	0.01	—
Turning-1	36.80	890.0	28.20	700.0
Turning-2	9.80	240.0	18.90	480.0
Turning-3	15.90	395.0	36.00	860.0
Loading-1	0.03	0.7	0.02	0.5
Loading-2	0.01	0.2	0.03	0.7
Screening	0.25	5.9	1.10	26.1

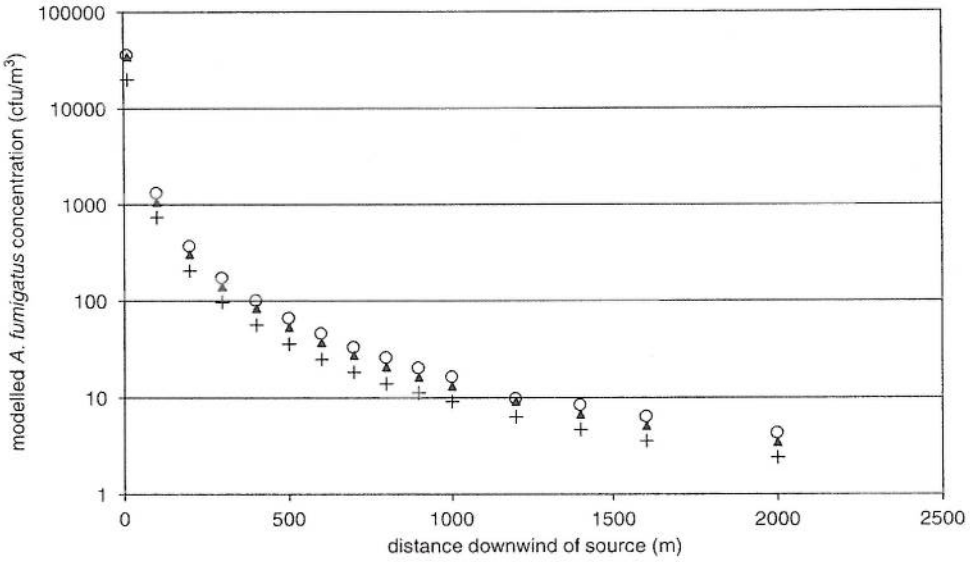


Fig. 6. Modelled source depletion curves for three series of modelled *A. Fumigatus* downwind of agitated compost windrows.

levels about 15 min after the agitation ceases (Millner et al., 1980). Kothary et al. (1984) reported a concentration range for *A. fumigatus* of 2–4 $\times$ 10^3 cfu m^{-3} close to the compost pile, with concentrations declining to less than 50 cfu m^{-3} at a distance of 250 m from the site. Similarly, Danneberg et al. (1997) reported concentration of 2×10^3 cfu m^{-3} for *A. fumigatus* near the source. Background concentrations are difficult to determine on account of the many ambient sources of bioaerosols. In our studies, we are frequently unable to detect *A. fumigatus* upgradient and away from the composting source. Others report *A. fumigatus* background concentrations of 10^3 cfu m^{-3} (Wheeler et al., 2001) and 42-1.6 (mean 79) $\times$ 10^3 cfu m^{-3} (Swan et al., 2002).

In contrast, bioaerosol concentrations measured 10 m adjacent to active processing operations are typically in the order of 10^7 cfu m^{-3} (for turning operations; Table 1; Fig. 4), 3-log higher that for passive release, confirming that mitigation should focus on minimising releases during compost turning. The concentrations measured here are more comparable with those recorded by Fischer et al. (2000) of 32×10^6 cfu m^{-3} for *A. fumigatus*. One must be cautious making strict comparisons between studies, locations and operations, however. Our *A. Fumigatus* concentrations vary by 1-log between the three agitation activities, for example. These variations are typical, the difference due to issues such as sampling technique (Eduard and

Heederik, 1998; Wheeler et al., 2001), wind conditions, properties of the compost windrows (such as pile age and moisture content), and between-turn variations in the method used during agitation (Sanches-Monedero and Stentiford, 2003).

In general, however, the recorded concentrations in this study are within the broad range reported by Wheeler et al. (2001), who cites that during shredding, turning and screening, fungi and bacterial counts are typically in the range of 10^3–10^7 cfu m^{-3}. Sanches-Monedero and Stentiford (2003) suggest that the concentration of bioaerosols released at composting facilities during normal operation are generally 10^2 higher than background levels.

One complication is that many studies only report figures for fungi and total bacteria, which makes direct comparisons difficult. For example, Weber et al. (1993) reported a range of 1–500 $\times$ 10^6 cfu m^{-3} and 0.6–800 $\times$ 10^6 cfu m^{-3} for fungi and total bacteria, respectively. Herr et al. (2003) report concentrations of total moulds of 1.3 $\times$ 10^5 cfu m^{-3} at 200 m downwind of a composting site. Clearly, as illustrated by our study, the distance should always be taken into account when analysing results from different studies, and the discrepancies highlight the need for guidance on bioaerosol sampling and monitoring. This said, a 3-log difference between passive and active bioaerosol concentrations measured at source is an important finding for regulators and risk analysts.

3.2. Depletion curves

Source depletion curves for *A. fumigatus* are provided in Figs. 5 and 6. These represent modelled curves based on emission flux from an authentic site. Our interest is in the extent of depletion with distance by reference to the current regulatory 'trigger' distance of 250 m, used as a distance below which regulatory risk assessments are being required in England and Wales. For the static windrows of varying geometries (Fig. 5) higher tonnage compost piles produce higher emissions that take longer to reduce to background concentrations when modelled using SCREEN3. The initial bioaerosol concentrations that approach 10^5 cfu m^{-3} (Fig. 5) warrant discussion. For static samples, these are a combined feature of the direct sampling method employed and the initial rise in modelled concentrations noted above. These concentrations are generally in excess of those measured close to the source by others and may represent a 'first flush', though this has not been substantiated in this study. For the active sampling initial results (Fig. 6), use of personal aerosol filter samplers is known to provide bioaerosol estimates up to 10 $\times$ those sampled using Anderson samplers (Wheeler et al., 2001; Taha et al., 2005). Stetzenbach et al. (2004) suggest this is because high impact samplers reduce the viability of bioaerosols captured directly onto agar gel. In this study, we have also sampled much closer to agitation activities (ca. 10 m distance from agitation operations) than in studies previously been reported (typically 50–250 m), in an attempt to gather authentic source term data for subsequent risk assessment.

All tonnages represented in Fig. 5 reduce steadily with distance from the source. By 250 m downwind, the three lowest tonnage piles have reduced to background concentrations (10^3 cfu m^{-3}). The highest tonnage pile does not reach this level within the 1000 m distance modelled; hence there are implications here for very large-scale facilities where 'trigger' distances might be revised. However this single study is insufficient evidence alone for this and at authentic sites, rather than modelled ones, it will be important to consider the combined releases from multiple compost piles rather than those from a single surface. Nevertheless, these results do show the importance of considering the amount of compost processed and the pile height when requiring and undertaking a risk assessment.

For the turning operations in Fig. 6, modelling was extended to 2000 m from the source term and undertaken in triplicate. Depletion to background concentrations of 10^3 cfu m^{-3} (Wheeler et al., 2001) of the bioaerosols released during turning occurs rapidly with distance from this facility (ca. 100 m). Here, the data appear to corroborate use of a generalised 'trigger' distance of 250 m as a conservative limit, below which, quantitative bioaerosol risk estimates are required for compost facilities in close proximity to housing (Environment Agency, 2001). For the site in this study and the data presented here, *A. fumigatus* concentrations released during turning operations appear to have depleted significantly by this distance to background concentrations. Again, this is only part of the story, as the source term contributions from the static piles on site are not aggregated with the episodic releases during turning, so again an incomplete picture is presented. Current work is resolving both combined effects and aggregation.

4. Conclusions

We have presented data demonstrating the ability to measure the concentration of bioaerosols emitted 'at source' during agitation activities. From these results, we have estimated the emission flux of bioaerosols from compost processing activities. We conclude that:

- Our methodology, developed in earlier studies (Taha et al., 2005) forms the basis for estimating specific bioaerosol emission rates from other activities, including shredding, screening, turning, vehicle movement, and waste loading and unloading.
- Agitation activities result in releases of bioaerosols in the order of 2–3 log higher than from static compost windrows.
- These data, and the bioaerosol characteristics that they help to illustrate, are important for environmental risk assessments that support the licensing of larger composting plants in sensitive locations.
- Improving bioaerosol risk assessments further needs to focus on better representation of microbiological processes in the air column (clumping, inactivation), combined source terms as single facilities and improved background data.
- Importantly, for risk-based regulation, data on dose–response curves for bioaerosols is urgently required to inform judgements on risk characterisation (risk significance).
- Future work will focus on improving the measurement and analysis of bioaerosols during compost processing and the integration of bioaerosol characteristics into improved dispersion analysis.

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Estimating fugitive bioaerosol releases from static compost windrows: Feasibility of a portable wind tunnel approach

M.P.M. Taha [a], S.J.T. Pollard [a,*], U. Sarkar [b], P. Longhurst [a]

[a] *Integrated Waste Management Centre, School of Industrial and Manufacturing Science, Cranfield University, Cranfield, UK*
[b] *Department of Chemical Engineering, Jadavpur University, Calcutta, India*

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Abstract

An assessment of the fugitive release of bioaerosols from static compost piles was conducted at a green waste composting facility in South East England; this representing the initial stage of a programme of research into the influence of process parameters on bioaerosol emission flux. Wind tunnel experiments conducted on the surface of static windrows generated specific bioaerosol emission rates ($SBER_2$s) at ground level of between 13 and 22×10^3 cfu/m^2/s for mesophilic actinomycetes and between 8 and 11×10^3 cfu/m^2/s for *Aspergillus fumigatus*. Air dispersion modelling of these emissions using the SCREEN3 air dispersion model in area source term mode was used to generate source depletion curves downwind of the facility for comparative purposes.
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1. Introduction

The operation of composting facilities in the vicinity of residential and public places has generated concerns over the potential impacts these facilities may pose to public health. Fugitive dusts emitted during waste decomposition releases a variety of bioaerosols (Fischer et al., 1999). In addition, the shredding of waste and the agitation and turning of compost during processing results in significant episodic releases to air. Bioaerosol particles are airborne organisms or biological agents that may act as toxicants. They include allergens such as bacteria, fungi, actinomycetes, arthropods, protozoa as well as microbial products such as endotoxin, microbial enzymes, β-1,3-glucans and mycotoxins (Millner et al., 1994). As a result of public health concerns and a need for operators to demonstrate the safe and responsible operation of these facilities, environmental regulators are now requesting risk assessments of operators prior to licensing composting plants. The estimation of bioaerosol exposures to downwind receptors is becoming important for large scale facilities sited in sensitive environmental settings close to the public.

Understanding the baseline emission of bioaerosols at source, and the factors and process variables that influence their generation and off-site dispersal is critical to meaningful risk assessment. Bioaerosol emission rate and dispersal are influenced by a large number of factors, including the materials being composted, the on-site processes involved, the associated vehicle movements, the process equipment used, individual bioaerosol properties and the geographical, topographical and meteorological conditions on- and off-site. This is a complex set of variables, and here we set out to understand one aspect alone; the baseline fugitive emissions and the influence of composting processing variables on bioaerosol flux at source.

This paper presents the initial results of a study on estimating fugitive emissions at source. We use a portable wind tunnel to capture bioaerosols directly above

* Corresponding author. Tel.: +44 1234 754 101; fax: +44 1234 751 671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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compost windrows in the absence of turning. The data generated provides a baseline assessment of fugitive emissions and has been used as input to an air dispersion model (SCREEN3) for assessing potential dispersal off-site under static conditions. Subsequent work will examine the influence of process variables on episodic bioaerosol flux from a range of on-site unit processes.

2. Materials and methods

The experimental and methodological rationale is summarised in Fig. 1. Bioaerosol flux measurements were conducted at a civic amenity green waste, open windrow composting facility in the SE of England where waste unloading, shredding, turning activities were concurrent. Fugitive emission rates were estimated from wind tunnel experiments and used to generate hypothetical source depletion curves at distance from the facility.

2.1. Wind tunnel measurements and control

A portable wind tunnel (Fig. 2) was located on top of compost windrows to allow the measurement of bioaerosol emission flux under static conditions. The fugitive dust emitted from the surface area was sampled within the horizontal air stream of the wind tunnel at a known velocity (ca. 3 m/s) across the surface (Table 1). In the tunnel, incoming air is filtered by activated carbon and blown into the inlet duct with a fan. A convective mass transfer takes place above the emitting surface and bioaerosols are then mixed into the bulk of the carrier air and vented from the hood. The base of the wind tunnel was embedded ca. 25 mm inside the surface of the pile to ensure no loss of air volume around the sides. Samples were taken from the hood outlet and the airflow velocity measured using a hot wire anemometer (Kestral 3000). Three compost pile locations were selected on the basis of access and suitability (the availability of power supply and of a flat surface). Ambient (i.e., on-site background) air bioaerosol concentrations were measured at 1.8 m height close to the compost windrow, downwind of the pile. A filled filter cassette was exposed without air pumping as a field blank.

2.2. Bioaerosol sampling

Bioaerosols were sampled using a medium flow personal aerosol filter sampler (SKC Universal dust and vapour sampling pump). Pumps were operated at 2.0 ± 0.1 l/min and fitted with SKC dust sampling IOM heads (25 mm) loaded with mixed cellulose ester filters (25 mm $\times$ 0.8 μm pore size). Sampling took place for ca. 30 min. As a control, a sample was taken directly from the outlet of activated carbon filter to measure the quality of the cleaned the inlet air supply. Microorganisms were quantified by using CAMNEA-method (Collection of airborne microorganisms on Nuclepore filters, Estimation and Analysis; Palmgren et al., 1986). After sampling, filters were placed inside a 30 ml vial containing 10 ml 0.05% v/v Tween-80 mixed with 0.1% w/w NaCl to prevent cell osmosis. On return to the laboratory, bioaerosols were re-suspended and cultured on to nutrient plates.

2.3. Bioaerosol enumeration

Aspergillus fumigatus (average size of 2–50 μm) and mesophilic actinomycetes (average size of 1 μm) were enumerated by visual inspection. Media preparation, inoculation, dilution and sterilisation were performed in accordance with BS 5763: Part 0. For mesophilic actinomycetes, two media were used and developed simultaneously: (i) half strength nutrient agar (Oxoid); and (ii) soil compost agar (a supernatant of 10% w/w of loam-based compost John Innes No. 1 compost in agar). After

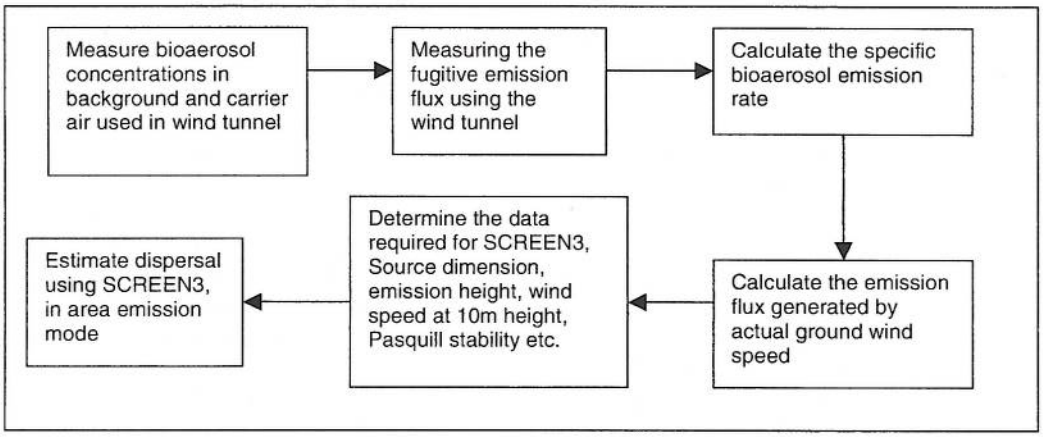


Fig. 1. Rationale and steps in measuring the emission flux and dispersal of bioaerosols.

Table 2
Estimated bioaerosol dispersal downwind of facility using SCREEN3

Wind tunnel and bioaerosols	Wind speed at 1.8 m (m/s)	Wind speed at 10 m	Pasquill stability	Concentrations estimated by SCREEN3 at various distances (m) from compost windrow $\times 10^3$ cfu/m^3 (1 h average)								
				1 m	10 m	30 m	50 m	100 m	200	250	500	1000
1 (Af)	1	1.33	A–B (1)	57.8	61.3	66.3	39.5	9.3	2.2	1.4	0.3	0.05
1 (Ac)				91.3	96.7	104.7	62.3	14.8	3.7	2.2	0.5	0.07
3 (Af)	0.8	1.06	A–B (1)	97.1	102.9	111.3	66.2	15.5	3.7	2.4	0.5	0.09
3 (Ac)				189.8	201.2	217.5	129.5	30.4	7.3	4.6	0.8	0.18

Wheeler et al. (2001) has suggested that the best available estimates for threshold limit values (background) for gram-negative bacteria, total bacteria and fungi in air are 300, 1000 and 1000 cfu/m^3, respectively, though the scientific consensus is limited. Some bioaerosol risk assessments have used low (5000 cfu/m^3), medium (10 000 cfu/m^3) and high (30 000 cfu/m^3) estimates of bioaerosol concentrations at proposed or existing facilities to represent source data for onward dispersion modelling. In this context, the ambient air concentrations of *A. fumigatus* (77 000 cfu/m^3) and mesophilic actinomycetes (10 300 cfu/m^3) measured in this study are high. Net fugitive bioaerosol data (Table 1) for windrow samples 1 and 3 samples in the wind tunnel outlet are of a similar order of magnitude, though lower than this ambient sample for *A. fumigatus* and higher for actinomycetes. In practice, large variations are associated with ambient bioaerosol monitoring data; for example on previous occasions at this facility, ambient *A. fumigatus* concentrations of 120×10^3 cfu/m^3 and 22×10^3 cfu/m^3 (cf. 77×10^3cfu/m^3) have been measured using an identical filter sampler technique. A further issue relates to the observation (Wheeler et al., 2001) that bioaerosol data collected using Anderson samplers frequently report an order of magnitude less than those collected using filter samplers. Irrespective, it is clear from our study that there are contributions to the site bioaerosol load beyond fugitive emissions from static windrows, as one would expect.

For the wind tunnel bioaerosol data, activated carbon influent air is demonstrably 'cleaned' by comparison with the ambient background sample, these data suggesting adsorption efficiencies of 99% and 92% w/w for *A. fumigatus* and actinomycetes, respectively. For the outlet data, fair agreement is demonstrated between locations 1 and 2 (Table 1) (with location 2 providing a greater flux for both determinands) suggesting less variability for consecutive wind tunnel experiments on material from a common source. Transformation of the concentration data provide fugitive specific bioaerosol emission rates ($SBER_2$s) at ground level of between 13 and 22×10^3 cfu/m^2/s for mesophilic actinomycetes and between 8 and 11×10^3 cfu/m^2/s for *A. fumigatus*. These rates are used as the area source emission input data for the air dispersion modelling of these emissions using the SCREEN3 air dispersion model to generate source depletion curves downwind of the facility for comparative purposes (Table 2).

The modelled *A. fumigatus* source depletion curves for these data using the area source term emission rates generated in wind tunnel experiments are shown in Fig. 3, alongside the literature data acquired by environmental sampling at distance from composting facilities (Fig. 4; wind tunnel data removed). Fig. 3 mixes modelled and monitored data and studies from a range of facilities. These studies are not directly comparable and used for illustrative purposes alone. Two observations are worthy of merit however, notwithstanding the additional difficulties and artificial nature of using Gaussian distribution models for bioaerosol dispersion. Comparing Figs. 3 and 4, one notices the rapid depletion of bioaerosol concentrations from source in both monitored and modelled data. Further, source depletion to proposed background values of 1000 cfu/m^3 typically occurs between 250 and 500 m from source in the wind tunnel data and typically within 250 m for the monitoring studies. We propose that the data generated by our

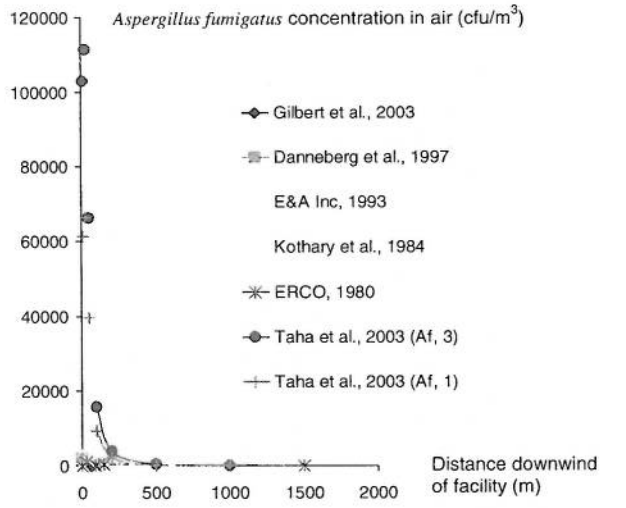


Fig. 3. Source depletion curves (cfu/m^3) for *Aspergillus fumigatus* from selected monitoring studies (Millner et al., 1994) alongside modelled data using fugitive emission rates generated in wind tunnel experiments.

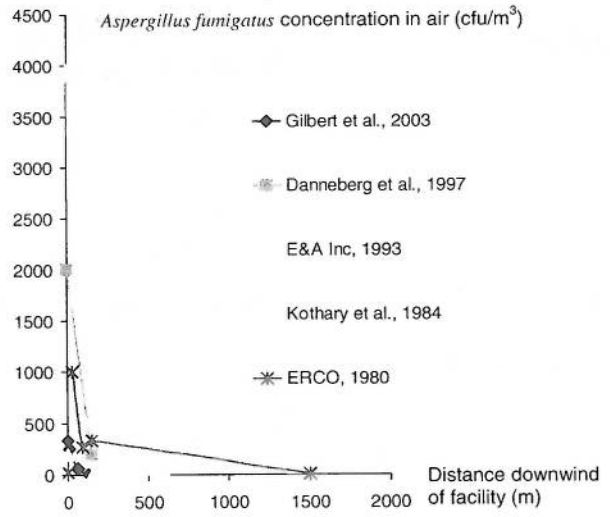


Fig. 4. Source depletion curves for *Aspergillus fumigatus* (cfu/m^3) from selected monitoring studies (Millner et al., 1994) (wind tunnel data removed; note scale).

study are generally consistent with the literature data. For example, for *A. fumigatus* and mesophilic actinomycetes, Sanches-Monedero and Stentiford (2003) have recently reported that at up to 40 m from composting sites the concentrations of these bioaerosols are between 3.8×10^3 and 98×10^3 cfu/m^3 and between 23×10^3 and 110×10^3 cfu/m^3, respectively.

4. Conclusions

We have presented initial data from a wind tunnel experiment demonstrating the ability to measure the fugitive emission flux of bioaerosols from static windrows. We conclude:

- wind tunnels can be used to measure the emission flux of fugitive bioaerosol that are aerosolized by wind energy;
- the emission fluxes estimated can be used within the SCREEN3 air dispersal model for estimating bioaerosol concentrations downwind of composting facilities;
- these data and the bioaerosol characteristics they help illustrate are important for environmental risk assessment that support the licensing of larger composting plants in sensitive locations;
- our methodology forms the basis for estimating specific bioaerosol emission rates from other activities, including shredding, screening, turning, vehicles movement, loading and waste unloading;
- future work will focus on improving the measurement and analysis of bioaerosols during compost processing.

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Improving bioaerosol exposure assessments of composting facilities — Comparative modelling of emissions from different compost ages and processing activities

M.P.M. Taha[a], G.H. Drew[a], A. Tamer[a], G. Hewings[b], G.M. Jordinson[c], P.J. Longhurst[a], S.J.T Pollard[a,*]

[a]*Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK*
[b]*Cardiff School of Engineering, The Research Office, Queen's Building, P.O. Box 925, Cardiff CF24 0YF, UK*
[c]*Environment Agency, Evenlode House, Howbery Park, Wallingford, Oxfordshire OX10 8BD, UK*

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Abstract

We present bioaerosol source term concentrations from passive and active composting sources and compare emissions from green waste compost aged 1, 2, 4, 6, 8, 12 and 16 weeks. Results reveal that the age of compost has little effect on the bioaerosol concentrations emitted for passive windrow sources. However emissions from turning compost during the early stages may be higher than during the later stages of the composting process. The bioaerosol emissions from passive sources were in the range of 10^3–10^4 cfu m^{-3}, with releases from active sources typically 1-log higher. We propose improvements to current risk assessment methodologies by examining emission rates and the differences between two air dispersion models for the prediction of downwind bioaerosol concentrations at off-site points of exposure. The SCREEN3 model provides a more precautionary estimate of the source depletion curves of bioaerosol emissions in comparison to ADMS 3.3. The results from both models predict that bioaerosol concentrations decrease to below typical background concentrations before 250 m, the distance at which the regulator in England and Wales may require a risk assessment to be completed.
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Keywords: Bioaerosols; Compost; Dispersion modelling; Emission rate; Exposure

1. Introduction

1.1. Background

Composting is reliant on the presence of various microorganisms, such as fungi and bacteria, which may become airborne and pose a risk to human health (Douwes et al., 2003). In response to perceived public health concerns, the Environment Agency of England and Wales (the environmental regulator) requires a risk assessment for licensed composting facilities that have a sensitive receptor within 250 m of their boundaries (Environment Agency, 2001). This must examine, among other hazards, the dispersal of airborne microorganisms or bioaerosols from the site (Wheeler et al., 2001;

*Corresponding author. Tel.: +44 1234 754101; fax: +44 1234 751671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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Environment Agency, 2002; Pollard et al., 2006). In this context, sensitive receptors may include a residence, school or office building. The aim of the risk assessment is to inform risk management. However, the quality of the risk assessment is dependant on the availability and quality of the bioaerosol source term data employed (Pollard et al., 2006). This data is frequently limited, in part because of the practical difficulties of microbiological analyses, but also due to cost constraints.

There is a growing body of research that examines the concentrations of bioaerosols in and around composting facilities (e.g. Danneberg et al., 1997; Swan et al., 2002; Sanches-Monedero and Stentiford, 2003; Taha et al., 2005, 2006). Many studies that attempt to predict the dispersal of bioaerosols from facilities use simple methods (e.g. Millner et al., 1980, Lighthart and Mohr, 1987; Swan et al., 2003; ADAS/SWICEB, 2005) and so are not able to take into account the full range of atmospheric and local conditions that could affect bioaerosol dispersion. Air dispersion models were developed to predict dispersion of pollutants, such as the nitrogen oxides, based on emissions and meteorological inputs, and have successfully been used for assessing odour dispersion from industry (e.g. Environment Agency, 2002). However, the use of these models for bioaerosol dispersion has been limited, as dispersion models may not be able to fully take into account the mechanisms of release of bacteria and fungi.

According to McCartney (1994), environmental factors such as wind speed, turbulence, humidity and water availability will influence when spores are released. Although these parameters are taken into account by dispersion models when predicting downwind concentrations, there are very few 'at source' measurements of bioaerosol concentrations that link these parameters to the concentrations measured. Furthermore, certain characteristics of bioaerosols complicate the use of dispersion models; in particular, their ability to form aggregates or clumps once released and the loss of viability that may occur as they are emitted from the compost windrow (Wheeler et al., 2001).

Our own research (Taha et al., 2004, 2005, 2006, 2007) focuses on improving the quality of regulatory risk assessments for composting by providing:

(i) accurate source term data at the point of release (Taha et al., 2006); and

(ii) developing new methods for improving sampling and enumeration of bioaerosols (Taha et al., 2007).

Here, we propose further improvements by presenting the refinement of air dispersion modelling for the prediction of downwind bioaerosol concentrations at off-site points of exposure.

1.2. Study rationale

We present results from measuring on site and predicting the dispersal of bioaerosols from a green waste composting research facility in southern Wales. The advantage of sampling at this facility was that the processes on site could be adjusted to aid the sampling activities; for example, timing of shredding and screening. The objectives of the study were (i) to characterise the source term bioaerosol emissions, taking into consideration storage properties, compost age and dispersal during agitation using a windrow turner, front-end loader, screener and shredder; and (ii) to compare the predicted downwind concentrations modelled by two separate dispersion models. We seek to improve bioaerosol exposure assessments by refining the methods currently used to estimate downwind dispersal of compost emissions.

In order to estimate the static pile emission flux rate and bioaerosol active dispersal emission rate during agitation, the single source Gaussian plume model SCREEN3 (USEPA, 1995) was used to initially estimate bioaerosol depletion curves (Taha, 2005). SCREEN3 is a screening-level model that adopts steady-state Gaussian plume algorithms and meteorological scenarios to estimate worst-case dispersal. This was followed by the application of advanced modelling using the ADMS 3.3 air dispersion model (Carruthers et al., 1994; CERC, 2003). ADMS is an advanced steady state, Gaussian-like dispersion model, capable of modelling continuous plumes, short duration releases and transport over complex terrain. The model simulates point, line, area and volume sources, and can estimate pollutant concentrations at a number of user defined receptors. The model has been shown to perform in a comparable manner to similar new generation models (Hanna et al., 2000). Using the model results, we infer the possible influences that bioaerosol properties such as inactivation and microbial agglomeration may have on the depletion curves (decrease in concentration with distance) produced by the models.

2. Material and methods

The study site is a research composting facility handling ca. 12000 m^3 of shredded green waste per annum in windrows under a 1500 m^2 building with open sides. Samples were taken from compost windrows (passive emissions) aged at 1, 2, 4, 6, 8, 12 and 16 weeks, and during agitation activities (active emissions) on site, such as turning, shredding and screening. For turning activities, measurement was conducted on 1, 4, 8 and 12 week old compost. Sampling was undertaken between January and March 2005.

2.1. Bioaerosol sampling

Direct sampling of bioaerosols from static compost windrows was undertaken using a portable wind tunnel (Jiang and Kaye, 2001; Taha et al., 2005, 2006) positioned on the compost windrows to allow the direct measurement of the bioaerosol flux. Incoming air, filtered through commercial granular activated carbon is blown into the inlet duct using a fan (Taha, 2005). Bioaerosols are mixed into the bulk of the carrier air and vented from the hood to the sampling device.

For safety and practical reasons, it was not possible to use the portable wind tunnel during compost processing. Instead, bioaerosols were sampled at the closest safe distance (5–10 m) downwind of various process activities. These distances are much closer to operations than in many other studies (e.g. ADAS/SWICEB, 2005). The airborne microorganisms were collected onto filter media using a medium flow pump followed by elution and plating. The flow rate was ca. 2 l min^{-1} and the filter media used was 0.8 mm polycarbonate. Mean wind speed (max and mean) and temperature (K) during sampling were recorded using a thermal anemometer (Testo 425). Three successive samples were taken over a 45 min sampling interval during turning. Samples were taken during green waste screening, compost turning, and compost loading operations.

Control (on-site background) bioaerosol concentrations were measured at a height of 1.8 m, at positions up- and downwind (5–30 m) of the compost windrows, using the method described above for active sampling. This method was also used to sample the air directly above the compost pile (0.3 m).

2.2. Sample collection and preservation

The methods used for sample collection and preservation are described in Taha et al. (2006). In both the active and passive release modes above, bioaerosols were sampled using a medium flow, personal aerosol filter sampler (SKC Universal dust and vapour sampling pump). The pump was operated at 2.0 ± 0.1 l min^{-1} and fitted with SKC dust sampling Institute of Occupational Medicine (IOM) heads (25 mm) (Wheeler et al., 2001), loaded with polycarbonate filters (25 mm × 0.8 μm pore size). Microorganisms were quantified using the collection of airborne microorganisms on nuclepore filters, estimation and analysis (CAMNEA) method (Palmgren et al., 1986). The filters were placed inside a 30 ml vial (Nalgene) containing 10 ml 0.05%v/v Tween-80 mixed with 0.1% w/w NaCl to prevent cell osmosis and stored within a cold box at <4 °C. On return to the laboratory, bioaerosols were re-suspended by agitating the filter, the filter casing and the amended Tween-80 solution together in the vial for ca. 2 min. The solution was diluted in a common logarithm order and inoculated within 48 h on agar plates to prevent sporulation of microorganisms leading to erroneous results.

2.3. Bioaerosol enumeration

Aspergillus fumigatus and actinomycetes sampled during active processing operations and from static compost windrows were enumerated by visual inspection. Media preparation, inoculation, dilution and sterilisation were performed in accordance with BS 5763: Part 0:1996. For actinomycetes, two media were used and developed simultaneously:

i. half strength nutrient agar (Oxoid); and
ii. soil compost agar (a supernatant of 10%w/w of loam-based compost John Innes No. 1 compost in agar).

Further details are reported in Taha et al. (2007). After preparation, both media were autoclaved (105 °C, 15 min), left to cool to below 47 °C and treated with 1% v/v antifungal cycloheximide, dissolved in less than 2 ml of ethanol. For *A. fumigatus*, malt extract agar (Merck) was mixed with 0.01% w/w antibacterial chloramphenicol (Sigma, UK). Nutrient agar plates and soil compost agar plates were incubated at 44 °C. Malt extract agar plates were incubated at 37 °C, the optimum

temperature for *A. fumigatus* (Swan et al., 2002). Colonies growing on both media were enumerated visually after 3–14 days. The 95% confidence interval of microorganisms dispersed in a solution was estimated using guidelines provided in the BS 5763 standard.

2.4. SCREEN3 depletion curves

Modelling the depletion of bioaerosols with distance downwind of a facility requires prior estimation of the bioaerosol flux. At any composting facility, the bioaerosol sources can be classified as either passive (the static windrows) or active (agitation activities such as turning or screening). As these sources display such different characteristics, they are modelled separately taking two separate approaches.

Firstly, the passive sources were standard sized windrows (80 m × 20 m) and were represented in the model as area sources. As there was no activity associated with these emissions, it was possible for the sampler to access the windrows directly. These were therefore modelled as direct source-sampled emissions.

For the active emissions, the health and safety of the sampler must be considered, so it is not always possible to sample at source. Samples were collected as close as possible to the activity. However this requires retro fitting of the down-wind micrometeorological sample to a dispersion curve, a technique that has been used to model odour emissions (Gostelow et al., 2003). This method has been tested for bioaerosols by Dowd et al. (2000) and Taha et al. (2006) and was considered appropriate given the limitations associated with sampling. As the active releases tend to occur at a specific location within the facility, they were represented as point sources in SCREEN3. The full model parameters used in these experiments are provided in Table 1.

Several simplifying and limiting assumptions are made in performing the modelling: (a) the particles displayed a Gaussian distribution in both lateral (crosswind) and vertical directions; (b) no gravitational deposition is assumed; (c) the source was assumed to be continuous; (d) the wind velocity and direction were constant over the modelled time and distance; (e) the modelled surface was relatively flat; (f) the effects of buildings were not taken into account; (g) the particle and wind velocity were assumed to be the same; and (h) microbial inactivation was not considered. In the light of these simplifications and methodological constraints, the results presented from the SCREEN3 model are considered to be initial estimates of downwind dispersion.

2.5. ADMS 3 depletion curves

The parameters and variables defined for the SCREEN3 modelling (Table 1) were used in ADMS 3.3, in order to provide a direct comparison between the two models. ADMS 3.3 was employed to address some of the simplifying assumptions used during SCREEN3 modelling. Several ADMS 3.3

Table 1
Model parameters used for the SCREEN3 modelling

Parameter	SCREEN3		ADMS	
	Active emissions	Passive emissions	Active emissions	Passive emissions
Source type	Point	Area	Point	Area
Source release height (m)	—	2	0	2
Source length (m)	—	80	—	80
Source width (m)	—	20	—	20
Receptor height (m)	1.8	1.8	1.8	1.8
Stack height (m)	3	—	3	—
Stack diameter (m)	3	—	3	—
Roughness length (m)	Rural	Rural	0.1	0.1
Stability class	D	D	D	D
Exit velocity (m)	0.2	—	0.2	0.3
Stack exit temperature	283 K	—	15 °C	15 °C
Buildings	No	No	No	No
Complex terrain	No	No	No	No

experiments were undertaken. The first replicated the SCREEN3 modelling, using the pre-defined stability classes and modelling each source separately. The second set of experiments modelled the sources as a group, producing a combined output for the facility as a whole. These experiments were repeated for both organisms measured (actinomycetes and *A. fumigatus*), and for the active and passive samples. The passive emission rates were modelled as area sources, to represent the windrows. As the active samples were taken at a point near the agitation activity, these were modelled as point sources.

3. Results and discussion

Bioaerosol concentrations measured using the wind tunnel and directly above the compost pile (passive emissions) are presented in Figs. 1 and 2. Background bioaerosol concentrations measured at the site boundary are shown in Table 2. Although measurements were taken upwind and downwind, *A. fumigatus* and actinomycetes were not detected. Bioaerosol concentrations and the estimated emission rates downwind from the various processing activities are presented in Table 3 and Fig. 3. The source depletion curves constructed for the passive emissions are presented in Fig. 4 (*A. fumigatus*) and Fig. 5 (actinomycetes). Similarly, the source depletion curves for the active emissions are shown in Figs. 6 and 7. The results of the combined sources modelling using ADMS 3.3 are presented in Figs. 8–11.

3.1. Bioaerosol concentrations (static emissions)

The concentration of *A. fumigatus* measured within the facility ranged between 10^3 and 10^4 cfu m^{-3} (Fig. 1). The concentration of actinomycetes was within a similar range, with a higher maximum concentration (10^3–10^5 cfu m^{-3}). The bioaerosol concentrations measured using the wind tunnel were generally less than the measured background concentrations, suggesting that the agitation activities contribute more to the overall emissions from this site.

The bioaerosol concentrations measured with the wind tunnel did not reveal a distinct trend as the compost aged (Fig. 1). It is not possible to state that emissions will increase or decrease as compost ages,

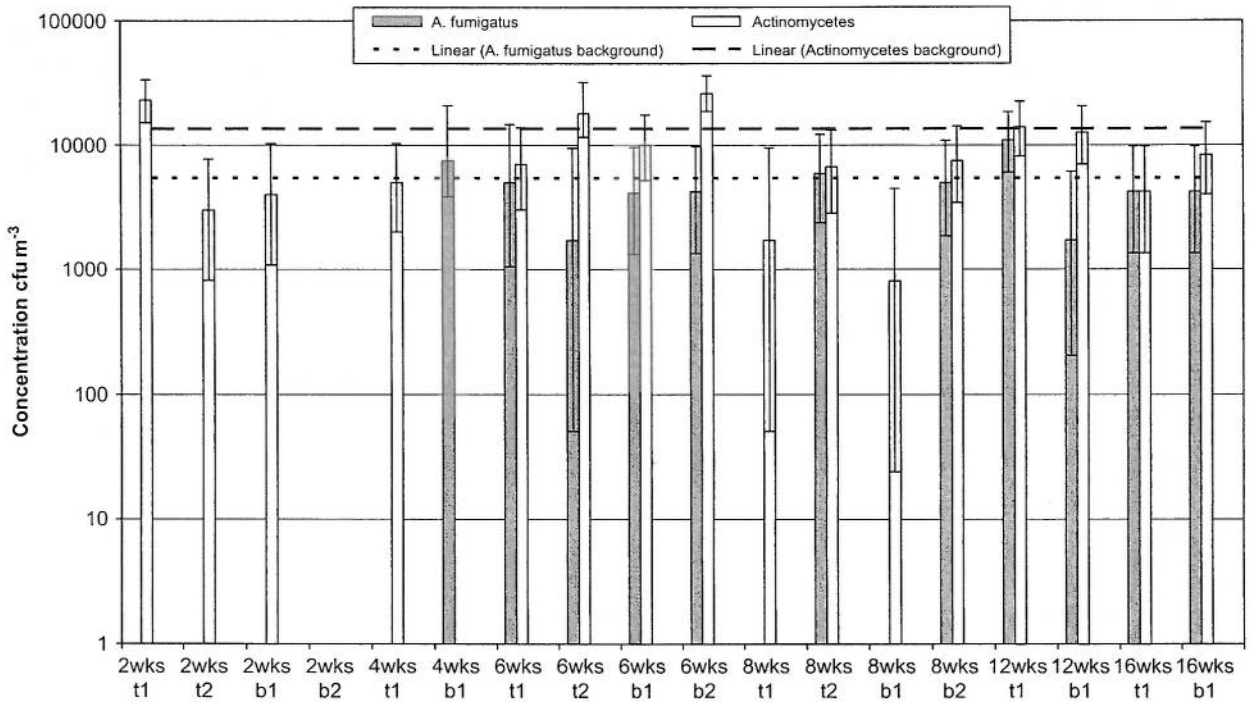


Fig. 1. The bioaerosols concentration measured in the mixing chamber of the wind tunnel during surface flux analysis (the errors bars show the confidence interval associated with each measurement).

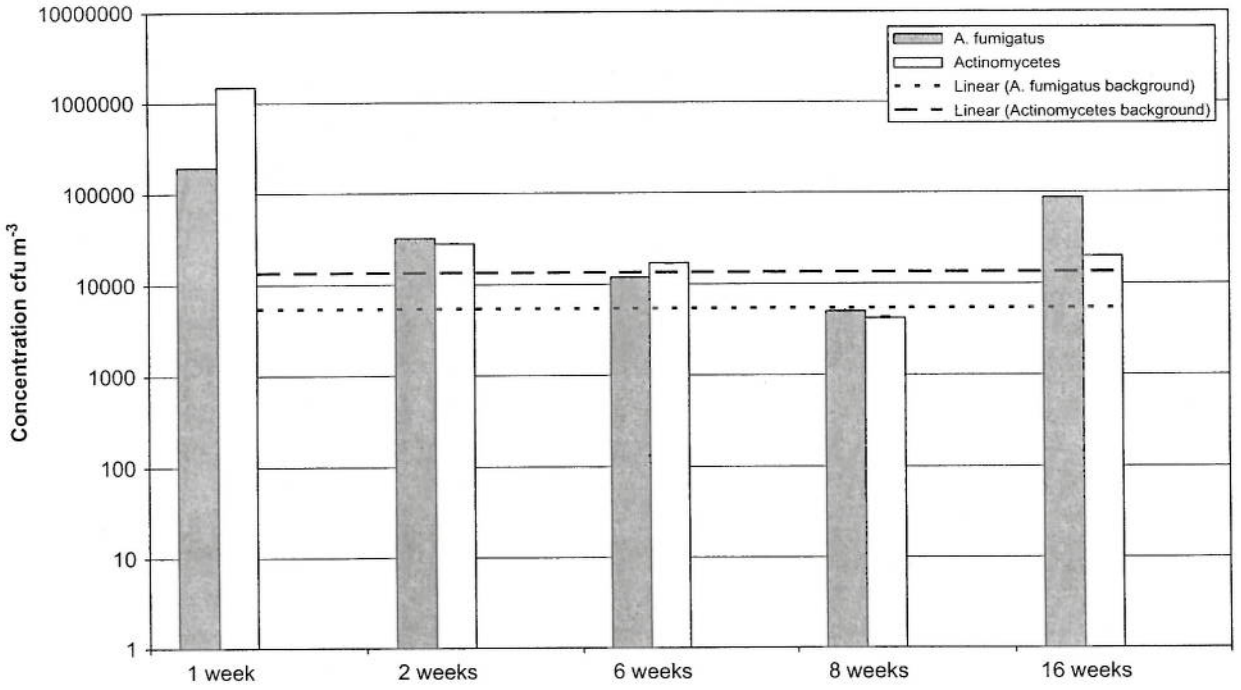


Fig. 2. Bioaerosols concentration measured in the air at about 300 mm from a surface of different compost pile ages (errors bars where visible show the confidence interval associated with each measurement).

Table 2
Background bioaerosol concentrations measured at the site

	Aspergillus fumigatus (cfu m^{-3})	Actinomycetes (cfu m^{-3})
Background January	2400	2500
Background February	7000	26,000
Background March	7000	12,000

based on these results. However, measurement in the air directly above the compost pile (0.3 m) presented higher bioaerosols concentrations at the early stage of composting, which reduced gradually until at 8 weeks. The emissions were less than measured background concentrations (Fig. 2). However, the concentration increased when the compost age was 16 weeks, which we believe may be due to different weather conditions or drying of the compost. These results indicated the presence of significant amounts of bioaerosols in the air close to the surface of the compost pile, under static conditions, in the early stages of composting. Wheeler et al. (2001) suggest threshold limit values for total fungi and total bacteria of 1000 cfu m^{-3}, although the dose–response relationships for these values are not established. These results show that on-site bioaerosol concentrations at source can exceed suggested threshold limit values.

The specific bioaerosol emission rates (SBERs) ranged from 100 to 1200 cfu $m^{-2} s^{-1}$ for all samples in which bioaerosols were detected. This range is lower by one log than the SBERs of 8000–22000 cfu $m^{-2} s^{-1}$ measured by Taha et al. (2006) at a full scale commercial facility. The contributing factor to this difference is the ambient wind velocity, as research has shown that higher wind velocities are required to release bioaerosols (McCartney, 1994; Tay et al., 2001). At this study site, the wind velocity average was 0.3 m s^{-1} due to the covered nature of the facility that reduces the wind velocity inside the facility boundaries.

3.2. Bioaerosol concentrations (dynamic emissions)

The dynamic release of bioaerosols was assessed by estimating the bioaerosol emission rate during different activities and for different compost ages. The activities studied here were shredding, turning and screening of the compost, similar to those

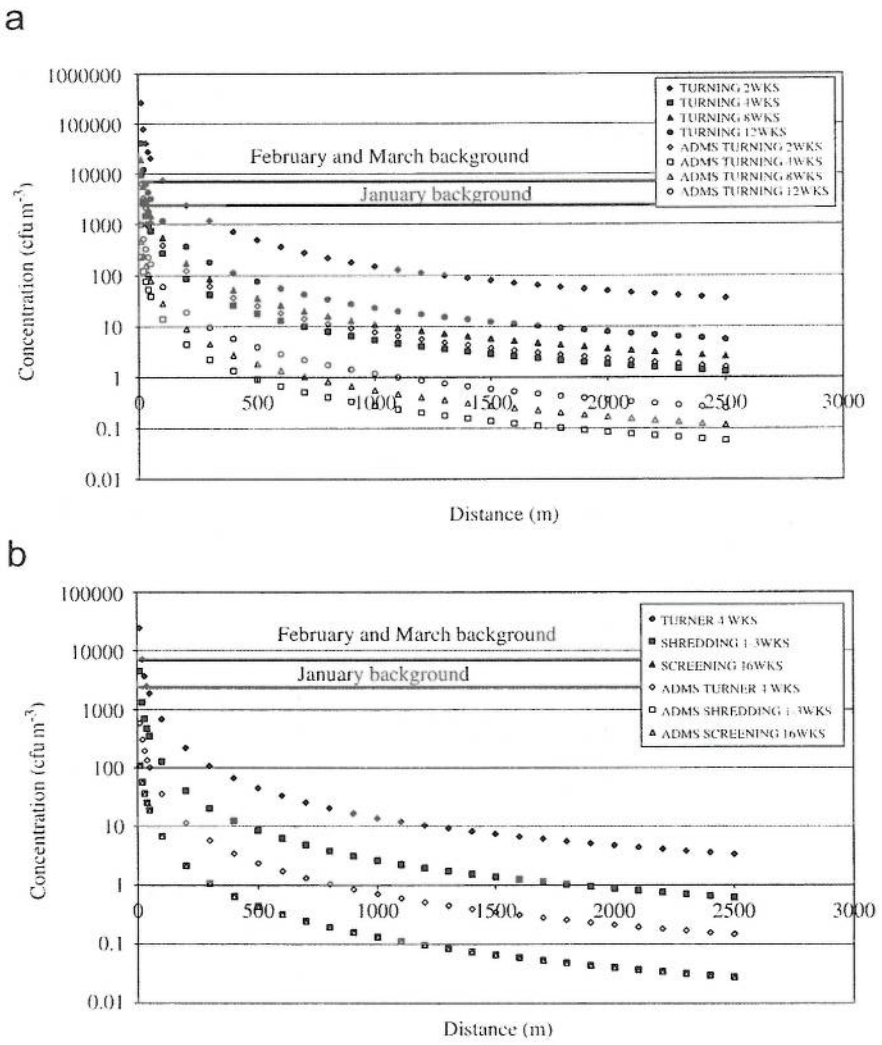


Fig. 6. (a) Source depletion curves of *Aspergillus fumigatus* from agitation activities (turning only) estimated using the SCREEN3 and ADMS dispersion models for stability class D (neutral conditions). The measured background levels are also shown. (b) Source depletion curves of *Aspergillus fumigatus* from agitation activities (specialised windrow turner, shredding and screening) estimated using the SCREEN3 and ADMS dispersion models for stability class D (neutral conditions). The measured background levels are also shown.

The results show that *A. fumigatus* emissions may differ depending on the age of the compost. During turning of 1 week old compost, the average *A. fumigatus* emission rate was 10^7 cfu s^{-1}, compared with an average of 10^5 cfu s^{-1} for the turning of compost age from 4 to 16 weeks. For actinomycetes, the average emission rates from turning of 1 and 4 week old compost were 6×10^6 and 1×10^6 cfu s^{-1}, respectively. The actinomycetes emission rates for 12 and 16 week old compost were 1-log lower than these rates. This is evidence that the stage of the composting process may influence the concentrations of bioaerosols released, as detected by the passive sampling described above. Emissions from shredding (1×10^5 and 8×10^4 cfu s^{-1}, for *A. fumigatus* and actinomycetes, respectively), and screening (1×10^5 cfu s^{-1} for both *A. fumigatus* and actinomycetes) tended to be slightly lower than from turning activities.

3.3. Depletion curves

The source depletion curves generated for the passive and active releases (Figs. 4–7) display a similar trend to analysis conducted by Taha et al. (2006). Wheeler et al. (2001) suggests that a

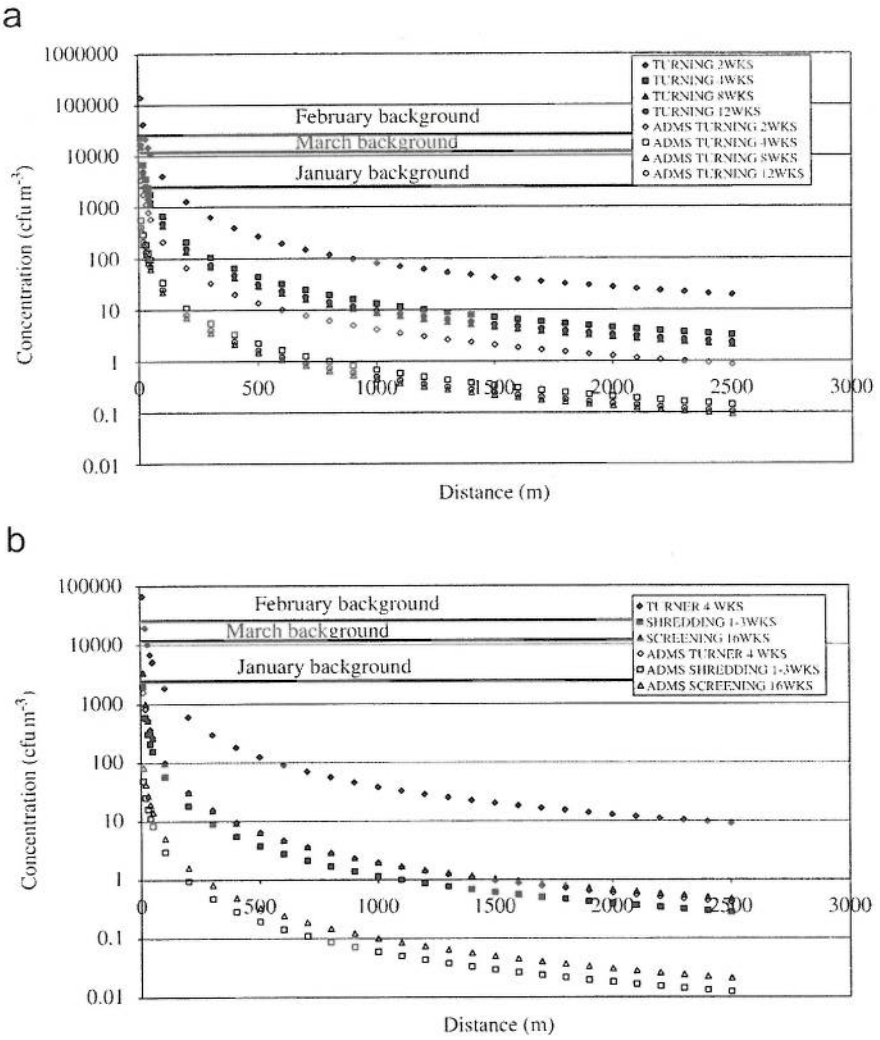


Fig. 7. (a) Source depletion curves of actinomycetes from agitation activities (turning only) estimated using the SCREEN3 and ADMS dispersion models for stability class D (neutral conditions). The measured background levels are also shown. (b) Source depletion curves of actinomycetes from agitation activities (specialised windrow turner, shredding and screening) estimated using the SCREEN3 and ADMS dispersion models for stability class D (neutral conditions). The measured background levels are also shown.

threshold limit value of 10^3 cfu m^{-3}. As no upwind concentrations could be detected, we sampled at the facility boundaries and these concentrations are shown in the figures for comparison. Ambient bioaerosol concentrations tend to vary greatly. For example, Haas et al. (1999) found a concentration of 494 cfu m^{-3} in an agricultural area and 18 cfu m^{-3} in a parking area. As the area surrounding the study area is predominantly rural, we have chosen to compare the samples with the concentration measured by Haas et al. (1999) in the agricultural area.

For the passive releases, the modelled concentration of *A. fumigatus* predicted using the SCREEN3 model from 12 week old compost shows the highest emissions and only reduces to below background (494 cfu m^{-3}) at a distance of approximately 400 m. For actinomycetes, the 12 week old compost again has the highest downwind concentrations and only reduces to below background by 600 m using the SCREEN3 model. However for both *A. fumigatus* and actinomycetes, the concentrations modelled using ADMS are predicted to be less than the background within 10 m from the source.

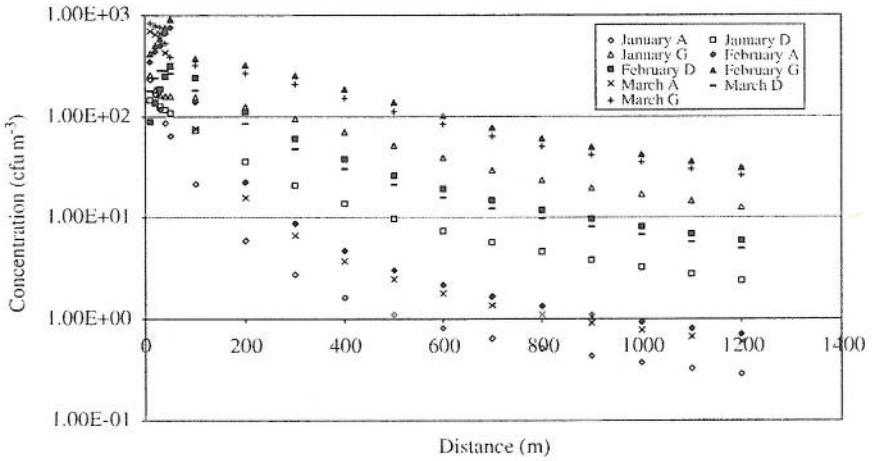


Fig. 8. Estimated depletion curves of *Aspergillus fumigatus* using the ADMS model for combined passive sources on three separate dates for three stability classes (A—very convective, D—neutral, and G—very stable).

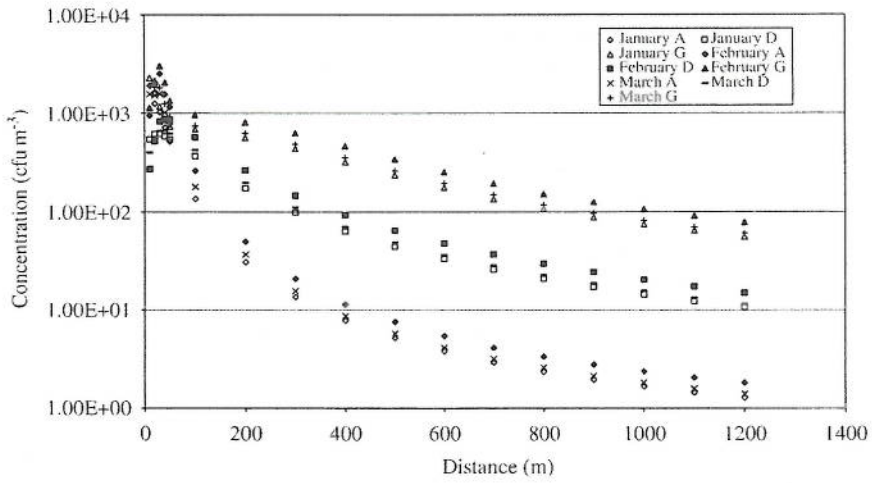


Fig. 9. Estimated depletion curves of actinomycetes using the ADMS model for combined passive sources on three separate dates for three stability classes (A—very convective, D—neutral, and G—very stable).

The agitation activities produce emissions of at least 1-log higher than the passive emissions. The SCREEN3 predictions show that most concentrations reduce to below background (494 cfu m^{-3}) by 200 m for *A. fumigatus* and actinomycetes, except for emissions from turning of 2 week old compost, which only reduces to below background by 500 m. The ADMS predictions suggest that the majority of emissions will have reduced to below background by 40 m, again apart from turning of 2 week old compost, which reduces to below background by 100 m.

The Environment Agency requires a risk assessment to be undertaken for any composting facility that has a sensitive receptor within 250 m of its boundary. The results presented here suggest that bioaerosol concentrations from both active and passive emissions reduce to below typical background levels before reaching the 250 m risk assessment requirement threshold, when modelled by the more advanced ADMS dispersion model.

Analysis of the figures reveals the differences between the two dispersion models. SCREEN3 is designed for scoping studies and therefore has a tendency to over-state concentrations, taking a more precautionary approach in its estimation than the advanced ADMS dispersion model. This is most likely due to the inclusion of an alternative mixing height algorithm (Brode, 1991), which uses the maximum of a predetermined mixing height or a

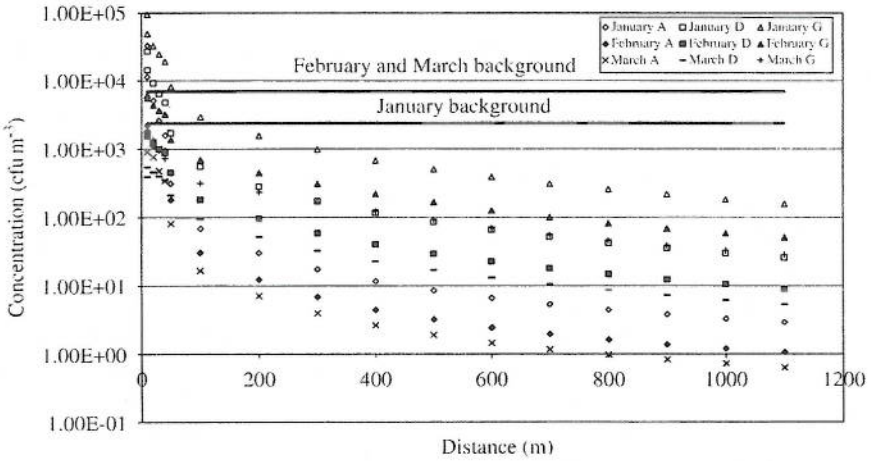


Fig. 10. Estimated depletion curves of *Aspergillus fumigatus* using the ADMS model for combined active and passive sources on three separate dates for three stability classes (A—very convective, D—neutral, and G—very stable). The measured background levels are also shown.

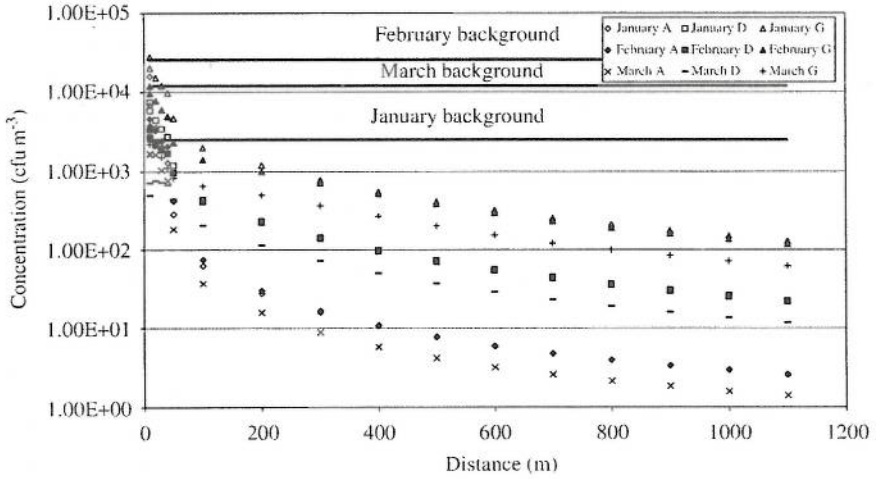


Fig. 11. Estimated depletion curves of actinomycetes using the ADMS model for combined active and passive sources on three separate dates for three stability classes (A—very convective, D—neutral, and G—very stable). The measured background levels are also shown.

value adjusted slightly higher than the plume height, based on stability class. The use of this alternative algorithm results in over-stated concentrations in comparison to those predicted by the USEPA's full Gaussian dispersion model, ISCST3 (USEPA, 1996). We therefore expect SCREEN3 results to be more precautionary when compared with another advanced Gaussian-like model such as ADMS 3.3, because SCREEN3 is designed to predict the worst case scenario.

ADMS predicts that the concentrations will decrease from 0 m, while SCREEN3 predicts an initial increase in concentrations for the passive emissions only, with the maximum concentration occurring at approximately 40 m from the source. This may be due to the different algorithms used when modelling different source types. The passive releases were modelled as area sources, to reflect the entire compost windrow, while the active releases were modelled as point sources, as by their nature these activities tend to occur at a single point within the facility. SCREEN3 takes into account the difference in temperature between the ambient air and the sampled air for point sources only, and uses this information to predict buoyancy effects for point sources (USEPA, 1995). This results in the initial increase in downwind concentrations seen for the point sources, but not for the area sources.

The ADMS dispersion model has the added capability of modelling more than one source. This provides a more realistic representation of dispersion from the facility, as each facility is likely to have several windrows of different ages on site at a single time, along with the possibility of at least one activity (shredding, screening or turning) occurring each day of operation. Figs. 8 (*A. fumigatus*) and 9 (actinomycetes) show the depletion curves predicted by ADMS for three different dates based on the combined passive sources sampled on that day. The concentration on all three days reduces to less than background (494 cfu m^{-3} as measured by Haas et al., 1999) before the 250 m Environment Agency threshold for risk assessments. For *A. fumigatus*, the maximum concentration is below the threshold limit value of 10^3 cfu m^{-3} suggested by Wheeler et al. (2001). The concentrations predicted are also not significantly higher than those for the single sources, which could be due to the spacing of the sources within the model's output grid.

Figs. 10 and 11 show the source depletion curves for the combined active and passive emissions for the three dates. The maximum concentrations are now within the range of 10^4–10^5 cfu m^{-3}, which shows that the active emissions are the main source of bioaerosols at these composting facilities. Despite these initial high concentrations, the depletion curves again show that concentrations reach the background levels measured by Haas et al. (1999) within the 250 m threshold for risk assessments. The exception is when modelling using stability class G (very stable) where concentrations may take up to 500 m to reduce below background levels.

4. Discussion

The source depletion curves presented by this study still have some caveats with them due to the clumping tendency of bioaerosol (physical decay) and deactivation (biological decay) caused by sunlight and heat. Although the clumping tendency of bioaerosols has been discussed in regard to their dispersion (e.g. Wheeler et al., 2001), there is little published research data to support any conclusions regarding this tendency, particularly in association with composting facilities. Previous literature suggests that fungal spores often form clumps when aerosolized (e.g. Lacey, 1991; Trunov et al., 2001), and that these clumps are within the respirable size (Karlsson and Malmberg, 1989). The same study found that clumping was more distinct for actinomycetes. Wider research has examined the tendency of bacteria and fungi to form clumps in media other than air, such as water and soil (Calleja et al., 1984).

Given the limited information regarding aggregation within air, we can only infer the possible characteristics that may be required for bioaerosols to form clumps, based on the existing literature. The literature suggests that random collision (Calleja et al., 1984) and faster air velocities (>0.3 cm s^{-1}) are needed to form aerobic clumps (Tay et al., 2001). The agitation activities that occur at composting facilities (e.g. shredding, turning and screening) produce sufficient air turbulence to result in random collisions of bioaerosols. Tay et al. (2001) also show that increasing temperatures are likely to increase clumping, suggesting that the high temperatures generated within compost windrows may encourage bioaerosol aggregation above piles, particularly during the more active stages of composting. However, further research is necessary to confirm this suggestion.

The mechanisms behind microbial clumping are linked with the physicochemical properties of the microbial cells such as surface hydrophobicity and charges on cell walls (Borrego et al., 2000; Dufrêne, 2000; Amanullah et al., 2001). Busch and Stumm (1968) reveal that, within the pH range of 5–9, bacteria have a net negative charge. The pH within composting piles is usually between 6 and 8.5, within this range. Clumps may, therefore, result from this negative charge attracting positively charged cell products. It is therefore important to begin taking the tendency of bioaerosols to form aggregations into account when predicting their dispersal. Current risk assessments are likely to be over-stating downwind concentrations as a result. Future work will aim to mimic clumping tendencies when using the advanced modelling functions in ADMS 3.3, such as the deposition options.

Bioaerosol viability also requires consideration because studies have shown that non-viable cell wall components, such as endotoxins, may cause adverse health effects (Castellan et al., 1987; Kennedy et al., 1987; Eduard et al., 1993, 2001; Lange et al., 2003). The actual fungal cells whether viable or not can prompt an allergenic response. Traditional monitoring methods capture air samples and then culture the viable bioaerosols from the sample. Some of these sampling methods (impaction and impingement) are known to impose significant stress on microorganisms (Lin et al., 2000) and Górny et al. (2002) show that a significant proportion of

bioaerosols released are considerably smaller than the spores released from surfaces contaminated with fungi. This might suggest that the non-viable components may be more numerous than the viable components, and that most published bioaerosol concentrations are underestimates of the true emissions. However, the practical difficulties associated with field sampling of bioaerosol components means that data to support this suggestion are not available. Given that dose–response relationships for bioaerosols are currently not well defined, it would appear prudent for the 250 m threshold to remain in place until further evidence is available regarding the dispersal of non-viable bioaerosol components.

Jones and Harrison (2004) show that meteorological factors (temperature, humidity and solar radiation) affect the dispersal of the airborne microorganisms, as well as their initial release. Elevated levels of fungi within buildings are also associated with higher temperatures and high humidity (Wan and Li, 1998). In addition, solar radiation has been shown to decrease the viability of bioaerosols (Ulevičius et al., 2000). It is generally accepted that composting windrows have a high humidity and high temperature, and are excellent environments for bioaerosols to proliferate. However, when considering their dispersal, little work has been done to examine the impact of the ambient environment on bioaerosol viability post-release, partly due to the complications involved in measuring non-viable bioaerosols in the field. Dust measurement and particle size ranges would have helped in supporting these results, and future work will aim to take this into account using field studies and by exploring the advanced options available in the ADMS 3.3 model.

5. Conclusions and future work

We have presented data demonstrating the ability to measure the concentration of bioaerosols emitted 'at source' during static conditions and for agitation activities, from compost of different ages. From these results, we have estimated the emission flux of bioaerosols from compost-processing activities, using a simple screening-level dispersion model and a more advanced new generation dispersion model. We have previously concluded that agitation activities result in releases of bioaerosols in the order of two to three log higher than from static compost windrows (Taha et al., 2006). The results presented here add further weight to this conclusion. In addition, we have shown that:

- the age of the compost has little effect on the concentration of bioaerosols emitted for passive windrow sources;
- emissions from turning compost during the early stages may be higher than during the later stages of the composting process;
- the simple screening-level model SCREEN3 takes a more precautionary approach and therefore provides a worst-case estimate of the source–depletion curves of viable bioaerosol emissions;
- the more advanced new generation model, ADMS 3.3 can be used to estimate bioaerosol dispersal from composting facilities;
- the source–depletion curves estimated by both models can still be considered as only preliminary estimates of bioaerosol dispersal, as both models are currently not able to take into account bioaerosol properties such as clumping and inactivation.

Future work will focus on improving measurement techniques for monitoring bioaerosol emissions, focussing on the clumping and inactivation properties. Further studies will be undertaken to examine the more advanced options within ADMS 3.3 in order to improve the dispersion modelling techniques. This research will further improve the science behind current bioaerosol risk assessment methodologies.

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Identifying source correlation parameters for hydrocarbon wastes using compound-specific isotope analysis

Rupert L. Hough [a], Martin Whittaker [b], Anthony E. Fallick [c], Tom Preston [c], John G. Farmer [b], Simon J.T. Pollard [a,*]

[a] *Integrated Waste Management Centre, Sustainable Systems Department, School of Industrial and Manufacturing Science, Cranfield University, Cranfield MK43 0AL, UK*
[b] *School of Geosciences, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK*
[c] *Scottish Universities Environmental Research Centre, East Kilbride, Glasgow G75 0QF, UK*

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Compound-specific isotope analysis (CSIA) is a promising method for identifying source correlation compounds in soils contaminated with heavy or weathered petroleum wastes.

Abstract

A preliminary evaluation of compound-specific isotope analysis (CSIA) as a novel, alternative method for identifying source correlation compounds in soils contaminated with residual heavy or weathered petroleum wastes is presented. Oil-contaminated soil microcosms were established using soil (sandy-loam, non-carbonaceous gley) amended with ballast-, crude- or No.6 fuel oil. Microcosms were periodically sampled over 256 days and $\delta^{13}C$ values (which express the ratio of ^{13}C to ^{12}C) determined at each time point for five *n*-alkanes and the isoprenoid norpristane using gas chromatography–isotope ratio mass spectrometry (GC-IRMS). Although some temporal variation was observed, no significant temporal shifts in the $\delta^{13}C$ values for the five *n*-alkanes were measured in all three oils. Isoprenoid isotope ratios ($\delta^{13}C$) appeared to be least affected by biotransformation, especially in the No.6 fuel oil. The research suggests that the $\delta^{13}C$ of isoprenoids such as norpristane, may be of use as source correlation parameters.
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1. Introduction

At sites featuring contamination of the soil environment by heavy oils or residual petroleum wastes, the vast complexity of the waste-soil-groundwater matrix and the hydrophobicity, inaccessibility and recalcitrance of individual waste components are such that resolution of these issues is fraught with uncertainties (Potter and Simmons, 1998; Pollard et al., 2004). Particular challenges that such sites present may be categorised into two broad themes; (i) analytical challenges associated with the chemical characterisation of these wastes (Pollard et al., 1994; Whittaker et al., 1996), and (ii) challenges associated with the assessment of biotransformation of heavy oil contaminants and their potential sources, particularly following prolonged weathering (Whittaker, 1996).

Fingerprinting of petroleum products in the environment is commonly undertaken to assess the source of a particular contamination event. It is commonly achieved through a qualitative comparison of mass chromatograms, but can also be achieved by quantifying the ratio of one biomarker to another. Fingerprinting is important for differentiating between potential contaminant sources and for establishing potential liability for a spillage; for example when contaminants migrate across boundaries of ownership (Douglas et al., 1992; Douglas and Uhler, 1993).

* Corresponding author. Tel.: +44 1234 754101; fax: +44 1234 751671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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Ratios of certain biomarkers, referred to as source correlation indices, are sensitive to the geological source of an oil, but remain consistent between related oils. Moreover, because of the environmental persistence of biomarker compounds, their values remain unaltered by oil weathering and biotransformation processes. The most commonly used source correlation indices are [pristane:phytane] and [17α(H),21β(H)-hopane: 17α(H),21β(H)-norhopane] (Whittaker et al., 1999). For heavy or residual petroleum contaminants, diagnostic fingerprinting creates uncertainties, especially because of the high degree of weathering experienced by the contaminants. Instead, diagnostic parameters that compare relative abundance of biomarker isomers and polyaromatic hydrocarbons (PAHs) in crude oils have been shown to be reliable source indices for marine spills (Douglas et al., 1992; Wang et al., 1994). However, there is little knowledge of the effectiveness of these indices for heavy oils in the contaminated soil, as opposed to the marine, environment.

Our own work, on the characterisation of heavy oils, has focused on improved analytical strategies and methods (Pollard et al., 1994; Whittaker et al., 1996, 1999; Pollard et al., 2004) for these problematic environmental matrices. Screening whole reference oils by stable carbon isotope fingerprinting without GC separation (Whittaker et al., 1996) demonstrated the utility of the technique for source term characterisation and highlighted the need for compound-specific studies. The advent of compound-specific isotope (CSIA) for assessing the isotopic signature of carbon in crude oils and crude oil fractions by gas chromatography-coupled isotope ratio mass spectroscopy (GC-IRMS) was first developed by Barrie et al. (1984). Since then, further technical examination and development of the method in crude oils and crude oil fractions has been undertaken (Reiley et al., 1991; Eakin et al., 1992; Merritt et al., 1994; Sessions et al., 2001). These refinements have elevated the characterisation of petroleum hydrocarbons to a level of sensitivity and detail unobtainable by conventional IRMS. CSIA yields data of the isotopic composition of a single compound relative to an international standard that are usually expressed as δ values in units of parts per thousand (‰). Because of this, CSIA is able to quantify isotopic composition and provide an additional (and often unique) means to (i) allocate and distinguish sources of organic compounds, and (ii) identify and quantify transformation reactions (Schmidt et al., 2004). CSIA is a continuous flow technique, which utilises the linking of a separation method (until now solely gas chromatography) via an on-line combustion/pyrolysis unit with a multicollector mass spectrometer. A review of CSIA principles and technical aspects has been published by Meier-Augenstein (1999).

CSIA has become a mainstay of petroleum geochemistry research, providing key information on the factors that influence the composition of oil components (Bjorøy et al., 1991; Sofer et al., 1991; Lichtfouse, 2000) and the determination of the source terms of oils and other organic matter (Mansuy et al., 1997; Rogers and Savard, 1999; Mazeas and Budzinski, 2002). In many cases, the CSIA of *n*-alkane and isoprenoid biomarkers has also provided a valuable set of correlation parameters for the identification of oil sources and depositional environments (Bowler et al., 1993) and the extent of biotransformation observed in crude oils (Killops and Killops, 1993). Chemical fingerprinting of the *n*-alkane fraction of crude oils and refined products in combination with isotopic characterisation of carbon in the individual homologues has been successfully used to allocate sources of sediment contamination and bird-feather oiling (Mansuy et al., 1997; Rogers and Savard, 1999; Mazeas and Budzinski, 2002).

In this paper, application of CSIA for the characterisation of heavy oil contaminants in soil is investigated. Source correlation index reliability was assessed according to the constancy of the $\delta^{13}C$ value during oil weathering. Indices that remain constant are useful as they allow the source of an oil to be determined (providing a sample of the fresh oil is available). Oil-amended soil microcosms were established and incubated at conditions optimum for oil biotransformation. An isotopic fingerprint of five *n*-alkanes and norpristane (phytane could not be sufficiently resolved in all samples) in oils at successive stages of microbial transformation was obtained. The aim of the study was to establish the utility of CSIA to determine source correlation parameters by assessing temporal variations in the isotopic fingerprint.

2. Materials and methods

2.1. Soil microcosms

Soil microcosms amended with one of three oils (Nigerian crude oil, ballast oil and No.6 fuel oil) were established in close accordance with British Standard 7755 (British Standards Institute, 1995). Microcosms were prepared in wide-necked, acid-washed 500-ml Erlenmeyer flasks. A total of 124 individual flasks were prepared: three oils sampled at nine different points in a time series, nine sterilised control flasks (one for each sampling point) and a total of 16 blank microcosm flasks. A sandy-loam (non-carbonaceous gley) soil (Table 1) which had not been used for agriculture for 8 years was sieved (<2.0 mm). Two hundred grams of soil and 4.0 g of oil (homogenised) were added to 108 flasks. Control microcosms were autoclaved (121 °C; 103.4 Pa) for 15 min and treated with a 1% w/w solution of mercuric chloride, $HgCl_2$, to suppress microbial activity (Chaineau et al., 1995). Blank microcosms containing no oil were prepared to assess contributions from soil organic matter (SOM). All microcosms were amended with a nutrient solution providing an equivalent molar C:N:P ratio of 100:8.75:1.75, believed optimum for oil biotransformation in soil (Chaineau et al., 1995; Heusemann, 1995).

Microcosms were arranged in a randomised block design and incubated at 30 °C for 256 days. Water content (weight) of microcosms was maintained to within ±5% with distilled de-ionised water. Control flask weight was maintained with $HgCl_2$ solution. Soil pH was monitored throughout the study. Sacrificial soil samples were taken at 0, 2, 4, 8, 16, 32, 64, 128 and 256 days. All samples were air dried under forced-draught in a fume cupboard prior to solvent extraction and analysis.

Solvent-extractable matter (SEM) was Soxhlet-extracted from soil subsamples (ca. 30 g) for 16 h using 150 ml HPLC-grade dichloromethane (DCM). DCM extracts were reduced overnight at ambient temperatures in a forced draught fume cupboard. Full experimental details of the column fractionation have been reported previously (Whittaker and Pollard, 1994). Component class fractionation was achieved using an adaptation of a classical chromatographic cleanup procedure (EPA Method 3611A, 1990). A Quick-Sep lateral reservoir flash chromatography apparatus was used to provide more rapid separation. The column (90 × 30 mm) was packed with neutral Aldrich STD grade alumina (80 mm, ca. 150 mesh, activated for 12 h at 130 °C), followed by anhydrous Na_2SO_4 (ca. 10 mm, dehydrated by heating at 400 °C for 4 h). The column was prepared by pouring equilibrated slurry of alumina stationary

Table 1
Chemical and physical properties of soil used in biotransformation study

Soil sampling details		Particle size analysis (% w/w)		Soil analysis	
Soil texture	Sandy clay loam	Clay (<0.002 mm)	21.5	pH (H_2O)	6.0
Sampling date	17 June 1995	Silt (0.002–0.063 mm)	21.2	Available P ($\mu g\ g^{-1}$)	10.0
Land use	Conservation beds in arboretum	Total sand (0.063–2.000 mm)	57.2	Available K ($\mu g\ g^{-1}$)	60.0
Sampling depth	0–26 cm	Very fine sand (0.063–0.250 mm)	16.0	CEC	13.1
Soil type	Non-calcareous gley	Fine sand (0.125–0.500 mm)	23.6	N ($mg\ g^{-1}$)	4.0
Previous agricultural use	None for 8 years	Medium sand (0.250–0.500 mm)	12.3	Field capacity moisture content (%)	38.7
		Coarse sand (0.500–1.000 mm)	4.7	Organic matter (%)	5.9
		Very coarse sand (1.000–2.000 mm)	0.7		

phase and *n*-pentane solvent down a glass rod into the chromatography apparatus. A piston air pump (Fisons, 50 W) was connected to the top of the column and the air pressure adjusted to produce a down-flow elution rate of ca. 20 ml min^{-1} (2% pump capacity). Component classes were obtained using an elution scheme reported by Pollard et al. (1992): 150 ml *n*-pentane (elution of saturates), 150 ml toluene (mono-, di- and polyaromatics), and 150 ml 50:50 dichloromethane/methanol mixture (polar compounds, highly polar aromatics, benzothiophenes and carbazoles). Further clean-up of the pentane fraction was performed using a method described by Rawluk (1991). Fractions were collected in pre-weighed acid-washed borosilicate flasks and reduced further under forced draught (ambient temperature).

2.2. Gas chromatography–isotope ratio mass spectrometry (GC-IRMS)

Solvent extracts were analysed in DCM solution at a concentration of ca. 10 $mg{\cdot}ml^{-1}$ using a VG ISOCHROM II GC-IRMS system. Individual compounds were isolated using an HP5890A gas chromatograph, equipped with a standard 30 × 0.00032 m i.d. neutral DB5 column (diphenyl/disiloxane (5%:95%) stationary phase) and a dedicated carbon isotope ratio mass spectrometer. Aliquots (2 μl) were injected in splitless mode. A linear temperature gradient was employed, the column temperature being held at 40 °C for 2 min following injection, ramped at 10 °C min^{-1} to 320 °C, then held at this temperature for a further 4 min. Injector and detector temperatures were set to 350 °C. Helium was used as a carrier gas at a flow rate of 7.5 ml min^{-1}. *n*-Alkane peaks were identified by comparing sample GC retention data with that obtained for a standard solution of five *n*-alkanes containing C_{15}, C_{20}, C_{25}, C_{30} and C_{40}. Conversion of oil class fraction subsamples to CO_2 for isotopic analysis was accomplished by dry combustion (850 °C; 6 h) in sealed, evacuated quartz tubes containing excess fired cupric oxide as an oxygen source. Isotope ratio data were obtained on a SIRA 10 isotope ratio mass spectrometer (VG Micromass 602D) and are reported relative to the international standard 'Vienna Pee Dee Belemnite' (VPDB; $^{13}C{:}^{12}C = 0.01118$ (Werner and Brand, 2001)) with corrections made for ^{17}O contributions. Isotope ratios are expressed in terms of $\delta^{13}C$ values (‰) calculated relative to the standard VPDB, according to the following relationship:

$$\delta^{13}C = \left(\frac{R_S}{R_R} - 1\right)1000 \quad (1)$$

where R_S is the ratio of ^{13}C to ^{12}C in the sample, and R_R is the ratio of ^{13}C to ^{12}C in the Vienna Pee Dee Belemnite standard (0.01118). The reproducibility of the individual isotopic measurements, determined through repeated analysis of a laboratory standard graphite sample, were $\pm -0.05‰$ (1σ); for each sample, the isotopic composition was determined in triplicate, with standard deviations generally less than ±0.3‰.

3. Results

3.1. Confirmation of oil biotransformation

A pre-requisite to investigating the performance of source correlation parameters was to verify that subject oils had undergone significant biotransformation over the 256-day microcosm study. This was verified by monitoring the bulk oil loadings and the changes in oil composition with time. It was confirmed that, for both ballast and crude oils, biotransformation reduced the amounts of oil in the microcosms by ~60% w/w (overall microbial degradation rate of 0.05 g kg^{-1} day^{-1}). Full details and results of these experiments have been reported elsewhere (Pollard et al., 1999).

3.2. Variation in solvent-extractable material (SEM)

Solvent-extractable material (SEM, $mg\ g^{-1}$ of air-dried soil) recovered from the treated and control soils was corrected for natural organic matter. Average recovery for the ballast oil-treated soils decreased most dramatically ($p < 0.05$), from a maximum of 14.54 ± 0.25 mg m^{-1} at $t = 0$ to 2.96 ± 0.54 mg g^{-1} after 256 days. Recoveries from the ballast oil control microcosms decreased much less sharply, from an initial 14.75 mg g^{-1} to 11.93 mg g^{-1} after 256 days. Average crude oil recoveries also decreased significantly ($p < 0.05$) over the course of the study, from 17.70 ± 0.44 mg g^{-1} to 6.47 ± 1.47 mg g^{-1}. Recoveries from the corresponding control microcosms were again much higher, decreasing from 17.96 mg g^{-1} to 16.94 mg g^{-1}. For the No.6 fuel oil microcosms, there was very little decrease in SEM over time (20.71 ± 0.90 mg g^{-1} to 19.85 ± 0.84 mg g^{-1} in the treated soils; 20.03 mg g^{-1} to 19.71 mg g^{-1} in the controls).

Using this information, the percentage loss of each oil due to abiotic and biotic processes at each sampling point was determined (Fig. 1). In the case of the ballast oil microcosms, abiotic weathering processes are significant in the early stages of the experiment, but this influence decreases over time. For the crude and No.6 fuel oil, abiotic weathering plays little role in the overall weathering process, apart from day 64 for the crude oil microcosms. Here, the role of abiotic weathering is highly significant ($p < 0.01$).

3.3. GC-IRMS analysis

Compound specific isotope analysis of microcosm extracts provided the $\delta^{13}C$ of the *n*-alkanes C_{14} (for ballast oil and crude oil only), C_{16} (for No.6 fuel oil only), C_{17}, C_{18}, C_{24} and C_{26}, and the isoprenoid alkane norpristane (iC_{18}) over the 256-day microcosm study. Mean isotope ratios, associated standard deviations and corresponding results from control

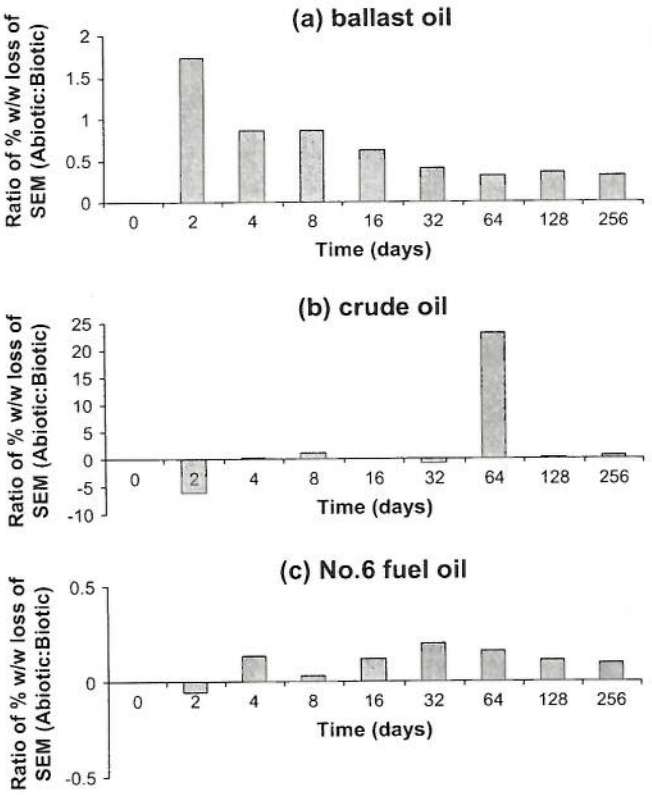


Fig. 1. Ratios of abiotic (control) to biotic (treated − control)% contributions to SEM variations for (a) ballast oil microcosms, (b) crude oil microcosms, (c) No.6 fuel oil microcosms.

microcosms for each compound at each sampling point for the ballast oil-, crude oil- and No.6 fuel oil-treated soils are provided in Tables 2, 3 and 4, respectively.

For ballast oil (Table 2), the $\delta^{13}C$ values for the *n*-alkanes did not, in general, vary according to any readily identifiable trend. The only obvious shift in isotopic composition was for C_{14}, which had a $\delta^{13}C$ of $-30.8 \pm 1.5‰$ after 2 days and $-28.4‰$ ($n = 1$) after 128 days (the compound was not detected at 256 days). Isotope ratios for C_{17}, C_{18}, C_{24}, C_{26} and norpristane did not vary by any significant amount from their initial values. The fluctuations in $\delta^{13}C$ for the compounds are shown in Fig. 2a. Similar results were obtained for the ballast oil control flasks with no significant variations in isotopic composition detected (Table 2).

For the crude oil extracts (Table 3), the isotopic composition of the five *n*-alkanes (C_{14}, C_{17}, C_{18}, C_{24}, C_{26}) and norpristane appeared to shift slightly in favour of the heavier C_{13} isotope and become less negative with increased oil weathering. However, a shift to more negative $\delta^{13}C$ values was observed at 64 days for all compounds (Fig. 2b). Overall, the shift was greatest for the C_{14}, C_{17}, C_{18}, C_{24} alkanes, which experienced statistically significant ($p < 0.05$) increases in $\delta^{13}C$ of between 1.5‰ and 2‰ over the 256 days. The isotope ratios of C_{26} and norpristane also increased with increased oil weathering, but the magnitude of the shift was not significant. Further, the $\delta^{13}C$ of these compounds could not be determined at 256 days, when the greatest isotopic shifts would have been expected.

For the No.6 fuel oil, the individual compounds within the extracts exhibited no significant shifts in $\delta^{13}C$ over the course of the study. All isotope ratios were found to lie between $-27.0‰$ and $-28.2‰$. A plot of compound $\delta^{13}C$ variation with time (Fig. 2c) indicates that the isotope ratios of the *n*-alkanes oscillated within the specified range over the course of the study. The isoprenoid $\delta^{13}C$ did not appear to undergo these fluctuations. The No.6 fuel oil microcosms, the isotope ratios of the *n*-alkanes and isoprenoid did not alter significantly over the course of the study.

4. Discussion

We sought to see whether significant changes in $\delta^{13}C$ occur during the weathering of heavy oil wastes. A previous study looking at the biotransformation of the same heavy oil wastes has reported significant losses in solvent extractable matter over time (Pollard et al., 1999). Significant changes in class fraction distribution were also reported. These changes demonstrated that significant biotransformation of the heavy oily wastes had occurred during the 256-day microcosm experiment. From an environmental forensics viewpoint, it is often necessary to allocate a contamination to a particular source in order to implement suitable risk reduction measures or to identify responsible parties in litigation (Morrison, 2000).

Results of the GC-IRMS analysis of ballast oil, crude oil and No.6 fuel oil extracts at successive stages of biotransformation (Tables 2–4) suggest that norpristane (the isoprenoid alkane biomarker) is isotopically heavier than in the *n*-alkanes in the fresh samples. This is in contrast to the results for pristane, which had previously been found to be isotopically lighter than *n*-alkanes in the same oils (Whittaker et al., 1996). A plausible explanation is the documented unpredictability of the nature of isotopic variations between these two compounds (Bjorøy et al., 1990, 1991; Sofer et al., 1991; Bowler et al., 1993).

For each oil, plots of the mean $\delta^{13}C$ variations of the five *n*-alkanes and norpristane over time (Fig. 2a–c) indicate that microbial degradation induces fluctuations in isotopic composition of these compounds, but generally the overall shifts in compound $\delta^{13}C$ over the 256 days were not substantial. For the ballast oil (Fig. 2a):

(i) The isotope ratios of the ballast oil *n*-alkanes and norpristane at 0 days of biotransformation were effectively the same (within ca. 0.5‰, the established reproducibility of the technique) as the values after 256 days of weathering, although for the *n*-alkanes some marked fluctuations in isotopic composition were observed.
(ii) The $\delta^{13}C$ of norpristane did not vary substantially during the study, experiencing less sizeable fluctuations in isotope ratio than the *n*-alkanes, and is therefore proposed as a possible oil diagnostic parameter.
(iii) All ballast oil compounds detected experienced a sharp decrease in $\delta^{13}C$ (1.0–1.5‰) over the first four days of

Table 2
Variation in isotopic composition of individual compounds in ballast oil-treated and control soils (‰)

Time	n1	n2	n3	Mean $\delta^{13}C$	SD	Control	Time	n1	n2	n3	Mean $\delta^{13}C$	SD	Control
C_{14}							C_{17}						
0	−29.16			−29.16			0	−29.23	−29.21	−29.84	−29.43	0.36	
2	−29.14	−32.05	−31.26	−30.82	1.50	−28.75	2	−29.84	−29.47	−30.27	−29.86	0.40	−29.65
4	−29.09		−28.83	−28.96	0.18	−28.98	4		−29.69	−29.83	−29.76	0.10	−29.69
8	−27.35			−27.35		−29.55	8		−29.46	−29.96	−29.71	0.35	−29.74
16	−29.26	−28.77		−29.02	0.35		16	−29.68	−29.59	−30.21	−29.83	0.34	
32		−28.37	−28.45	−28.41	0.06		32	−29.76	−29.32	−29.21	−29.43	0.29	
64							64						−30.04
128			−28.44	−28.44			128		−29.30	−30.01	−29.66	0.50	−30.15
256						−29.14	256	−30.14	−29.83	−29.30	−29.76	0.42	−29.14
C_{18}							C_{24}						
0	−29.02	−28.95	−29.23	−29.07	0.15		0	−29.13	−28.76	−29.49	−29.13	0.37	
2	−29.84	−29.59	−29.51	−29.65	0.17	−29.55	2	−29.98	−30.30	−29.97	−30.08	0.19	−28.82
4	−31.26	−29.69	−29.72	−30.22	0.90	−29.82	4	−32.49	−29.40	−29.30	−30.40	1.81	−29.21
8		−29.64	−29.99	−29.82	0.25	−29.72	8	−29.22		−29.37	−29.30	0.11	−29.42
16	−29.65	−29.54	−30.07	−29.75	0.28		16	−29.25	−28.86	−29.79	−29.30	0.47	
32	−29.74	−29.17	−29.17	−29.36	0.33		32	−29.51	−28.88	−28.64	−29.01	0.45	
64		−27.73		−27.73		−29.78	64			−28.87	−28.87		−29.11
128	−29.01	−29.98		−29.50	0.69	−29.96	128	−28.07	−29.43	−28.98	−28.83	0.69	−29.07
256	−29.92	−29.61	−29.08	−29.54	0.42	−29.28	256	−29.24	−29.35		−29.30	0.08	−28.7
C_{26}							Norpristane						
0	−29.37	−28.86	−29.17	−29.13	0.26		0	−29.01	−28.57		−28.79	0.31	
2	−30.00	−30.58	−30.51	−30.36	0.32	−28.92	2	−28.92	−28.65	−28.90	−28.82	0.15	−28.73
4	−30.60	−29.51	−29.49	−29.87	0.64	−28.96	4	−28.57	−28.68		−28.63	0.08	−28.96
8	−29.32			−29.32			8	−28.42	−28.39	−28.87	−28.56	0.27	−28.81
16	−29.52			−29.52			16	−28.57	−28.48	−29.10	−28.72	0.34	
32							32	−28.45	−27.89		−28.17	0.40	
64			−28.89	−28.89		−28.76	64			−28.44	−28.44		
128	−28.19	−29.35	−29.06	−28.87	0.60	−29.10	128		−28.48	−28.48	−28.48	0.00	−28.72
256	−28.97	−29.21		−29.09	0.17	−28.95	256	−29.21	−28.92		−29.07	0.21	−28.22

Table 3
Variation in isotopic composition of individual compounds in crude oil-treated and control soils (‰)

Time	n1	n2	n3	Mean $\delta^{13}C$	SD	Control	Time	n1	n2	n3	Mean $\delta^{13}C$	SD	Control
C_{14}							C_{17}						
0	−28.32	−28.57		−28.45	0.18			−28.35	−28.60		−28.48	0.18	
2	−27.96	−28.88		−28.42	0.65	−27.39	2	−28.29			−28.29		−27.35
4	−28.27	−28.58	−28.63	−28.49	0.20	−27.11	4	−27.94	−28.36	−28.36	−28.22	0.24	−27.44
8	−27.05	−27.56	−27.63	−27.41	0.32	−26.87	8		−27.18	−27.33	−27.26	0.11	−27.12
16	−27.21	−27.40	−27.79	−27.47	0.30		16	−27.26	−27.40	−27.45	−27.37	0.10	
32	−27.71	−28.20	−29.34	−28.42	0.84		32	−27.22	−28.04	−28.53	−27.93	0.66	
64	−29.72	−30.34	−31.04	−30.37	0.66		64	−29.92	−29.99	−30.58	−31.16	0.36	
128	−28.75	−29.07	−26.36	−28.06	1.48		128	−28.55	−29.10	−27.32	−28.32	0.91	
256		−27.27	−26.72	−27.00	0.39	−26.91	256	−27.05	−26.84	−26.48	−26.79	0.29	−27.08
C_{18}							C_{24}						
0	−28.46	−28.43		−28.45	0.02		0	−28.68	−28.25		−28.47	0.30	
2	−27.47	−28.27		−27.87	0.57	−27.08	2	−28.67	−28.88		−28.78	0.15	−27.32
4	−27.88	−28.08	−28.43	−28.13	0.28	−27.28	4	−28.15	−28.50	−29.33	−28.66	0.61	−27.57
8	−26.15	−27.12	−27.06	−26.78	0.54	−26.87	8	−27.11	−27.65	−27.41	−27.39	0.27	−26.96
16	−26.98	−27.55	−27.56	−27.36	0.33		16	−27.32	−27.73	−27.68	−27.58	0.22	
32	−27.05	−27.78	−28.38	−27.74	0.67		32	−27.73	−28.07	−28.90	−28.23	0.60	
64	−28.97	−29.93	−30.52	−29.81	0.78		64	−29.04	−29.90	−30.77	−29.90	0.87	
128	−28.11	−28.93	−27.03	−28.02	0.95		128	−28.45	−28.97	−26.85	−28.09	1.10	
256	−26.90	−26.54	−26.27	−26.57	0.32	−27.11	256		−26.78	−26.29	−26.54	0.35	−27.21
C_{26}							Norpristane						
0	−28.65	−28.74		−28.70	0.06		0	−27.80	−27.90		−27.85	0.07	
2	−29.53	−29.54		−29.54	0.01	−27.59	2	−28.13	−28.94		−28.54	0.57	−27.04
4	−28.62	−28.52	−30.02	−29.05	0.84	−27.65	4	−28.42	−28.63	−28.80	−28.62	0.19	−27.09
8	−27.82	−28.11	−27.83	−27.92	0.16	−27.49	8	−27.09	−27.73	−27.61	−27.48	0.34	−26.61
16	−27.69	−28.21	−28.00	−27.97	0.26		16	−27.41	−27.41	−27.92	−27.58	0.29	
32	−28.34	−28.41	−29.11	−28.62	0.43		32	−27.72	−28.21	−29.02	−28.32	0.66	
64	−29.29	−29.81	−30.19	−29.76	0.45		64	−29.92	−30.39	−31.27	−30.53	0.69	
128	−28.69	−29.06	−27.08	−28.28	1.05		128	−28.61		−26.46	−27.54	1.52	
256						−27.44	256						−27.24

Table 4
Variation in isotopic composition of individual compounds in No.6 fuel oil-treated and control soils (‰)

Time	n1	n2	n3	Mean $\delta^{13}C$	SD	Control	Time	n1	n2	n3	Mean $\delta^{13}C$	SD	Control
C_{16}							C_{17}						
0	−27.15	−27.25	−26.60	−27.00	0.35		0	−27.46	−26.30		−26.88	0.82	
2	−28.25		−27.29	−27.77	0.68		2	−28.17	−26.97	−27.51	−27.55	0.60	−28.37
4		−27.48		−27.48	0.00		4	−27.88	−27.67		−27.78	0.15	−27.68
8	−26.97	−27.14		−27.06	0.12	−27.39	8	−27.27	−27.45		−27.36	0.13	−27.59
16	−27.91	−27.92		−27.92	0.01		16		−27.99	−28.17	−28.08	0.13	
32	−26.89	−28.26		−27.58	0.97		32	−27.57	−27.89		−27.73	0.23	
64	−27.80	−28.47		−28.14	0.47		64	−28.07	−28.28		−28.18	0.15	
128	−27.04	−27.25	−27.13	−27.14	0.11		128	−27.32	−27.49	−27.54	−27.45	0.12	
256			−27.16	−27.16		−26.91	256		−28.31	−27.52	−27.92	0.56	−27.64
C_{18}							C_{24}						
0	−28.61	−27.33	−27.79	−27.91	0.50		0	−27.75	−27.38		−27.57	0.26	
2	−27.89	−26.89	−27.32	−27.37	0.50	−27.80	2		−27.24	−27.90	−27.57	0.47	
4	−27.07	−27.40		−27.24	0.23	−27.48	4	−28.19	−27.97		−28.08	0.16	
8	−27.05	−27.44		−27.25	0.28	−27.44	8		−27.61	−27.51	−27.56	0.07	−27.82
16	−27.97	−28.06		−28.02	0.06		16	−28.06	−28.13		−28.10	0.05	
32	−27.24	−27.84	−27.33	−27.47	0.32		32	−27.41	−27.85	−27.35	−27.54	0.27	
64	−28.06	−28.12		−28.09	0.04		64	−27.72	−27.85		−27.79	0.09	
128	−27.32	−27.93	−27.56	−27.60	0.31		128	−27.48	−27.75	−27.82	−27.68	0.18	
256		−28.31	−27.43	−27.87	0.62	−27.60	256			−27.60	−27.60		−27.37
C_{26}							Norpristane						
0	−27.74	−27.54		−27.64	0.14		0	−28.01	−27.35	−27.53	−27.63	0.34	
2		−27.28	−27.63	−27.46	0.25		2	−28.00	−26.97	−27.31	−27.43	0.52	
4		−27.83		−27.83			4	−27.41	−27.52		−27.47	0.08	
8	−27.51	−27.27		−27.39	0.17	−27.71	8	−27.06	−27.15		−27.11	0.06	−27.20
16	−28.24	−26.69		−27.47	1.10		16	−27.41	−27.65		−27.53	0.17	
32	−27.34	−28.11	−27.58	−27.68	0.39		32	−27.17	−27.53	−27.71	−27.47	0.27	
64	−27.76	−27.93		−27.85	0.12		64	−27.56	−27.38		−27.47	0.13	
128	−27.24	−27.65	−27.60	−27.50	0.22		128	−27.24	−27.26	−27.19	−27.23	0.04	
256			−27.73	−27.73		−27.53	256	−26.87		−27.12	−27.00	0.18	−26.96

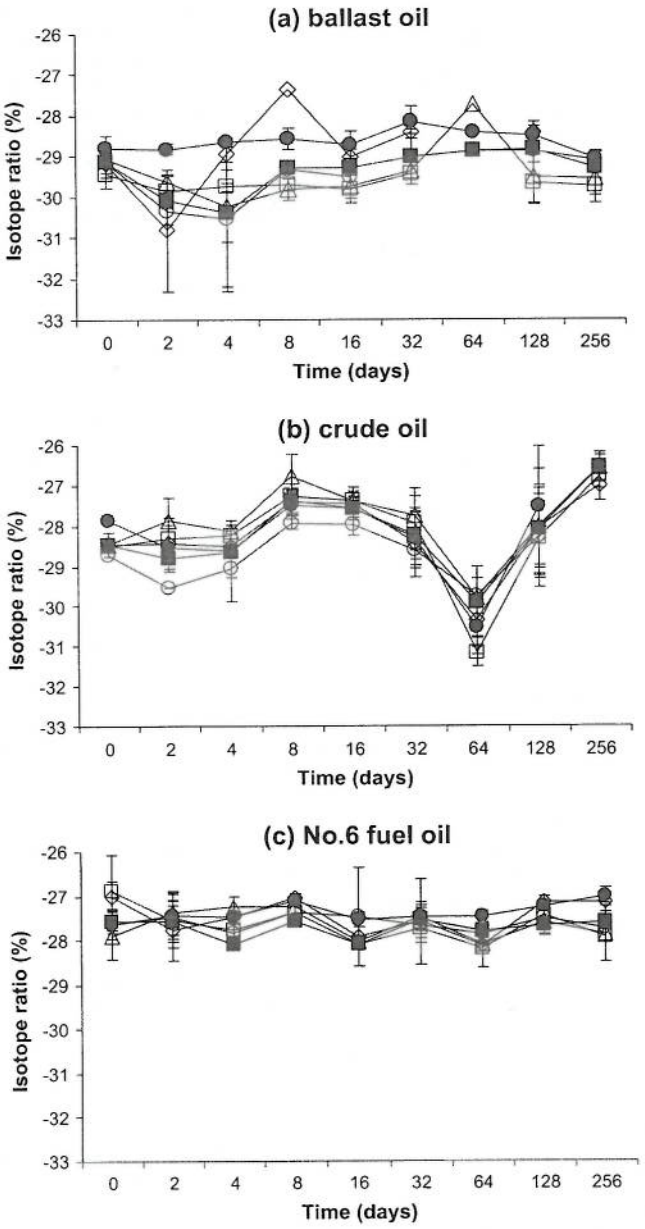


Fig. 2. Variation in *n*-alkane and norpristane isotope ratios ($\delta^{13}C$) for (a) ballast oil microcosms, (b) crude oil microcosms, (c) No.6 fuel oil microcosms; where ◇ represents C_{14} (or C_{16} in the case of No.6 fuel oil); □ represents C_{17}; △ represents C_{18}; ■ represents C_{24}; ○ represents C_{26}; and ● represents norpristane.

the study. This may be due to preferential loss of ^{13}C to abiotic weathering processes, which were shown to be most influential over the initial stages of the study (Fig. 1). Following this, the C_{14}, C_{24} and C_{26} $\delta^{13}C$ gradually increased over the course of the study to return to their original values. The $\delta^{13}C$ of C_{17} and C_{18} varied to a much lesser degree.

(iv) This latter variation, although small, may be the result of microbial action on the C_{14}, C_{24} and C_{26} alkanes, causing the heavier isotope to gradually accumulate in these compounds. Previous studies document that a shift in the order of 1–2‰ might be expected to result from microbial activity (e.g. Bowler et al., 1993). The reason that this effect is diminished in C_{17} and C_{18} is because of co-elution of pristane and phytane with these compounds.

For the crude oil samples (Fig. 2b):

(i) Isotope ratios in the crude oil samples appeared to shift in favour of the heavier isotope over the course of the study, typically by 1.5–2.0‰. This suggests that biotransformation of this oil may be monitored through the detection of compound isotope ratios, which increase as biotransformation proceeds and the lighter isotope is preferentially removed during microbial catabolism.

(ii) The trend observed in (i) is reversed by a decrease in all isotope ratios by day 64. This may be due to a sudden shift in the rate of oil biotransformation, causing a marked rearrangement in compound isotopic fractionation. This is corroborated by the evidence presented in Fig. 1, which shows a highly significant increase ($p < 0.01$) in the proportion of weathering due to abiotic processes.

(iii) There is no clear difference between the isotopic variations of the *n*-alkanes and those of norpristane. Thus in this case, the use of isoprenoid $\delta^{13}C$ would not be a reliable source diagnostic parameter.

For the No.6 fuel oil (Fig. 2c):

(i) No overall shift in isotope ratio was observed for any of the compounds over the course of the study.

(ii) Individual values did appear to fluctuate in value between 0 and 256 days, but by less than ±0.5‰. This is within the reproducibility of the technique and cannot be interpreted as a genuine manifestation of microbial activity.

The influence of microbial activity on oil isotopic composition has been studied by several authors (Schmidt et al., 2004; Griebler et al., 2004). Stahl (1980) examined the nutrient-enhanced degradation of crude oil over 42 days by determining compositional and stable carbon isotope variations within different class fractions. Although the aromatic and polar fraction $\delta^{13}C$ values remained constant (−27.6‰ and −27.1‰, respectively), the saturate fraction became isotopically heavier by 0.7‰ and the asphaltene fraction isotopically lighter by 1.1‰. Other, compound-specific, studies using GC-IRMS have found no change in the isotopic composition of individual *n*-alkanes of a variety of crude oils with biotransformation (Sofer et al., 1991; Mazeas et al., 2002).

The results presented here for ballast and crude oil reveal shifts in *n*-alkane $\delta^{13}C$ values of up to 2.5 times those observed by Stahl (1980). Although no studies were carried out on the effect of microbial activity on the whole oil isotope ratio, it would seem logical that an oil consisting predominantly of saturate class fraction components would also undergo shifts in isotope ratio. The use of oil $\delta^{13}C$ as source correlation parameters would, in such cases, be undermined. However, the results presented in this paper do suggest that

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A sensitive and robust method for the determination of alkylphenol polyethoxylates and their carboxylic acids and their transformation in a trickling filter wastewater treatment plant

Yoong K.K. Koh [a], Tze Y. Chiu [b], Alan R. Boobis [a], Elise Cartmell [b], Simon J.T. Pollard [c], Mark D. Scrimshaw [d,*], John N. Lester [b]

[a] Faculty of Medicine, Division of Experimental Medicine and Toxicology, Imperial College London, Hammersmith Campus, London W12 ONN, UK
[b] Centre for Water Science, School of Applied Sciences, Cranfield University, Bedfordshire MK43 0AL, UK
[c] Centre for Resource Efficiency and Management, Sustainable Systems Department, Cranfield University, Bedfordshire MK43 0AL, UK
[d] Institute for the Environment, Brunel University, Uxbridge, Middlesex UB8 3PH, UK

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ABSTRACT

This paper presents a method for the determination of alkylphenols, alkylphenol polyethoxylates (APEO) and alkylphenol ethoxycarboxylates (APEC) in the aqueous and particulate phase of wastewater samples. Quantification was achieved by liquid chromatography-tandem mass spectrometry. The sensitivity of the method is demonstrated by low detection limits, in the dissolved phase 1.2–9.6 ng l^{-1} for alkylphenol, $AP_{1-3}EO$ and APEC and 0.1–4.1 ng l^{-1} for longer chain alkylphenol polyethoxylates. The method detection limit for particulate phase samples ranged from 6 to 60 ng g^{-1} for AP, $AP_{1-3}EO$ and APEC; with the longer chain APEO being from 0.5 to 20 ng g^{-1}. Matrix effects were noted in complex matrix rich samples. There was a distinct change in the distribution of alkylphenol ethoxylates during biological treatment of the wastewater, with the major biotransformation products observed being carboxylated derivatives at concentrations of up to 1768 ng l^{-1}. Shorter chain APEO were present in higher proportions in the suspended solids, due to their higher affinity to particulate matter compared to the long-chain oligomers.

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1. Introduction

Alkylphenol polyethoxylates (APEO) are non-ionic surfactants widely used in commercial and domestic applications with a worldwide production of approximately 500 kilotons (Petrovic and Barceló, 2001; Langford and Lester, 2002). A voluntary ban on the use of APEO in household cleaning products was introduced in northern Europe during 1995, with further restrictions on their use for industrial cleaning in 2000 (OSPAR, 2006). However, octylphenol ethoxylates (OPEO) and nonylphenol ethoxylates (NPEO) continue to be used in industrial applications, as evidenced by their continuous discharge into sewage treatment works and subsequent release into the aquatic environment (Cheng et al., 2006; Cailleaud et al., 2007).

Environmental concern in relation to these compounds results from their estrogenic activity (Routledge and Sumpter, 1996). Biodegradation of APEO during biological wastewater treatment can occur under both aerobic and anaerobic conditions and results in the production of more persistent and estrogenic metabolites consisting of AP mono- to triethoxylates (NP_1EO, NP_2EO and NP_3EO), carboxylated intermediates and the alkylphenols (AP), nonylphenol (NP) and octylphenol (OP) (González et al., 2007; Langford et al., 2007; Petrovic et al., 2007). Understanding the transformation of these compounds during biological wastewater treatment processes is important for the development of strategies to control their discharge to the environment and sensitive and selective analytical methods are an essential tool for gaining the required data.

The analysis of APEO and their metabolites is a complex process due to the ethoxylated oligomers and alkyl-chain isomers which can be present (Scrimshaw et al., 2004). Gas chromatography (GC) and liquid chromatography (LC) are now commonly used for the determination of APEO. The use of GC for direct analysis is limited to APEO with lower numbers of ethoxy groups, while metabolic products and long-chain ethoxylates require derivatization to increase volatility. Traditionally, LC analysis with fluorescence (Ahel et al., 2000; Marcomini et al., 2000) or ultraviolet (Zhou et al., 1990) detection has been widely used. However, these techniques often lack the sensitivity and specificity required at low concentrations and LC coupled with tandem mass spectrometry (MS/MS) is now increasingly being used to determine these compounds (Loyo-Rosales et al., 2003, 2007; Petrovic et al., 2003). Most studies describe LC/MS/MS analysis of only a limited number of the possible oligomers and metabolites, focussing on either NPEO and NPECs

* Corresponding author. Tel.: +44 (0)1895267299; fax: +44 (0)1895269761.
E-mail address: mark.scrimshaw@brunel.ac.uk (M.D. Scrimshaw).

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(Houde et al., 2002; Petrovic et al., 2003), $AP_{1-3}EOs$ and AP (Ferguson et al., 2001), or $AP_{1-5}EOs$, AP and APEC (Loyo-Rosales et al., 2003; Loos et al., 2007). Furthermore, these works focus on the dissolved phase only, and the significance and distribution of these compounds on the particulate phase remains to be evaluated.

This study aims to develop a sensitive and selective analytical method to detect nonyl- and octylphenol, their ethoxylates ($NP_{1-12}EO$, $OP_{1-12}EO$) and carboxylated metabolites with up to three ethoxy units in sewage matrices. Compounds are determined in both the dissolved and particulate phases and attempts are made to achieve improvements in existing detection limits. The method was successfully applied to study a trickling filter (TF) biological wastewater treatment works, which are of particular interest due to their relatively common use. For example, a typical region in the South East of England has more TF (around 800) sites than those using the activated sludge process and few studies in the literature have reported on the fate of APEO in this process.

2. Experimental section

2.1. Reagents and chemicals

The technical 4-nonylphenol mixture of chain isomers and 4-*tert*-octylphenol were obtained from Sigma–Aldrich (Gillingham, Dorset, UK). The long-chain NPEO and OPEO were available in technical mixtures (Igepal CO210, CO520, CO720) and (Igepal CA210, CA520, CA720), respectively, containing a range of oligomers (Sigma–Aldrich). Nonyl- and octyl-phenoxy acetic acid (NP_1EC, OP_1EC), 4-nonyl- and octylphenolmono- and diethoxylate ($NP_{1-2}EO$, $OP_{1-2}EO$) were obtained from QMX Laboratories (Thaxted, Essex, UK). Standards for NP_2EC, NP_3EC, OP_2EC and OP_3EC were not available commercially. Due to the absence of commercially available standards, NP_2EC and NP_3Ec were quantified with NP_1EC standard, assuming similar response factors. Similarly OP_2EC and OP_3EC were determined with OP_1EC.

Acetone, ethylacetate, acetonitrile, methanol and dichloromethane were obtained from Rathburn (Walkerburn, Scotland, UK) and acetic acid from Sigma–Aldrich. Single standard stock solutions were prepared in acetonitrile. Reagent grade MilliQ-water (18.2 MΩ) (Millipore, Watford, UK) was used for spikes and preparation of solutions. The working standard solutions were prepared by further diluting the stock standard solutions with acetonitrile/MilliQ-water (50:50 v/v).

2.2. Trickling filter

The wastewater treatment works studied consisted of: primary treatment followed by a single high rate nitrifying filter with BIO-dek® structured plastic media (diameter 12 m; media depth 1.8 m); two Biochemical Oxygen Demand (BOD) percolating filters with random Biofil® plastic media (diameter 12 m; media depth 1.8 m) operating in parallel; and a single tertiary trickling filter with stone media (5 m × 10 m; media depth 4 m). This 2800 population equivalent works treated a dry weather flow of 650 $m^3\ d^{-1}$ with the only industrial inputs of <10% being from a local airfield. Their use of surfactants or degreasers was limited to methyl ethyl ketone (MEK). Spot water samples of settled sewage (primary effluent) and final effluent were taken on the morning of 28th March 2007.

2.3. Analytical procedure

For determination of dissolved concentrations, settled sewage (100 ml) or final effluent (250 ml) was filtered through a 1.2 μm Whatman GF/C filter (Whatman, Maidstone, UK). The filtered aqueous phase was then extracted using solid phase extraction (SPE) using a syringe barrel tC18 (500 mg, 3 cm^3) cartridge (Waters Ltd., Watford, UK). The appropriate volume of sample was loaded onto the cartridges which were preconditioned with 5 ml methanol followed by 5 ml MilliQ-water. The flow rate for sample extraction was kept constant between 5 and 10 ml min^{-1} using a vacuum manifold. When the sample had passed through, 4 ml of reagent grade water was used to rinse the cartridge, which was dried by drawing air through it for half an hour. The analytes were eluted using 10 ml ethylacetate, 10 ml dichloromethane followed by 5 ml 0.1% acetic acid in methanol. A rotary evaporator (Heidolph Instruments, Schwabach, Germany) was employed to concentrate the extracts to 1 ml which was then evaporated to complete dryness under a gentle stream of nitrogen. The extract was reconstituted with 0.25 ml acetonitrile/MilliQ-water (50:50 v/v) and transferred to an autosampler vial prior to analysis using LC/MS/MS.

The determination of alkylphenolic compounds in the particulate phase was also performed in this study. The filter papers with suspended solids were freeze-dried, shredded and subsequently extracted using 10 ml methanol/acetone (1:1) by shaking on a Multi-Reax system (Heidolph UK, Germany) for half an hour in a 25 ml Teflon tube. The solids were separated by centrifugation at 1500*g* for 10 min and the supernatant decanted off. This procedure was repeated twice and the combined extracts (20 ml) were then cleaned by passing through a 500 mg and 3 cm^3 silica SPE cartridge (Waters Ltd., Watford, UK) and eluted using 10% acetic acid in 10 ml methanol prior to drying, reconstitution with 0.25 ml acetonitrile/MilliQ-water (50:50 v/v) and quantification by LC/MS/MS.

2.4. LC/MS/MS analysis

Analytes were determined using LC/ESI/MS/MS consisting of an HPLC (Waters Alliance HPLC system 2695) coupled to a Waters Quattro Premier XE mass spectrometer with a *Z*-Spray ESI source (Micromass, Manchester, UK). The AP, APEC and APEO were separated on a Gemini C18 column (3 μm particle size, 100 mm × 2 mm i.d., Phenomenex, Macclesfield, UK). The mass spectrometer was operated in the negative electrospray ionisation (ESI^-) (AP and APEC) or positive electrospray mode (ESI^+) (APEO) using multiple reaction monitoring (MRM). Nitrogen was used as the nebuliser gas and argon as the collision gas. The conditions for detection by the mass spectrometer were as follows, capillary voltage, 3.20 kV in the positive mode and −2.3 kV in the negative mode, extractor lens at 3.0 V, RF lens at 0.5 V in the positive mode and 1.0 V in the negative mode, multiplier voltage, 650 V, desolvation gas flow, 1000 l h^{-1}, cone voltage as shown in Table 1, cone gas flow at 50 l h^{-1}, desolvation temperature at 350 °C and source temperature at 120 °C.

Two separate chromatographic runs were used, one for the separation of $AP_{3-12}EO$; and the other for $AP_{1-2}EO$, APEC and APs. In both cases, separation was achieved using MilliQ-water containing 20 mM NH_4OH (solvent A) and acetonitrile containing 20 mM NH_4OH (solvent B). The use of ammonia results in formation of the NH_4^+ adduct ions by the APEO, rather than more stable sodium adducts, which facilitates fragmentation of parent ions in the collision cell of the MS/MS (Table 1). The gradient conditions for $AP_{3-12}EO$ were; time zero, 45% solvent B (5 min) followed by a linear increased in gradient to 80% solvent B which was maintained for 40 min. Following this gradient, the conditions were maintained at 90% solvent B for 5 min before the column was re-equilibrated to starting conditions at 20% solvent B. The total run time was 50 min and A sample volume of 10 μl was injected at a flow rate of 0.2 ml min^{-1}.

Conditions for the $AP_{1-2}EO$, APEC and APs started with 20% solvent B increasing to 45% over 10 min (Fig. 1). This was followed by

Table 1
Characteristic LC/MS/MS parameters and detection limits of alkylphenol polyethoxylates (NPEO and OPEO)

Compounds	*m/z* Precursor $[M+NH_4]^+$	Cone (V)	Product ions (collision potential)	Retention time (min)	IDL (pg)	Recoveries % (RSD)	Matrix suppression (%)	MDL (ng l^{-1})	MDL (ng g^{-1})
NP_3EO	370	40	353(10)[a], 226.5(20)	27.87	0.2	84(2)	10	0.1	0.5
NP_4EO	414	30	397(14)[a], 270(20)	27.71	4.7	91(5)	8	1.5	7.5
NP_5EO	458	30	440(20)[a], 315(25)	27.63	7.9	85(2)	9	2.1	10
NP_6EO	502	30	485(20)[a], 359(30)	27.47	13.4	90(2)	8	2.7	13
NP_7EO	546	30	529(23)[a], 403(25)	27.23	8.3	90(3)	8	0.8	4
NP_8EO	590	30	573(25)[a], 447(27)	27.07	3.5	90(3)	8	0.7	4
NP_9EO	634	30	617(25)[a], 335(30)	26.82	2.9	88(2)	9	2.2	11
$NP_{10}EO$	678	30	661(25)[a], 132.5(40)	26.66	3.0	98(3)	8	2.1	10
$NP_{11}EO$	722	30	705(25)[a], 291(40)	26.42	1.9	89(3)	8	0.9	4.5
$NP_{12}EO$	766	30	749(30)[a], 291(35)	26.26	1.0	90(2)	9	1.1	5.5
OP_3EO	356.5	20	338.5(10)[a], 227(10)	22.84	4.9	80(5)	11	1.8	9
OP_4EO	400.5	20	382.5(15)[a], 270.5(15)	22.84	5.9	85(3)	10	4.1	20
OP_5EO	444	20	426.5(10)[a], 315(10)	22.76	0.2	80(3)	9	1.4	7
OP_6EO	488	30	471(15)[a], 359(20)	22.68	6.0	79(6)	9	3.0	15
OP_7EO	532	30	515(20)[a], 403(20)	22.60	8.6	79(9)	8	0.6	3
OP_8EO	576	30	559(20)[a], 447(25)	22.43	7.9	93(3)	8	1.3	6.5
OP_9EO	620	30	603(20)[a], 491(25)	22.27	5.5	85(4)	9	2.0	10
$OP_{10}EO$	664	30	647(20)[a], 535(30)	22.11	3.0	90(7)	8	0.8	4
$OP_{11}EO$	708	30	690(20)[a], 579(30)	22.03	0.1	88(9)	8	0.1	0.5
$OP_{12}EO$	752	30	735(20)[a], 623(30)	21.87	0.1	82(2)	9	0.5	2.5
NP_1EO[b]	282	25	127(25)[a], 265(25)	29.11	40	86(2)	10	1.2	6
NP_2EO[b]	326	40	183(40)[a], 121(40)	28.88	7	73(2)	11	2.5	12
NP_1EC[c]	263.5	20	205(20)[a], 106(30)	11.32	3	94(3)	9	2.5	12
NP_2EC[c]	307	20	205(20)	11.32	N/C			N/C	N/C
NP_3EC[c]	351	20	205(20)	11.32	N/C			N/C	N/C
OP_1EO[b]	268	15	113(10)[a], 250(20)	25.92	58	81(3)	10	9.6	48
OP_2EO[b]	312	20	183(10)[a], 295(10)	25.73	5	73(2)	11	5.1	25
OP_1EC[c]	277.5	20	219(18)[a], 133(40)	10.87	3	97(6)	8	12	60
OP_2EC[c]	321	20	219(18)	10.87	N/C			N/C	N/C
OP_3EC[c]	365	20	219(18)	10.87	N/C			N/C	N/C
NP[c]	219	30	132.5(30)[a], 147(35)	29.43	5	73(2)	11	2.3	11
OP[c]	205.5	30	134(25)[a], 106(20)	26.32	4	72(1)	9	6.9	34

Recoveries and matrix suppression for determination of the dissolved phase in final effluent samples. IDL were calculated by a S/N of 3 from the MRM chromatograms of the standard solution mixture. MDL for dissolved phase from spiked MQ (0.1 μg l^{-1}) in 250 ml reagent water; MDL for the particulate phase from 0.125 μg g^{-1} in 0.2 g sludge dry weight. N/C: not calculated (no unique standards available).

[a] MRM used for quantification.
[b] $[M+NH_4]^+$.
[c] $[M-H]^-$.

a linear increased to 80% solvent B which was maintained for 20 min. Following the increase gradient from 80% to 90% solvent B, the conditions were maintained at 90% solvent B for 5 min before the column was re-equilibrated to starting conditions at 20% solvent B for 10 min prior to next run. Similarly, the total run time for this analysis was 50 min with 10 μl sample volume injected and flow rate was kept at 0.2 ml min^{-1}.

3. Results and discussion

3.1. Optimisation of LC and MS/MS conditions

Identification of the alkylphenolic compounds was ensured by monitoring two characteristic precursor-product ion transitions and obtaining a retention time match. For quantification, the most sensitive transition was used. However, some compounds produced only one sensitive product ion (Table 1). Quantification using external calibration with standard solution mixtures was used. In all instances the calibration curves exhibited $r^2 \geqslant 0.99$ for all compounds.

The APEO exhibit a high affinity for alkali metal ions resulting in the formation of sodium adducts $[M+Na]^+$ rather than the protonated molecules in unmodified mobile phases (Koh et al., 2005). However, the sodium adducts tend to be stable and do not fragment in the collision cell, and the ammonium adducts have been

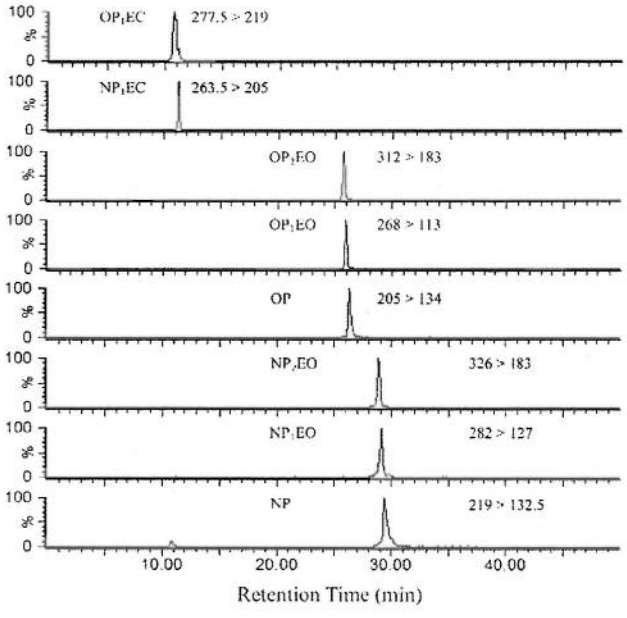


Fig. 1. Chromatograms of alkyphenolic compounds. Standard concentrations 0.5 mg l^{-1} (only one product ion for each alkylphenolic oligomer is shown).

favoured for MS/MS (Jonkers et al., 2003; Loos et al., 2007). In this study, the use of ammonium adducts for MRM detection improved the detection limits due to the high degree of fragmentation in the collision cell.

3.2. Evaluation of method performance

The recoveries and relative standard deviations were determined in experiments where the analytes in the dissolved phase were in the concentration range of 0.1 $\mu g\,l^{-1}$ (low spike) and 1 $\mu g\,l^{-1}$ (high spike) using MilliQ-water and wastewater samples ($n = 3$). Filtration of the wastewater samples was undertaken prior to SPE to remove particles. Recoveries in MilliQ-water (low and high spiking levels) ranged from 71% to 98% for AP, APEO and APEC. Generally, the relative standard deviations (RSDs) were in the range of 2–7%. Typically, recoveries for settled sewage (low and high spiking levels) ranged from 62% to 98% for AP, APEO and APEC. Relative standard deviations obtained were 2–8% for these alkylphenolic compounds. Recovery values and RSD were similar for spiked (low and high) final effluent samples for all alkylphenolic compounds.

The recoveries and relative standard deviations were also determined for particulate samples where the analytes were in the concentration range of 0.125 $\mu g\,g^{-1}$ (low spike) and 1.25 $\mu g\,g^{-1}$ (high spike) using suspended solids samples ($n = 3$) and sludge samples ($n = 3$). The total suspended solids were 437.5 $mg\,l^{-1}$ and 23.5 $mg\,l^{-1}$ for settled sewage and final effluent samples. Recoveries for APEO sorbed to the particulate phased ranged from 51% to 105% for AP, APEO and APEC for low and high spikes and their corresponding RSDs were in the range of 1–14%. Recoveries in spiked sludge ranged from 51% to 104% for AP, APEO and APEC and their RSDs ranged from 1 to 8. This methodology demonstrates that consistent recovery values and low RSD could be obtained from different matrices.

The method detection limit (MDL) was determined by subjecting the entire analytical extraction and detection procedure to the determination of spiked reagent water, settled sewage and final effluent samples in both the dissolved and particulate phases. The MDL determined for the entire SPE/LC/MS/MS ranged from 1.2 to 9.6 $ng\,l^{-1}$ for (AP, APEO and APEC) and from 0.1 to 4 $ng\,l^{-1}$ for long-chain APEO (Table 1). The direct comparison of MDL with values reported by other authors is difficult due to the use of a range of sample matrices, the number of analytes and the lack of information on how the limits have been derived. In comparison to methods that allow the determination of selected APEO, APEC and AP in aqueous samples, the sensitivity of the method presented here is generally greater than other studies, however, the work by Jahnke et al. (2004) appears particularly sensitive (Table 2). These authors utilised greater sample volumes (1 l) than in this study, and made their samples to a final volume of 100 µl, an overall ten times greater concentration factor than in this study, possibly accounting for much of the difference.

The detection limits for compounds on the particulate phase (removed by filtration with the GF/C filters) were calculated based on determination of ~0.2 g of total suspended solids. The MDL determined for the entire SPE/LC/MS/MS ranged from 6 to 60 $ng\,g^{-1}$ for AP, short chain APEO and APEC and 0.5–20 $ng\,g^{-1}$ for long-chain APEO.

3.3. Matrix effects

A common problem when analysing APEOs and their degradation products in wastewater samples by MS is the suppression of the analyte signal as a result of co-eluting compounds impairing ionisation in the ESI source. As a result, LC/MS/MS signals of external standard samples, usually prepared in pure solvent, may be enhanced in relation to those from samples prepared from an environmental matrix (Petrovic and Barceló, 2002).

To evaluate and quantify the impact of matrix effects on signal intensity, the methodology was applied to water, settled sewage and effluent matrices which were unspiked or spiked with the alkylphenolic compounds (low and high spike of 0.1 $\mu g\,l^{-1}$ and 1 $\mu g\,l^{-1}$, respectively). The relative signal suppression was derived using Eq. (1) (Vieno et al., 2006) and the result expressed as a percentage

$$\frac{A_s - (A_{sp} - A_{usp})}{A_s} \times 100\% \quad (1)$$

where A_s is the peak area of the analyte in pure standard solution, A_{sp} is the peak area in the spiked matrix extract and A_{usp} is the peak area in the unspiked matrix extract.

Matrix effects resulted in a suppression of the analyte signal of 8–24% in the $AP_{1-12}EO$ (dissolved phase), with greater matrix effects observed in the settle sewage of 12–24% compared to the final effluent at 8–11% (dissolved phase). Significantly higher matrix interference was observed for solid samples of up to 27% in sewage sludge for $AP_{1-12}EO$ and up to 24% for settled sewage for $AP_{1-2}EC$ and APs. The matrix effect can be reduced by a careful and selective extraction procedure and sample clean-up and the addition of mobile phase additives (Petrovic and Barceló, 2001). Such approaches, along with a smaller injection volume (10 µl) and longer analysis time (~50 min) to give well separated chromatography, were incorporated within this study to minimise matrix effects. Overall matrix effects on the signal were less than those observed by Jahnke et al. (2004), who reported suppression from 32% to 79%, and commented that "for high enrichment factors, matrix interferences are distinct", and it is apparent that there is a trade-off in utilising high enrichment to increase sensitivity against uncertainty resulting from matrix effects and that matrix effects are sample dependent.

Table 2
Comparison of method detection limit ($ng\,l^{-1}$) with other publications

Analyte	MDL (this study)	MDL (Jahnke et al., 2004)[a]	MDL (Petrovic et al., 2002)[b]	MDL (Rudel et al., 1998)[c]	MDL (Loos et al., 2007)[d]	MDL (Houde et al., 2002)[e]	MDL (Jonkers et al., 2003)[f]
NP_1EO	1.2	10	100	14.4	100	50	15
NP_2EO	2.5	0.2	40	13	100	20	6
NP_1EC	2.5	0.1	20	86.7	1	10	13
OP_1EO	9.6	12	100	10	100	–	–
OP_2EO	5.1	0.1	40	3.3	100	–	–
OP_1EC	12	0.04	20	–	1	–	–
NP	2.3	2.0	20	8.4	10	–	11
OP	6.9	4.0	20	6.1	5	–	–

[a,d,e] $[APEO+NH_4]^+$ adducts and $[M-H]^-$ ions (AP and APEC) monitored using LC/ESI/MS/MS.
[b,f] $[APEO+NH_4]^+$ adducts and $[M-H]^-$ ions (AP and APEC) monitored using LC/ESI/MS.
[c] GC/MS after derivatization.

3.4. Concentration of alkylphenolic compounds in a trickling filter works

The method was applied to evaluate the transformation of the APEO during biological treatment through analysis of settled sewage and final effluent at a trickling filter wastewater treatment plant. There was a change in the distribution of the NPEO oligomers during treatment (Fig. 2) which was also observed for the OPEO (data not shown). In the settled sewage, the higher ethoxylates ($NP_{4-12}EO$) accounted for 91% of the nonylphenol compounds, however, following biological treatment, the distribution of both nonyl- and octylphenol compounds changed and the carboxylated metabolites ($NP_{1-3}EC$) were predominant amongst the nonylphenol compounds (58%) and increased in the octylphenols (20%). Taking into account the presence of the carboxylated intermediates, 64% of the nonylphenol compounds and 86% of the octylphenols passed through treatment to the final effluent. These results support observations by other workers who have determined carboxylated intermediates, and demonstrates their significance in discharges (Jahnke et al., 2004; Loyo-Rosales et al., 2007) and that there was a shift in the distribution of oligomers due to cleavage of ethoxy units and carboxylation through the biological treatment process.

The major biotransformation products of the NPEO, $NP_{1-3}EC$, formed during the wastewater treatment, were present in the final effluent at relatively high concentrations (35–1768 ng l^{-1}) as a result of biodegradation. As demonstrated in this study progressive shortening of the ethoxylate chain occurs during the biological stage of wastewater treatment, although this is not efficient enough to remove all of the higher oligomers ($AP_{4-12}EO$) which were

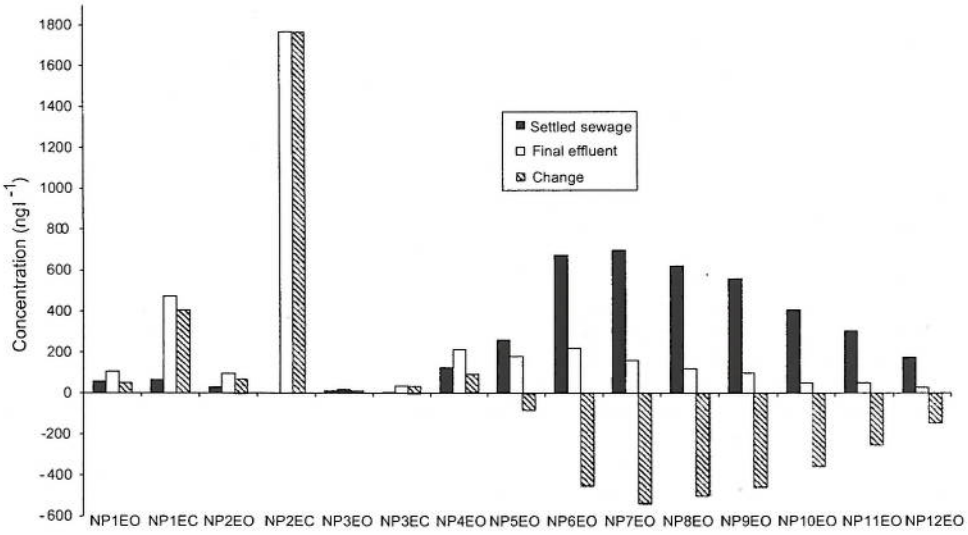


Fig. 2. Concentrations of the NPEO and $NP_{1-3}EC$ in settled sewage and final effluent with the change in concentrations during the process highlighted.

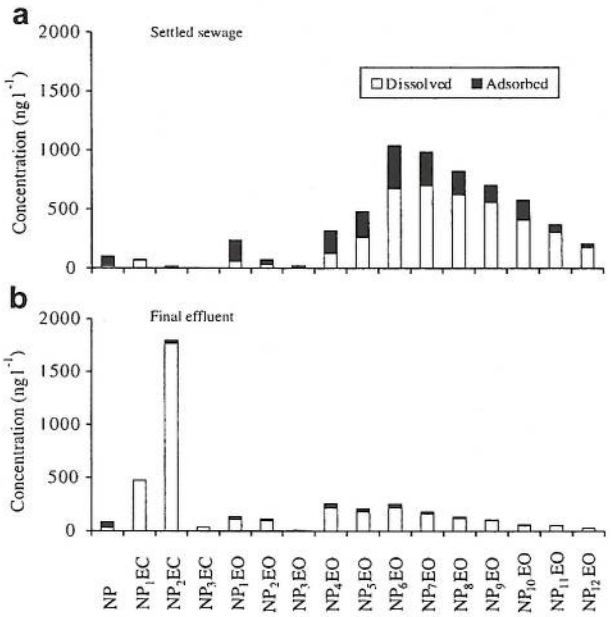


Fig. 3. Concentrations of NP, $NP_{1-3}EC$ and $NP_{1-12}EO$ showing partitioning between the dissolved and particulate fraction in settled sewage (A) and final effluent (B).

still observed in the final effluent. This study corroborated the findings of others cited in this manuscript in that APEO do degrade; however, estrogenic carboxylated metabolites were generated in the process. In this study, the NP_2EC predominated in the effluent (Fig. 2), a characteristic also observed in activated sludge processes, though these metabolites are more effectively removed in membrane reactors (González et al., 2007).

The determination of these compounds on the particulate phase demonstrates the significance of sorption to solids, with 68% of the hydrophobic NP (and 50% of the OP) being associated with the suspended solids (Fig. 3). Suspended solids in the final effluent at the treatment plant were 23.5 mg l^{-1}. Although at this site the final effluent concentration of nonylphenol would meet the PNEC value set by the UK Environment Agency (330 ng l^{-1}), it would fail for octylphenol (6 ng l^{-1}). Whilst there are as yet no environmental quality standards for the carboxylated intermediates these compounds appear to be discharged at relatively high concentrations and their solubility will mean the ability to remove them from effluents with conventional biological treatment is likely to be challenging.

4. Conclusions

An analytical method for alkylphenolic compounds has been developed, consisting of a SPE extraction (dissolved phase); and solvent extraction with silica clean-up (particulate phase) followed by LC/MS/MS detection. Evaluation of the methodology indicates the importance of considering matrix effects, in particular if concentration factors are increased to give lower detection limits and more complex, or "dirty" samples are analysed. The results of determining the transformation of the compounds during biological wastewater treatment demonstrate the importance of determining not only the alkylphenols and ethoxylates, but also the APEC intermediates, as the highest concentrations found in the final effluent were for NP_1EC and NP_2EC.

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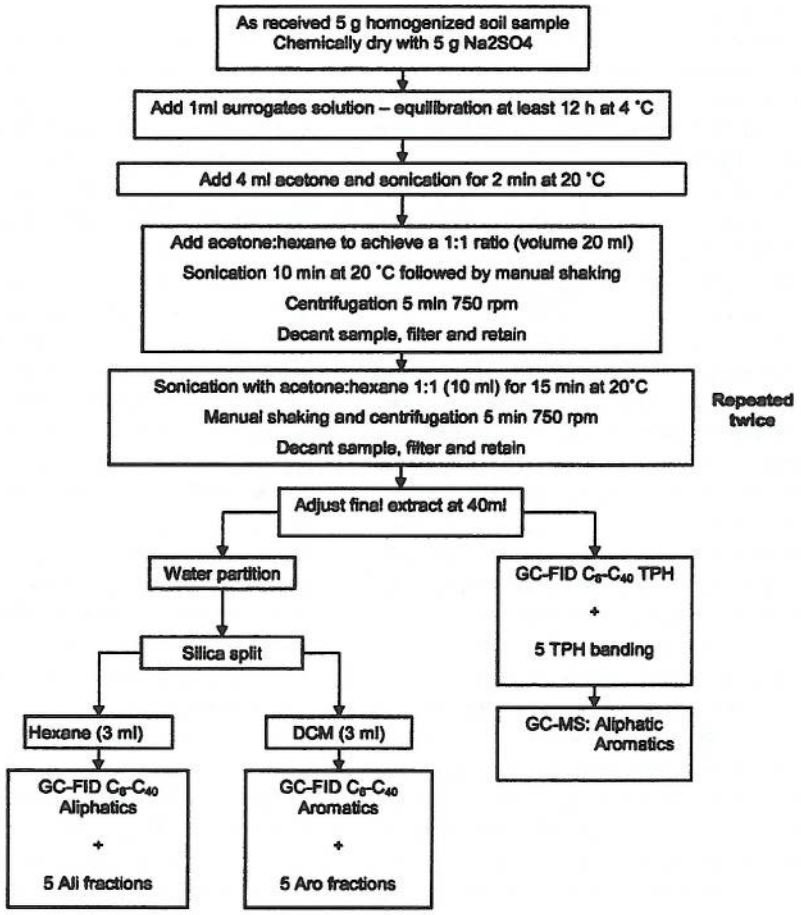


Figure 1. Analytical schematic recommended for analyzing soil contaminated with weathered hydrocarbons.

not cover polar compounds but only nonweakly polars as they are usually not considered for evaluating human health risk from petroleum hydrocarbons in soils.[1,9] A silica gel column chromatography procedure was used to split the extracted hydrocarbons into aliphatic and aromatic class fractions (Figure 1). Approximately 80 mL of polished water and a spatula of sodium chloride (baked at 400 °C for 4 h) were added to the sample extracts, partitioning out any acetone into the water and ensuring the removal of the nonpolar content. TPH silica cleanup was then carried out by passing 1 mL of the upper phase from the partitioned samples through a silica gel column, eluting with 3 mL of dichloromethane (DCM). In contrast, the split of the aliphatic/aromatic fractions was realized by eluting with 3 mL of hexane followed by 3 mL of DCM, respectively.

Instrumental Analysis. Quantification of TPH content was carried out using a gas chromatograph fitted with a flame ionization detector (GC-FID Agilent model 6890). Chromatography was performed on a fused-silica capillary column (15 m × 0.32 mm internal diameter) coated with HP-5 (0.25-μm film thickness; Agilent). Helium was used as the carrier gas at 2.5 mL min^{-1}, and the FID detector temperature kept at 350 °C. Pulsed splitless injection with a sample volume of 3 μL was applied. The oven temperature was increased from 45 to 250 °C at a gradient of 120 °C min^{-1}, then increased to 300 at 100 °C min^{-1}, and finally increased to 340 at 90 °C min^{-1} and held at this temperature for 4 min. The total run time was 6.2 min. Quantification of TPH and subranges of hydrocarbons including Texas banding compounds (Texas 1–5),[12] diesel range organic (DRO), kerosene range organic (KRO), and mineral oil range organic (MRO) compounds in soils was made by integrating peak areas using Agilent Chemstation Software Revision B.01.01 (164) SR1 (2001–2005) and by comparison of these peaks with the response of a known concentration of diesel and mineral oil standards. External multilevel calibrations were carried out for both diesel/mineral oil fractions and surrogates, quantification ranging from 0.5 to 2500 $\mu g\ mL^{-1}$ and from 1 to 5 $\mu g\ mL^{-1}$, respectively.

Surrogate standards were used to determine the extraction efficiency of the method. For quality control, a 500 $\mu g\ mL^{-1}$ diesel standard and mineral oil were run every 10 samples. In addition, duplicate blank controls and reference material were systematically used. The blank control was treated in exactly the same manner as the samples but contained no soil. When analyzed, if the blank concentration exceeded the method reporting limits either of 2 or 10 mg kg^{-1} for Texas banding and the TPH, DRO, MRO, and KRO hydrocarbon ranges, respectively, the samples series was re-extracted. The reference material was an uncontaminated soil of known characteristics and was spiked with a diesel and mineral oil standard at a concentration equivalent to 16 000 mg kg^{-1}.

Polycyclic aromatic hydrocarbons were identified and quantified by GC/MS using an Agilent 6890 gas chromatograph coupled to an Agilent 5975 mass spectrometer operated at 70 eV in positive ion mode. Splitless injection with a sample volume of 1 μL was applied. The oven temperature was increased from 80 to 150 °C

Table 1. Mean Concentration, Precision, and Bias for Duplicate Sample Extraction for Each Soil Matrix

matrix	spike concentration, mg kg^{-1}	mean concentration, mg kg^{-1}	precision, mg kg^{-1}	precision, % RSD	bias, mg kg^{-1}	bias, %	total error, %
silty soil	0	65	7	11	n/a	n/a	n/a
	1000	942	38	4	−58	−6	14
	5000	5876	235	4	876	18	26
	10000	9988	300	3	−12	0	6
	30000	29280	878	3	−720	−2	8
clay soil	0	81	23	28	81		56
	1000	487	15	3	−513	−51	57
	5000	5479	219	4	479	10	18
	10000	10142	710	7	142	1	15
	30000	30104	2107	7	104	0	14
sandy soil	0	9	6	62	n/a	n/a	n/a
	1000	510	15	3	−490	−49	55
	5000	5387	215	4	387	8	16
	10000	9727	389	4	−273	−3	11
	30000	28759	575	2	−1241	−4	8
madeground[a]	0	286	63	22	n/a	n/a	n/a
	1000	616	18	3	−384	−38	44
	5000	5588	224	4	588	12	20
	10000	10802	324	3	802	8	14
	30000	31166	1558	5	1166	4	14
Matrix RTC CRMPR 9583	9510	11124	334	3	1614	17	23

[a] Madeground, a granular matrix comprising ash, brick, and concrete fragments, which was selected to represent surface soil found on many industrial sites (n/a not applicable).

at 30 °C min^{-1} and then increased to 320 at 15 °C min^{-1} and held at this temperature for 4 min. The mass spectrometer was operated using the full scan mode (range m/z 50−500) for quantitative analysis of target PAHs. For each compound, quantification was performed by integrating the peak at specific m/z. Internal multilevel calibration was carried out ranging from 0.01 to 5 ng μL^{-1}. For quality control, a 1.0 ng μL^{-1} PAH Calibration Mix 5 Standard solution (Restek) was analyzed every 15 samples.

Validation Procedure. Validation provides confidence that the established performance characteristics are based on robust experimental determinations and are statistically sound. Each spiked soil matrix was allowed to stand for 24 h at room temperature before commencing extraction, to allow the spike to interact with the soil matrix. Performance characteristics were determined with a minimum of 10 degrees of freedom by analyzing each certified reference material or spiked samples in duplicate in different analytical batches. Eleven batches of duplicates were analyzed for each matrix at each spiking level thus providing 10 degrees of freedom in each validation experiment.

RESULTS AND DISCUSSION

The sequential solvent ultrasonic method presented here has been evaluated using several different soils and concentration levels in addition to the use of a certified reference material. The mean TPH concentrations achieved for each tested soil, concentration levels, precision, and bias of the samples are shown in Table 1. The results showed that the method had good extraction efficiency and recovery independently of soil type with relative standard deviation (RSD) values for all the soils of below 10% for all of the spiked soils. However, recoveries below 5000 mg kg^{-1} would not be quite as high but at least ≥50% recovery may be expected by using this technique. The relatively high bias obtained may be due to the lack of evaporation step within the method. The highest degree of variability was obtained in the clay soil (Table 1), a trend also reported in a previous study,[21] where it was suggested that the organic compounds were strongly binding to the clay matrix bounds, reducing extractability and increasing variability. It is important to validate extraction efficiencies using certified reference materials as the recoveries obtained with spiked compounds may not be representative of those obtained with native compounds. This is because spiked analytes are usually lightly coated on the surface of the matrix, whereas native compounds can be strongly absorbed to the soil matrix. Although important, to the best of our knowledge, very few certified commercial data sets are available within the open literature. Extraction of certified reference matrix RTC CRMPR 9583 gave good precision (Table 1). Here a RSD of 3% (Table 1) was achieved, which is a better degree of precision than that achieved by Sanz-Landaluze et al.[14] of 14% when validating their method using a reference material.

These results are in good agreement with those of Banjoo and Nelson,[13] where extraction efficiency greater than 90% for optimized sonication method was obtained. Differences between the method used in our study and those of Banjoo and Nelson[13] occur in extraction duration, solvent volume, and addition sequence. Additionally, samples were not agitated in the Banjoo and Nelson method. In the present study, agitation was used to ensure full contact between sample and solvent increasing extraction efficiency. Banjoo and Nelson[13] used evaporative techniques in their postextraction sample preparation. Here, no such step is required, which may first minimize loss of volatiles and second account for some of the differences in extraction efficiencies of these two methods, as losses may have occurred during extract concentration steps. While chemical analysis used in this work did not quantify directly the potential loss of volatiles compounds of the front end bands ranging between C_8 and C_{12}, some of our current work undertaken on kerosene extraction from soils suggests that retention of the lighter end compounds is very good (i.e., recovery

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Table 2. DRO, KRO, and MRO Hydrocarbon Banding Mean Concentration Extracted, Precision, and Bias for Soils Spiked with 20 and 80% of Typical Hydrocarbon Concentration Found in Environmental Samples

		silty soil		clay soil		sandy soil		madeground	
carbon band	% spike level[a]	mean, mg kg^{-1}	precision, mg kg^{-1} (% RSD)	mean, mg kg^{-1}	precision, mg kg^{-1}	mean, mg kg^{-1}	precision, mg kg^{-1}	mean, mg kg^{-1}	precision, mg kg^{-1}
DRO C_{10}–C_{24}	20	8401	1092 (13)	6574	526 (8)	6468	323 (5)	7052	212 (3)
	80	18957	568 (3)	19801	1584 (8)	19135	382 (2)	20677	1034 (5)
KRO C_8–C_{14}	20	1663	66 (4)	1641	148 (9)	1639	82 (5)	1724	69 (4)
	80	4963	198 (4)	4986	499 (10)	5005	150 (3)	5201	364 (7)
MRO C_{22}–C_{34}	20	3933	158 (4)	3708	334 (9)	3527	141 (4)	4123	124 (3)
	80	11415	342 (3)	10862	760 (7)	10451	523 (5)	11513	461 (4)

[a] Percentage of expected concentration range encountered in environmental samples.

Table 3. Texas Risk Bandings Mean Concentration Extracted, Precision, and Bias for Soils Spiked with 20 and 80% of Typical Hydrocarbon Concentration Found in Environmental Samples

		silty soil		clay soil		sandy soil		madeground	
carbon band	% spike level*	mean, mg kg^{-1}	precision, mg kg^{-1} (% RSD)	mean, mg kg^{-1}	precision, mg kg^{-1}	mean, mg kg^{-1}	precision, mg kg^{-1}	mean, mg kg^{-1}	precision, mg kg^{-1}
TPH C_8–C_{10}	20	224	11 (5)	234	30 (13)	231	28 (12)	228	23 (10)
	80	669	20 (3)	673	47 (7)	655	33 (5)	642	39 (6)
TPH C_{10}–C_{12}	20	531	21 (4)	550	33 (6)	536	27 (5)	556	22 (4)
	80	1593	48 (3)	1697	102 (6)	1633	33 (2)	1690	152 (6)
TPH C_{12}–C_{16}	20	2317	116 (5)	2383	167 (7)	2328	93 (4)	2502	125 (5)
	80	7173	287 (4)	7615	533 (7)	7340	147 (2)	7832	548 (7)
TPH C_{16}–C_{21}	20	2363	47 (2)	2523	177 (7)	2445	73 (3)	2653	80 (3)
	80	6783	271 (4)	7352	515 (7)	6919	138 (2)	7531	301 (4)
TPH C_{21}–C_{35}	20	4304	215 (5)	4173	334 (8)	3880	155 (4)	4471	134 (3)
	80	12143	364 (3)	12100	847 (7)	11461	458 (4)	12678	380 (3)

>70%; data not shown). Further research will need to be performed with light hydrocarbons such as isooctane, nonane, or decane to test this out.

As also shown in Table 1, certified and some spiked compounds gave recovery of >100% and higher recovery efficiency was observed with clay soil rather than sandy soil. The reasons for the observed over-recoveries are quite common with reference compound recoveries and may be associated with inherent integration error with unresolved complex mixtures at the baseline or possible coelution of analytes.[19,27] In addition, calibration variance observed in analytical systems particularly where bias is small may contribute to this observation.

Ensuring reliability and validity of the results is an important consideration. Quality control is built into this method to allow for continued evaluation and validation of the method, through the analysis of a reagent blank and a spiked reference material with every ≤20 samples. Additionally, sample recovery is monitored using surrogate spikes. Analyses of KRO, DRO, MRO, and Texas risk carbon banding fractions show RSD values ranging between 2 and 13% with the highest overall degree of variability occurring when analyzing the lightest fractions including DRO C_{10}–C_{24} ranges and TEXAS1-TPH C_8–C_{10} ranges (Tables 2 and 3). With the exception of the madeground soil, a higher degree of precision was typically observed when extracting higher concentrations of hydrocarbons. It is only when analyzing the aromatic fraction (Table 4) where RSD values rise above 20%. The greatest degree of variability was observed when extracting low concentrations of the C_8–C_{10} range for all of the soils tested, possibly due to volatile losses or thermal decomposition of compounds. Here, the diminution curve showed that precision was lower due to the detection limits of the GC used (data not shown). This is consistent with the precision obtained for ultrasonic methods elsewhere. Shin and Kwon[21] and Sanz-Landaluze et al.[14] demonstrated RSD values of <10 and 14%, respectively, when optimizing sonication methods. Within the silty and sandy soils, a greater degree of precision was achievable at higher concentrations, whereas within the clay and madeground soils, precision was higher when extracting lower concentrations. Overall, the results showed that the ultrasonic sequential solvent extraction method has a high degree of accuracy, achieving an extraction efficiency of ≥95%.

Sanz-Landaluze et al.[14] optimized sonication parameters when using an ultrasonic probe to give good extraction efficiencies with satisfactory accuracy confirmed using certified reference materials, when extracting the 16 U.S. EPA priority PAHs. Although the method described by the authors does not require a cleanup step, concentration through evaporation is employed, which could lead to volatile losses. Ultrasonic probes are more expensive to purchase than ultrasonic baths; however, in real terms this cost is in no way prohibitive. However, the additional health and safety requirements of ultrasonic probe use could be an issue. Sonic probes as shown by Sanz-Landaluze et al.[14] also require an understanding of and optimization of amplitude and ultrasonic power/energy.

Previous investigations have shown that the water within soil samples can significantly influence extraction efficiency of organic compounds.[10] A mixture of two solvents such as 1:1 acetone/hexane or 1:1 hexane/DCM is commonly used for organics

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Table 4. Aliphatic and Aromatic Fractions, Mean Concentration Extracted, Precision, and Bias for TPH DRO, KRO, MRO, and Texas Risk Bandings[a]

	aliphatic hydrocarbons				aromatic hydrocarbons			
carbon band	mean, mg kg^{-1}	precision, mg kg^{-1} (% RSD)	bias mg kg^{-1}	bias %	mean mg kg^{-1}	precision, mg kg^{-1} (% RSD)	bias, mg kg^{-1}	bias, %
TPH	160	29 (18)	100	0.1	166	27 (16)	104	4
DRO	83	12 (15)			84	14 (16)		
KRO	31	5 (15)			12	2 (14)		
MRO	77	13 (17)			89	15 (17)		
$>C_8 \rightarrow C_{10}$[b]	10	2(16)						
$>C_{10} \rightarrow C_{12}$	10	2 (15)			8	2 (22)		
$>C_{12} \rightarrow C_{16}$	21	3 (16)			29	6 (20)		
$>C_{16} \rightarrow C_{21}$	22	4 (18)			33	5 (16)		
$>C_{21} - C_{35}$	77	14 (18)			94	16 (17)		

[a] Certified reference materials for aliphatic and aromatic fractions are not available consequently the spiked matrix data were used to determine the accuracy and precision of the method. The level of spike used throughout was 160 mg kg^{-1}. [b] PAH mixed used to spike the soil contained no aromatic PAH $>C_8-C_{10}$ fraction

extraction.[10,23] Here, the extraction of field moist samples can suffer interference from water when hydrophobic solvents (hexane and DCM) are used, reducing extraction efficiencies. Within the method described in this paper, acetone, a hydrophilic solvent, allows penetration and extraction of contaminants from field moist samples, simultaneously disrupting the soil matrix and enhancing extraction rates. This, followed by the addition of hexane, enables the extraction of nonpolar compounds. This initial use of a polar solvent negates the need for oven or freeze-drying, which has been shown to reduce extraction efficiencies,[13,24,25] particularly for the lower molecular weight equivalent carbon fractions. The effectiveness of this step in overcoming this interference from water has been reported elsewhere.[13,24]

The effectiveness of polar solvents such as acetone was also shown by Schwab et al.,[22] when investigating the effect of solvent, soil type, extraction cycles, soil quantity, and aging on the efficiency of mechanical shaking. The authors found that soil moisture played a key role and of the solvents studied acetone was the least effected by soil moisture and type.

Banjoo and Nelson[13] optimized an ultrasonic extraction procedure for the determination of PAHs and aliphatic hydrocarbons ranging from C_{12} to C_{24}, in sediments. This was compared against a reflux with the methanolic KOH method. The investigation showed that ultrasonic extraction of dried sediment with acetone/hexane mix (1:1) gave a concentration of the PAHs studied comparable to the reflux method, with lower variation in the reproducibility. The advantage of using acetone prior to the addition of other solvents was highlighted. The authors found that extraction efficiency increased when samples were initially sonicated with acetone only prior to addition of hexane. Additionally, no increase in efficiency was seen upon increasing extraction duration from 30 to 60 min, and the optimum number of extraction cycles was four.

The effect of solvent choice has also been demonstrated by Shin and Kwon[21] and Sanz-Landaluze et al.,[14] where acetone/DCM (1:1, v/v) and hexane, respectively, were shown to be the solvents of choice during sonication.

Bergknut et al.[24] compared pressurized liquid extraction (PLE) to Soxhlet extraction and also assessed the effects of other parameters of the PLE process. The effects of different organic solvents, pretreatment, and extraction time on the availability of PAHs extracted by PLE was assessed by sequentially extracting soil in water, methanol, 1-butanol, acetone, *n*-hexane, and toluene by PLE. Here the sample was extracted using the solvents one after the other. PLE extraction using methanol demonstrated equivalent extraction efficiency in 14 min as a 2-h toluene Soxhlet extraction. The studies highlighted the different solvents' affinity for different molecular weight PAHs. Toluene and acetone extracted roughly even concentrations of all PAHs tested in the study comprising 2-, 3-, 4-, and 5-fused rings, whereas 1-butanol extracted higher concentrations of high molecular weight PAHs (>4- and 5-fused rings).

Many of the methods currently in use for the analysis of weathered petroleum hydrocarbon-contaminated soils incorporate, where necessary, a sample cleanup method.[1,25,26] In some cases, methods will, in the same step, fractionate a sample into aliphatic and aromatic fractions.[1,26] Risk assessments are increasingly evaluating aliphatic and aromatic compounds separately; therefore, it is important that this is incorporated into methods not only to satisfy the risk assessment requirements but to ensure the results are not skewed by the presence of biogenic TPH. The method described here uses a microscale silica gel column chromatography method to fractionate extracts into aromatic and aliphatic fractions and where required remove interfering polar compounds.

Comparison against other available methods is helpful in evaluating the applicability of a method to the extraction of weathered hydrocarbons in soil on a broader analytical scale, enabling its position within the group of weathered hydrocarbon soil extraction methods to be defined. Alternative methods have been demonstrated to give a range of efficiencies from 75 and 77% for supercritical fluid extraction[15] and Soxhlet,[27] respectively, up to ≥97 and 99% for accelerated solvent extraction[15] and microwave-assisted extraction,[27] respectively. In this study, a

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minimum recovery of ≥95% has been demonstrated with maximum recoveries in the range >99%, easily positioning this methods within the best of the alternatives to Soxhlet methods.

The method is compatible with the current risk assessment frameworks, allowing for carbon banding and class fractionation. The method is faster than a typical Soxhlet method, allowing 24 (or more depending upon size of centrifuge and sonic bath) samples to be extracted within ~70 min. If no cleanup/fractionation step is required, extracts can be directly analyzed by GC/MS without further evaporation. Soxhlet methods can take between 2 and 24 h (depending on the protocol), often produce relatively dirty samples requiring sample cleanup, and often require sample evaporation. Soxhlet also requires more glassware that is fragile and comparatively expensive to that used in sonication. Soxhlet extraction protocols can require up to 250 mL of extracting solvent, whereas the sonication method described here uses 40 mL. Lower solvent consumption not only reduces costs but reduces the environmental impact of their subsequent disposal and health risks to the operator. Other authors have had success with adapted sonication techniques. In comparing USEPA Methods 3540 (Soxhlet) and 3550 (Sonication), for example, Ilias[28] presented a rapid fuel isolation, identification, and quantitation method for TPH in soils, reportedly one-third of the cost of conventional Soxhlet techniques. Our work reinforces this observation as the cycle time of the sequential ultrasonic method presented here was good as most the apparatus was used once and disposable, keeping capital outlay low and minimizing cross-contamination.

CONCLUSIONS

This sequential ultrasonic extraction method for contaminated soils allows high efficiency for several levels of analysis, TPH concentration ranges, various hydrocarbon banding, aliphatic and aromatic fractions (with and without hydrocarbon banding), and specific target compound identification. The extraction method is the same for all the different levels of analytical detail achievable; here the use of column chromatography and GC-FID and GC/MS integration techniques allows for the additional data to be easily extrapolated. Thus, this method meets the needs of the current risk assessments while also enabling the provision of data important for bioremediation studies.

We believe that the ultrasonic solvent extraction method described here is an improvement on conventional methods, as it saves time and lowers solvent consumption. Further, there are no evaporation steps preventing the potential loss of front end hydrocarbon bands, and the use of water partitioning facilitates an effective solvent exchange prior to fractionation. The method involves fewer handling steps, and disposable apparatus eliminates potential cross-contamination. Importantly, it is easy and simple to reproduce.

The method is also environmentally friendly, due to its reduced chlorinated solvent usage. The method has shown a good potential for implementation as a standard method, potentially capable of providing (through use) further insight and knowledge to the contaminated land sector.

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MULTI-PHASE PARTITIONING AND CO-SOLVENT EFFECTS FOR POLYNUCLEAR AROMATIC HYDROCARBONS (PAH) IN AUTHENTIC PETROLEUM- AND CREOSOTE-CONTAMINATED SOILS

Michael G. Zemanek,[a] Simon J. T. Pollard,[b] Sandra L. Kenefick[c†] and Steve E. Hrudey[c*]

[a]*Contaminated Sites Decommissioning Branch, Chemicals Assessment and Management Division, Alberta Environmental Protection, 9820 - 106 Street, Edmonton, Alberta, Canada, T5K 2J6*

[b]*Environmental Strategy Directorate, Scottish Environment Protection Agency, Head Office, Erskine Court, The Castle Business Park, Stirling FK9 4TR, Scotland, UK*

[c]*Eco-Research Chair in Environmental Risk Management, Environmental Health Program, Department of Public Health Sciences, Faculty of Medicine, University of Alberta, Edmonton, Alberta, Canada, T6G 2G3*

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Abstract

The residual oil phase, present at substantial levels in hydrocarbon-contaminated soils, was found to be the principal medium for retention of polynuclear aromatic hydrocarbons (PAH). Using authentic petroleum and creosote-contaminated soils containing 2 6% w/w solvent extractable matter, individual PAH were shown to exist in the oil phase at values between 84 and 95% w/w of the total mass of each compound in the system, with the exception of naphthalene (70% w/w). Evaluation of the phase partitioning of PAH in creosote-contaminated soil confirmed that PAH were predominantly in the creosote oil phase, with substantially lower proportions associated with soil organic matter and soil water. In the aqueous phase, solubility enhancement was observed for PAH with the degree of enhancement more evident for the hydrophobic PAH. A normalised solubility enhancement factor (ESF') was derived to illustrate the combined effect of increased PAH solubility in the aqueous phase. Values of log ESF' varied from −4.97 (naphthalene) to 0.09 (benzo[ghi]perylene). The findings suggest limitations exist for successful remediation of PAH contamination in the soils evaluated and indicate that the focus of remediation must be on the residual oil phase if total PAH are to be removed. © *1998 Elsevier Science Ltd. All rights reserved*

INTRODUCTION

The presence of polynuclear aromatic hydrocarbons (PAH) at hydrocarbon-contaminated waste sites often drives the processes of risk assessment and remediation because these compounds are persistent in the environment, they exhibit documented carcinogenic, mutagenic and toxic effects, and because stringent assessment criteria have been developed for their control (Hrudey and Pollard, 1993). PAH are well-recognised as constituents of hydrocarbon oils. Because they are non-polar and hydrophobic, they reside primarily in the residual oil phase at these sites, although they may partition to other organic phases such as soil organic matter (SOM). An understanding of the behaviour and distribution of hazardous components within the oil–soil–water matrix at oil-contaminated sites is fundamental to evaluating human, animal and plant exposures and risks, for predicting air, soil and groundwater conditions and ultimately for selecting remediation strategies (Sims, 1990; Pollard *et al.*, 1992).

The distribution of individual PAH between oil, soil and water can be predicted by extending the isotherm models developed for two-phase systems to the three phase 'oil–soil–water system' encountered at oil-contaminated sites. The relative concentrations of PAH between each of the three distinct phases provides an explicit measure of the propensity for PAH to exist in each phase and yields information for predicting treatment potential, contaminant migration, biological uptake and human exposure. In this paper, we examine the chemical partitioning of PAH in a multiphase soil environment using authentic contaminated soils obtained from petroleum and creosote sites in Alberta, Canada.

The ratio of equilibrium concentrations of a solute partitioned between two immiscible solvents under steady-state conditions is constant, and independent of relative volumes. The Nernst Distribution Law, for two liquid phases, and Henry's Law, for a gas and a liquid phase describe this linear relationship for the partitioning of small amounts of solutes between two immiscible phases. In general, for a system at equilibrium:

*To whom correspondence should be addressed.
†Present address: Department of Chemistry, Okanagan University College, 3333 College Way, Kelowna, BC, Canada, V1V 1V7.

$$K = \frac{C_1}{C_2} \quad (1)$$

where K is the partition coefficient and C_1 and C_2 are equilibrium solute concentrations in their respective phases. For the oil-contaminated soil environment, both oil and SOM can act as organic phases in a water/immiscible 'solvent' partition model (Hamaker *et al.*, 1972; Chiou *et al.*, 1979; Karickhoff *et al.*, 1979; Means *et al.*, 1979).

Soil/water partitioning for hydrophobic compounds, including PAH, is linear over a broad range of concentrations. The behaviour is described by the partition coefficient:

$$K_p = \frac{X}{C} \quad (2)$$

where K_p is the soil-water partition coefficient; X, the equilibrium concentration of sorbate bound to the sediment; and C, the equilibrium concentration in the water phase. Departure from isotherm linearity occurs when aqueous concentrations typically approach 60 to 70% of a compound's saturated water solubility. K_p values can be related to the organic carbon content of the soil organic matter and standardized for a given soil fraction using the relationship:

$$K_{oc} = \frac{K_p}{f_{oc}} \quad (3)$$

where K_{oc} is the organic carbon-water partition coefficient; and f_{oc}, the fraction of organic carbon in the soil. K_{oc} is considered to be a unique property of the compound being sorbed, implying that sorption of PAH is relatively independent of other sorbent related properties of the soil, such as ion exchange capacity, pH and clay mineralogy. A considerable research effort has been based on this premise and sorption models developed around the concept of SOM as a homogenous 'solvent' for hydrophobic compounds in soils (Gauthier *et al.*, 1987; Rutherford *et al.*, 1992). However, the chemical nature of SOM itself appears to have some degree of control over the binding of PAH. Organic matter associated with larger particle size soil fractions is significantly less effective as a sorbent than that associated with finer particle sizes, suggesting a stronger affinity of the organic compound for organic matter in later stages of decomposition (Karickhoff *et al.*, 1979; Evans *et al.*, 1990).

With respect to oil phase partitioning, an analogous situation exists. Free oil and 'residual saturation' in the unsaturated zone can both be treated as a homogenous partition medium or as a mixture of co-solvents. The complexity, varying solubility and degree of weathering for the oil phase will influence the distribution of PAH in the aqueous phase. At, or near waste disposal or spill sites, soil pore water is most likely to be a mixture or emulsion of water and several organic co-solvents (Rao *et al.*, 1985; Rao, 1990). Fu and Luthy (1986*a*,*b*) demonstrated that an increase in the volume of miscible solvent in an aqueous phase produces a semi-logarithmic increase in solubility of PAH and attending decrease in soil sorption. The level of enhanced solubility caused by co-solvents for individual non-polar solutes appears in proportion to the solute hydrophobicity. It follows that co-solvents may enhance the solution of 'low solubility' (i.e. more hydrophobic) PAH in the water phase to a greater extent than PAH of 'higher solubility'.

Movement of oil in soil and subsequent entrapment in the soil matrix creates a residual organic phase from which PAH can potentially distribute into fixed SOM or into aqueous solution. SOM has been shown to be a significant medium for the uptake of PAH but, by its very hydrophobic nature and as the source of PAH in the soil, the residual oil phase itself acts as the primary sink for PAH. Sun and Boyd (1991) have suggested that a threshold exists at which the oil content in soil reaches a critical level and forms a discrete sorptive phase highly effective in removing hydrophobic compounds from aqueous solution. These workers determined that 0.1% w/w oil (1000 mg kg^{-1}) in soil is sufficient for the oil phase to function as a distinct partitioning phase, separate from SOM. In its simplest form, a relationship based on partition theory may exist whereby the concentrations in the oil and SOM phases can be expressed as:

$$\frac{M_{po}}{V_o} = K\frac{M_{ps}}{M_s} \quad (4)$$

where $\frac{M_{po}}{V_o}$ is the concentration of the PAH in the liquid organic phase (μg ml^{-1}); $\frac{M_{ps}}{M_s}$ the concentration of the PAH in the solid soil phase (μg g^{-1}); M_{po} the mass of PAH existing in the liquid organic phase (μg); V_o the volume of liquid organic phase (ml); M_{ps}, the mass of PAH adsorbed by the soil (μg); M_s, the mass of soil (g); and K, the liquid organic phase/soil partition coefficient (g ml^{-1}). Rearranging (4):

$$M_{po} = (K)(M_{ps})\frac{V_o}{M_s} \quad (5)$$

For the purposes of the experimental rationale explained below, it is useful to express this equation and view the mass fraction of PAH in the oil phase as a relationship between the volume of oil and the mass fraction of PAH sorbed on soil:

$$\frac{M_{po}}{M_T} = (K)\frac{M_{ps}}{M_T} \bullet \frac{V_o}{M_s} \quad (6)$$

where M_T is the total mass of PAH in the system (μg).

Evaluation of these relationships and parameters for authentic contaminated site soils yields important

information as to the direction of partitioning in multi-media systems, hence valuable data with respect to exposure assessment. We discuss our rationale for the experimental design and our approach below.

METHODS

Experimental rationale

PAH-contaminated soil contains PAH dissolved in the oil and pore water phases, and sorbed on SOM. These PAH are at indeterminate levels because neither the oil nor soil can be independently extracted for quantitative analysis. However, using an approach analogous to that for 'standard additions' in analytical chemistry, the volume of the oil phase (V_o) can be artificially increased by batch equilibration of the soil with a small amount of non-polar organic solvent, such as dichloromethane (DCM), which is completely miscible with the oil and easily separated by centrifugation. Miscibility between oil and DCM implies that the two liquids have a similar non-polar nature. Addition of DCM causes a shift in the soil's equilibrium countered by a change in PAH concentration in SOM. At equilibrium, the organic DCM dissolves all organic compounds from the residual free oil phase plus some organics partitioned from the fixed SOM, because the hydrophobic solutes have a greater affinity for the additional, non-polar solvent (Sun and Boyd, 1991). Consequently, the total mass of PAH in the combined organic liquid phase (M_{po}) would increase from the original soil condition. A plot, based on Equation (6), of the mass fraction of PAH in the liquid organic phase against the volume of added organic liquid, standardized to the weight of soil, can then be constructed from a series of soil batch equilibria with known and varied volumes of added solvent followed by mass quantitation of PAH in the solvent phase. The PAH existing in the original oil phase can then be estimated by back extrapolation, as in a 'standard additions' method, to the original condition of the soil where no organic solvent is added.

Site descriptions

Soil samples from five priority hydrocarbon waste sites in Alberta were used for investigation (Pollard *et al.*, 1992). An abandoned oilfield battery site in east central Alberta was selected as representative of similar plants operating in the 1940s–1950s. At these sites, crude oil was dewatered and desalted, lighter fractions removed for further processing off-site and the residual heavy oil process wastes disposed of on-site, typically in unlined pits. Wastes identified at this site include spilled crude oil, flowing heavy oil seepage and consolidated asphaltic material. Creosote-contaminated soils were obtained from the process area of a former wood-treatment facility in central Alberta which, over a period of 60 years, used pentachlorophenol, coal-tar creosote and chromated copper arsenate treatment solutions for wood preservation. Surficial soils comprising the 'drip pad' of the process area were highly contaminated with creosote solutions, most visibly in front of the creosote pressure treatment retorts.

Sampling and analysis

On-site sampling and sample preparation of soil sub-samples has been reported previously (Pollard *et al.*, 1992). Approximately 10 to 20 g of soil was Soxhlet extracted with 150 ml of double distilled DCM solvent (16 h). Extracts were dried through a Na_2S0_4 column and concentrated to < 50 ml on a rotary evaporator at 30°C. Extracts were washed into 50 ml volumetric flasks, brought up to volume, then stored in Teflon lined screwcap vials at 4°C until required. Ten millilitre aliquots of concentrate were placed in shallow, preweighed aluminum dishes and allowed to dry in a fumehood for approximately 1 h for complete evaporation of the DCM. Recovery of solvent-extractable organic maker was calculated from:

$$\% \text{ solvent extractable matter} = \frac{(M_{DE} \times RFE)}{M_s} \quad (7)$$

where M_{DE} is the mass of dried extract (g); RFE, the reciprocal of the fraction of the whole extract used in analysis (50 ml 10 ml^{-1} = 5); and M_S, the mass of soil used in Soxhlet extraction (g). A Florisil solid-phase extraction (SPE) cartridge was conditioned with two column volumes of DCM and dried. A 1-ml aliquot of extract was applied and the cartridge eluted with three column volumes of DCM. The eluate was reduced by N_2 blow-down and exchanged into 1 ml hexane to precipitate interfering asphaltenes. Extracts still contained interfering aliphatic and polar compounds requiring removal by further alumina column cleanup. A 10×254 mm champagne column was packed with approximately 10 g of 80–200 mesh alumina activated at 225°C for 16 h. The packing was topped with 1 cm of Na_2S0_4 and conditioned with 50 ml hexane. Extracts from the preceding Florisil cleanup, were deposited on top of the packing, followed by three 2 ml hexane rinsings of the vial containing the extract. The column was then washed with a final 10 ml volume of hexane. All eluate from the hexane application was discarded. PAH were then desorbed with 100 ml DCM. These eluates collected were reduced to approximately 5 ml by rotary evaporation and N_2 blowdown.

Concentrations of PAH in 1 ml of cleaned extracts were determined on a Hewlett Packard 5890 gas chromatograph (70°C to 280°C; 10°C min^{-1}) fitted with a 30 m×0.25 mm i.d. DB-1301 (J&W Scientific) column of 0.25 μm film thickness connected to a 5970 mass selective detector (GC/MS). Major ions and two minor ions of each PAH were monitored using selected ion monitoring (SIM) and analyte quantitation was based on the signal response of the major selected ions for each PAH compound compared to a 5-component deuterated internal standard (Supelco cat. #4-8902) which was added prior to extraction.

Compound recoveries were determined in triplicate on 20-g sub-samples of two standard sediments (HS-3

and HS-6; National Research Council). Extracts were spiked with the deuterated internal standard and the 16 PAH quantified by GC/MS. Extracts of these sediments were found to be relatively free of interfering analytes and cleanup was not necessary prior to analysis. Additionally, PAH analyte levels in the standard sediments were cross-analyzed by thermal desorption for confirmation of the efficiency of the Soxhlet extraction. The efficiency of the Florisil and alumina cleanup was examined by running an extract from a creosote-contaminated site through the Florisil and the combined Florisil-alumina cleanup method. The original and cleaned extracts were analyzed using SIM GC/MS. Similarly, recovery from the cleanup procedure was checked by running a 16 component nondeuterated PAH standard (Supelco cat. #4-8905) in DCM through the Florisil cleanup and the combined Florisil-alumina cleanup procedure. The original standard and resulting cleaned extracts were analyzed by GC/MS to quantify possible losses in each cleanup step.

Quantitation of PAH in oil and soil phases for creosote-contaminated soil

Creosote-contaminated soil (CCS) was chosen for the study of multiphase partitioning of PAH in soil after preliminary evaluations exhibited high levels of the 16 USEPA priority PAH. To evaluate required equilibration times, batch experiments were performed on the CCS with DCM at a 1:8 weight ratio. The solvent and soil were combined in 35-ml centrifuge tubes and mixed using a rotary tumbler at 20°C for 12, 24, 48 and 72 h. Mixtures were centrifuged at 2500 rpm for 1 h and a 200-ml aliquot extracted and cleaned for GC/MS analysis. Analysis on the CCS soil samples in a soil/organic solvent phase system allowed examination of the differences in PAH concentrations between the oil and soil organic phases. Approximately 10-g sub-samples of CCS were combined with varying volumes of oil-miscible solvent (DCM) in 35 ml centrifuge tubes. The lowest feasible soil:solvent weight ratio of 1:0.5 was visually determined by progressively adding solvent to just saturate the soil system when agitated. Saturation of the soil with DCM was imperative so as to dissolve the entire free oil phase and maintain homogeneity of the organic liquid. Triplicate samples of soil:solvent weight ratios ranging between 1:0.5 to 1:8 were brought to equilibrium at 20°C in a shaker over a 72-h period. Individual tubes were then centrifuged at 2500 rpm (1 h). Supernatants were drawn off and analyzed by GC/MS for 16 PAH. The remaining slurry in the tube was Soxhlet-extracted and the PAH quantified for mass balance. PAH concentrations from the Soxhlet extraction were corrected for the analyte mass that remained in the solvent volume that could not be removed after centrifugation. Total PAH, liquid organic phase PAH and soil bound PAH concentrations were evaluated by this method, the principal assumption being that the difference between the total mass of PAH and the mass of PAH in the solvent was equivalent to the mass of PAH remaining soil bound.

Quantitation of PAH in the aqueous phase for creosote-contaminated soil

Air dried aliquots of DCM extracts, derived from the Soxhlet extraction, were heated with the soil at 103°C for 16 h. The weight difference between the soil in the original state and the oven dried condition was attributed to 100% w/w water loss plus loss from all volatilized organics. Field capacity of the CCS soil was determined by saturating the soil in excess distilled/deionized water (DDW). After a period of one week, approximately 100-g samples of the over-saturated soil were loaded onto glass funnels lined with a pre-wetted filter and the water allowed to drain under gravity. Corrected water contents were determined on the soil when gravitational flow halted. The amount of water added to bring the soil to field capacity was determined by difference. DDW was artificially added to four glass jars, each containing approximately 500 g of a CCS, to the point of field capacity. The jars were turnbled at 20°C and equilibrated over 7 days. The resulting slurry was centrifuged at 10 000 rpm leaving an aqueous supernatant that was drawn off and passed through a 0.45 μm cellulose nitrate filter. Triplicate 10-ml aliquots of the filtrate were extracted with DCM, dried over sodium sulphate and concentrated to 1 ml. The concentrated extracts were then subjected to GC/MS analysis for PAH.

RESULTS AND DISCUSSION

Soxhlet extraction efficiencies

Recoveries of PAH analytes from the standard reference sediments are shown in Table 1. Analyte concentrations from Soxhlet extraction revealed recoveries from 50 to 180% w/w, with the exception of acenaphthylene (246% w/w and 236% w/w). This range in PAH recoveries is considered typical of heavy, weathered oil matrices. PAH in the standard soil extracts were not separated from the bulk solvent extract by cleanup prior to GC/MS analysis, and interferences from co-eluting peaks of additional organic compounds present may be responsible for deviations in recovery, particularly the case for acenaphthylene. Thermal desorption confirmed the efficiency of the Soxhlet extraction with similar recoveries generally ranging between 50 to 180% w/w (Table 1). Acenaphthylene recovery by thermal desorption in both sediments (1133% w/w and 1090% w/w) was inconsistent with the reference concentrations provided by the NRC. For most PAH analytes, recoveries by thermal desorption were typically greater than those recovered by solvent extraction, but differences were minor.

Solvent extractable oil contents and concentrations of PAH in soils collected at five petroleum- and creosote-contaminated sites are shown in Table 2. Oil contents in individual samples ranged between 2 and 6% w/w. PAH concentrations in two soil samples collected from 'hot-spot' locations at the creosote-contaminated site (site 2) are also shown in Table 2 (samples CSS-1 and CSS-2).

Table 1. Soxhlet extraction and thermal desorption recoveries of two standard NRC reference sediments

	NRC reference soil HS-3					NRC reference soil HS-6				
	NRC concentration ($\mu g\ g^{-1}$)	Soxhlet recovered[a] concentration ($\mu g\ g^{-1}$)	Thermal desorption[b] concentration ($\mu g\ g^{-1}$)	Soxhlet recovery (%)	Thermal desorption recovery (%)	NRC concentration ($\mu g\ g^{-1}$)	Soxhlet recovered[a] concentration ($\mu g\ g^{-1}$)	Thermal desorption[b] concentration ($\mu g\ g^{-1}$)	Soxhlet recovery (%)	Thermal desorption recovery (%)
Naphthalene	9	8.3 ± 0.2	12.6 ± 1.2	92.7	139.4	4.1	4.5 ± 0.08	9.5(single)	110.7	231.7
Acenaphthylene	0.3	0.7 ± 0.03	3.4 ± 0.5	245.5	1133.3	0.2	0.4 ± 0.02	2.0 ± 0.6	235.7	1070.2
Acenaphthene	4.5	4.2 ± 0.2	5.9 ± 0.6	93.3	130.4	0.2	0.2 ± 0.01	0.2 ± 0.06	66.1	104.3
Fluorene	13.6	11.1 ± 0.4	11.4 ± 0.5	81.3	83.6	0.5	0.3 ± 0.03	0.7 ± 0.3	73.7	144.7
Phenanthrene	85	83.4 ± 1.3	83.6 ± 4.5	98.1	98.4	3	3.8 ± 0.08	3.8 ± 0.7	127.1	125.6
Anthracene	13.4	8.0 ± 0.4	23.3 ± 0.3	60	173.6	1.1	1.3 ± 0.06	3.7 ± 0.7	115.2	336.4
Fluoranthene	60	84.9 ± 2.8	59.4 ± 3.2	141.5	99	3.5	6.4 ± 0.1	3.5 ± 0.4	180.2	97.9
Pyrene	39	20.7 ± 0.7	41.3 ± 1.8	53.1	105.9	3	2.1 ± 0.4	3.1 ± 0.3	70.2	103.3
Benz[*a*]anthracene	14.6	16.1 ± 0.1	16.9 ± 0.9	110.6	116	1.8	2.0 ± 0.5	2.3 ± 0.2	109.9	125.9
Chrysene	14.1	9.6 ± 0.3	13.7 ± 0.5	68	97.2	2	2.3 ± 0.3	2.4 ± 0.2	116.6	118.3
Benzo[*b* + *k*]fluoranthene	10.5	13.1 ± 0.9	8.1 ± 0.6	124.3	76.8	4.2	4.8 ± 0.1	2.8 ± 0.2	114.6	66.2
Benzo[*a*]pyrene	7.4	5.3 ± 0.2	7.8 ± 0.6	72.1	105	2.2	1.8 ± 0.1	2.8 ± 0.4	83	125.8
Indeno[1,2,3-*cd*]pyrene	5.4	7.0 ± 0.7	3.0 ± 0.3	128.7	54.9	2	2.2 ± 0.2	1.2 ± 0.1	114.8	63.2
Dibenz[*a*,*h*]anthracene	1.3	1.7 ± 0.2	0.8 ± 0.1	134.2	61.3	0.5	0.7 ± 0.08	0.3 ± 0.04	143.5	55.8
Benzo[*ghi*]perylene	5	4.8 ± 0.4	6.5 ± 1.7	95.9	130	1.8	1.6 ± 0.2	2.7 ± 0.2	92.5	153.6

[a]Analyte concentration values based on triplicate soxhlet extractions on each standard reference sediment.
[b]Analyte concentration values based on triplicate thermal desorption analysis on each standard reference sediment.

Table 2. Typical polycyclic aromatic hydrocarbon concentrations and soil parameters in petroleum- and creosote-contaminated soils from five Alberta sites

	Contaminated site location						
	Site 1	Site 2			Site 3	Site 4	Site 5
PAH compound		CSS-1	CSS-2	CSS-3			
	PAH concentration ($\mu g\ g^{-1}$)						
Naphthalene	0.1	24.1	18.8	2.5	0.1	0.2	4.0
Acenaphthylene	N.D.	8.2	12.0	0.2	N.D.	N.D.	N.D.
Acenaphthene	N.D.	644.5	434.3	0.7	0.1	0.2	1.4
Fluorene	N.D.	344.6	445.6	0.4	N.D.	0.6	10.1
Phenanthrene	0.4	393.7	873.2	7.7	0.2	4.6	84.4
Anthracene	0.1	735.9	633.3	2.3	0.1	0.8	11.1
Fluoranthene	0.4	1363.7	967.8	59.6	0.1	0.6	9.9
Pyrene	9.6	1088.1	845.2	55.4	0.1	4.0	40.4
Benz[*a*]anthracene	1.3	176.5	136.2	10.9	N.D.	N.D.	12.5
Chrysene	3.5	251.0	181.6	28.6	0.2	4.5	25.9
Benzo[*b* + *k*]fluoranthene	1.3	225.4	177.9	29.6	0.1	0.5	7.1
Benzo[*a*]pyrene	2.1	96.0	63.7	8.7	0.1	1.0	9.8
Indeno[1,2,3-*cd*]pyrene	0.6	38.3	23.3	8.0	0.3	0.7	4.2
Dibenz[*a*,*h*]anthracene	0.4	6.6	5.1	2.8	0.2	0.6	4.3
Benzo[*ghi*]perylene	1.8	41.0	27.1	12.7	0.3	2.1	11.4
	Contaminated soil parameters						
Oil content (% w/w)	2.4	5.7	3.9	3.3	4.1	5.8	5.4
Natural water content (% w/w)	2.6	14.2	10.8	1.3	4.8	2.0	4.2
Field capacity (%)	—	40.1	37.8	—	—	—	—
Sand (% w/w)	18	51	42	84	38	60	67
Silt (% w/w)	40	24	27	11	43	32	30
Clay (% w/w)	42	25	31	5	18	8	4
Total organic carbon (% w/w)	4.5[a]	10.5[a]	6.4[a]	6.2[a]	12.6[a]	7.2[a]	19.4[a]
	1.6[c]	4.2[b]	2.8[b]		2.3[c]	0.9[c]	3.0[c]
		2.0[c]	2.0[c]				
pH	7.9	7.6	7.4	7.6	7.7	5.6	6.3

N.D.: Not detected (detection limit 0.05 $\mu g\ g^{-1}$).
[a]Total organic carbon of the soil including oil contamination.
[b]Total organic carbon of the soil excluding oil contamination (i.e. measured on extracted soil).
[c]Total organic carbon of similar uncontaminated background soil collected at the site.
All weights and concentrations are based on total dry soil weight.
Natural water contents and field capacities are corrected for organic volatiles lost through heating at 103°C during standard gravimetric analysis.
Creosote contaminated soil CSS-1 was chosen for the soil, oil and water multiphase PAH equilibrium partitioning study.

Both soils exhibited similar water contents and PAH levels, but displayed differing oil contents. Soil CSS-1 was chosen for oil, soil and water multiphase partitioning studies because it exhibited a higher oil content.

PAH distribution in the oil and soil phases

Soil/DCM batch equilibration at 1:8 soil/solvent weight ratios over various times show that PAH equilibrium concentrations were essentially reached in the first 24 h, with no subsequent increases in concentration (Table 3). Equilibrium concentrations of seven PAH with various ratios of volume of DCM to weight of soil are presented in Table 4. Naphthalene, acenaphthene, phenanthrene, anthracene, chrysene, benzo[*a*]pyrene and benzo[*ghi*]-perylene were examined because they represent a range of PAH chemical properties differing in molecular structure and aqueous solubility. The ratio of the mass of each PAH partitioned into the organic liquid phase to the total mass of PAH in the system, was plotted against the relative volume of solvent added (standardized to the weight of soil used in the analysis). A trend of an initial linear increase in PAH partitioning into the solvent phase with increasing solvent volume is observed. In accordance with the experimental rationale, the y-axis intercept of this linear trend (Fig. 1) provides an estimate of the total mass of PAH in the oil phase for the soil's original state, free of added solvent. These graphical relationships assume a two compartment partitioning model of liquid organic phase (oil and solvent) and a soil-bound SOM phase. In reality, the soil water represents a third phase into which PAH can partition. Due to their hydrophobic nature, however, the percentage of the total PAH in the water phase was subsequently found to be extremely low. Consequently, for the estimation of soil adsorbed PAH, water phase PAH concentrations were treated as negligible. The relative mass of PAH adsorbed by the soil can then be approximated by:

Table 3. Batch equilibrium time experiment for a creosote contaminated soil and solvent system

PAH compound	Equilibrium time (h)			
	12	24	48	72
	Concentration in the solvent (dichloromethane) phase[a] ($\mu g\ g^{-1}$)			
Naphthalene	14.4	15.3	20.5	20.5
Acenaphthylene	12.1	11.7	11.8	11.2
Acenaphthene	619.6	641.2	627.5	629.0
Fluorene	349.3	377.1	375.1	411.0
Phenanthrene	591.9	605.7	589.9	633.8
Anthracene	630.7	548.7	565.4	711.0
Fluoranthene	1613.3	1680.1	1617.6	1615.3
Pyrene	803.2	796.3	811.1	754.7
Benz[*a*]anthracene	176.8	186.8	181.4	184.7
Chrysene	203.4	207.3	201.4	207.6
Benzo[*b* + *k*]fluoranthene	136.3	131.7	130.5	129.5
Benzo[*a*]pyrene	69.9	66.6	64.2	67.3
Indeno[1,2,3-*cd*]pyrene	32.7	28.0	27.0	26.2
Dibenz[*a,h*]anthracene	11.6	15.1	17.5	9.7
Benzo[*ghi*]perylene	46.1	35.0	31.8	32.4

[a]Ratio of weight soil:weight solvent = 1:8.

$$\% \text{ PAH adsorbed by soil} \cong 100\% - \% \text{ PAH in oil phase} \quad (8)$$

Based on this assumption, individual PAH exist in the oil phase at values between 84 and 95% w/w of the total mass of each compound in the system, with the exception of naphthalene (70% w/w) the most water-soluble PAH tested. Therefore, sorption to soil organic matter was estimated to account for less than 5 to 16% w/w (30% w/w for naphthalene) of the total mass of PAH. The slope of the initial linear portion of the desorption curve represents the propensity of individual solutes to exist in the solvent phase, or to remain sorbed to the SOM complex. A positive slope indicates that partitioning from SOM into the liquid organic phase occurs with increasing solvent volume. Naphthalene, acenaphthene and phenanthrene represent the more water soluble of the 16 priority PAH compounds and each exhibited a positive increasing slope with increased solvent volume. Estimates of associations of these three compounds with the oil phase indicate that a decrease in aqueous phase solubility correlates with a greater association with the oil phase as would be expected (Tables 5 and 6). Conversely, the more hydrophobic PAH are less likely to be bound to SOM when an oil phase is present, because the direction of partitioning in the presence of hydrophobic oil medium is from SOM to the oil, and the more hydrophobic PAH should prefer the oil phase to SOM. An initial flat portion of the plot (Fig. 1) indicates the total mass of PAH in the organic liquid phase remains unchanged with increases in solvent volume. Benzo[*ghi*]perylene exhibits this tendency (Fig. 1(c)), signifying that either: (1) a large proportion of the compound already exists in the oil phase; (2) the quantities of SOM available in the soil to adsorb the PAH have little effect; or (3) the compounds are tightly or irreversibly bound to the SOM under the existing equilibrium conditions. If any of these circumstances were to exist, the amount of PAH existing in the oil phase might be more adequately estimated at higher solvent volumes, where errors and quantitative variation associated with losses through sample transfer and mass balance determination are at a minimum. Under such conditions, a maximum limit of PAH in the oil phase can be estimated. Table 4 (sample nos. 25 to 28) shows that possible maximum levels of acenaphthene, phenanthrene, anthracene and chrysene in the oil phase are greater than 97% w/w of the total PAH in the system, while naphthalene, benzo[*a*]pyrene and benzo[*ghi*]-perylene might be present in the oil at maximum values between 90 and 95% w/w. In cases where PAH adsorption to SOM is reversible by solvent equilibrium, however, near complete desorption of the PAH analytes from the SOM at higher solvent volumes likely occurs so that these maximum estimates may erroneously include some original SOM-bound PAH levels.

At higher DCM volumes, acenaphthene, phenanthrene, anthracene and chrysene become fully desorbed (Table 4, sample nos 25 to 28). Nearly 100% w/w of these PAH solutes originally present in the waste matrix partition into the solvent at volume solvent/mass soil ratios greater than 4.0 ml g^{-1} (Table 4). At higher DCM volumes, the curves for naphthalene, benzo[*a*]pyrene and benzo[*ghi*]perylene, however, are horizontal with solvent phase PAH values less than 100% (Fig. 2). This phenomena may be due to solvent-organic matter swelling interactions.

Lyon and Rhodes (1991) reported the swelling of various natural organic materials such as peat, pollen, chitin and cellulose in contact with various organic solvents. They described the swelling of these materials as a volumetric manifestation of bulk sorption of organic liquids into the macromolecular solid. Freeman and Cheung (1981) proposed a gel partition model for swelling of soil organic matter. They viewed the SOM as a non-polar humic-kerogen structure consisting of highly branched polymeric chains, connected by crosslinks to form a three dimensional, randomly oriented network. They further explained that solvent absorption will cause swelling of the network to create a gel-like structure that provides greater accessibility for organic solute diffusion into the non-polar gel. The solute partitioning between liquid and gel then depends on competing attractive effects due to solute–liquid and solute–gel interactions. Fu and Luthy (1986*b*) used this model to describe enhanced sorption of naphthalene in miscible solvent/water mixtures. They concluded that the solvent caused an organic maker swelling phenomena which improved accessibility of naphthalene to the nonpolar soil organic matter which impeded partitioning into the co-solvent phase. In the present study, complete desorption of naphthalene, benzo[*a*]pyrene and benzo[*ghi*]-perylene during batch equilibration may be obstructed by competitive sorption effects created by a solvent

Table 4. Solvent/soil ratios and weight percent PAH in solvent phase

Sample number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Wt soil(g)	10.7072	10.1931	12.3758	13.5103	11.2229	11.5407	12.1915	14.8358	16.5578	12.2214	11.1596	12.7679	12.1274	10.5288	11.8215	10.7635	10.7509	11.5792
Wt solvent(g)	5.3553	5.1356	6.1977	6.7508	7.5176	7.7186	8.1834	14.8358	16.5578	10.1142	9.2682	10.5944	12.1122	10.5329	11.8154	16.1693	17.3683	
Wt solvent/wt soil	0.50	0.50	0.50	0.50	0.67	0.67	0.67	1.00	1.00	0.83	0.83	0.83	1.00	1.00	1.00	1.50	1.50	1.50
Vol solvent/wt soil	0.66	0.67	0.66	0.66	0.88	0.88	0.89	1.32	1.32	1.09	1.10	1.10	1.32	1.32	1.32	1.98	1.98	1.98
	PAH in solvent phase/total PAH (%)																	
Naphthalene	75.3	67.4	78.4	81.3	76.8	71.3	69.8	83.0	87.7	75.3	75.0	74.5	71.0	77.4	82.3	80.2	84.4	81.0
Acenaphthene	88.1	83.4	93.8	94.1	90.2	91.4	90.0	89.5	95.6	91.6	90.9	91.7	91.8	93.0	94.0	95.7	94.7	94.5
Phenanthrene	96.0	91.8	97.4	97.1	94.1	91.6	92.7	91.3	96.9	94.1	94.5	93.9	94.3	94.7	93.2	97.4	97.0	96.3
Anthracene	88.2	86.3	92.4	92.1	85.9	90.1	85.4	89.8	95.9	87.8	89.1	85.9	89.4	88.9	88.9	94.6	95.0	93.5
Chrysene	99.0	92.9	98.0	97.4	92.0	91.8	96.2	90.0	95.4	94.2	96.6	97.6	97.3	95.0	92.9	95.5	95.3	96.1
Benzo[*a*]pyrene	109.9	87.5	81.7	77.9	82.4	87.2	87.0	81.5	82.4	87.3	89.7	91.7	89.5	85.7	83.1	96.4	95.7	92.0
Benzo[*ghi*]perylene	121.4	105.3	75.0	75.2	94.7	71.9	105.2	82.1	90.8	70.7	96.2	101.6	100.8	87.8	88.3	100.3	100.7	105.2

Sample number	19	20	21	22	23	24	25	26	27	28	Linear regression	
Wt soil(g)	11.4658	10.4589	10.5454	8.5423	7.6369	8.4563	7.9919	5.6446	6.8212	6.2472	y-intercept	Sample numbers for linear regression
Wt solvent(g)	22.9271	20.9402	21.0901	25.6498	22.9289	25.3599	39.9595	28.2230	54.5696	49.9776	(estimate of proportion of PAH in the oil phase (%))	
Wt solvent/wt soil	2.00	2.00	2.00	3.00	3.00	3.00	5.00	5.00	8.00	8.00		
Vol solvent/wt soil	2.64	2.64	2.64	3.96	3.96	3.96	6.60	6.60	10.56	10.56		
	PAH in solvent phase/total PAH (%)											
Naphthalene	86.9	85.2	84.0	82.7	85.8	88.0	92.9	91.5	90.7	90.7	70	1–21
Acenaphthene	96.9	96.1	96.9	97.7	99.5	99.5	100.3	101.2	99.5	98.6	88	1–21
Phenanthrene	96.9	96.9	96.9	98.4	99.3	99.7	99.2	99.7	98.5	98.5	93	1–24
Anthracene	94.5	94.5	94.4	95.4	98.6	98.5	99.0	98.7	98.4	97.1	87	1–15
Chrysene	97.8	97.0	98.2	98.7	98.8	99.1	98.7	99.5	97.1	97.6	96	1–18
Benzo[*a*]pyrene	86.8	84.6	87.7	90.3	89.6	90.7	95.8	92.3	95.1	93.1	84	1–24
Benzo[*ghi*]perylene	83.1	79.1	86.9	93.1	87.0	89.7	94.3	92.9	93.2	92.1	90	1–24

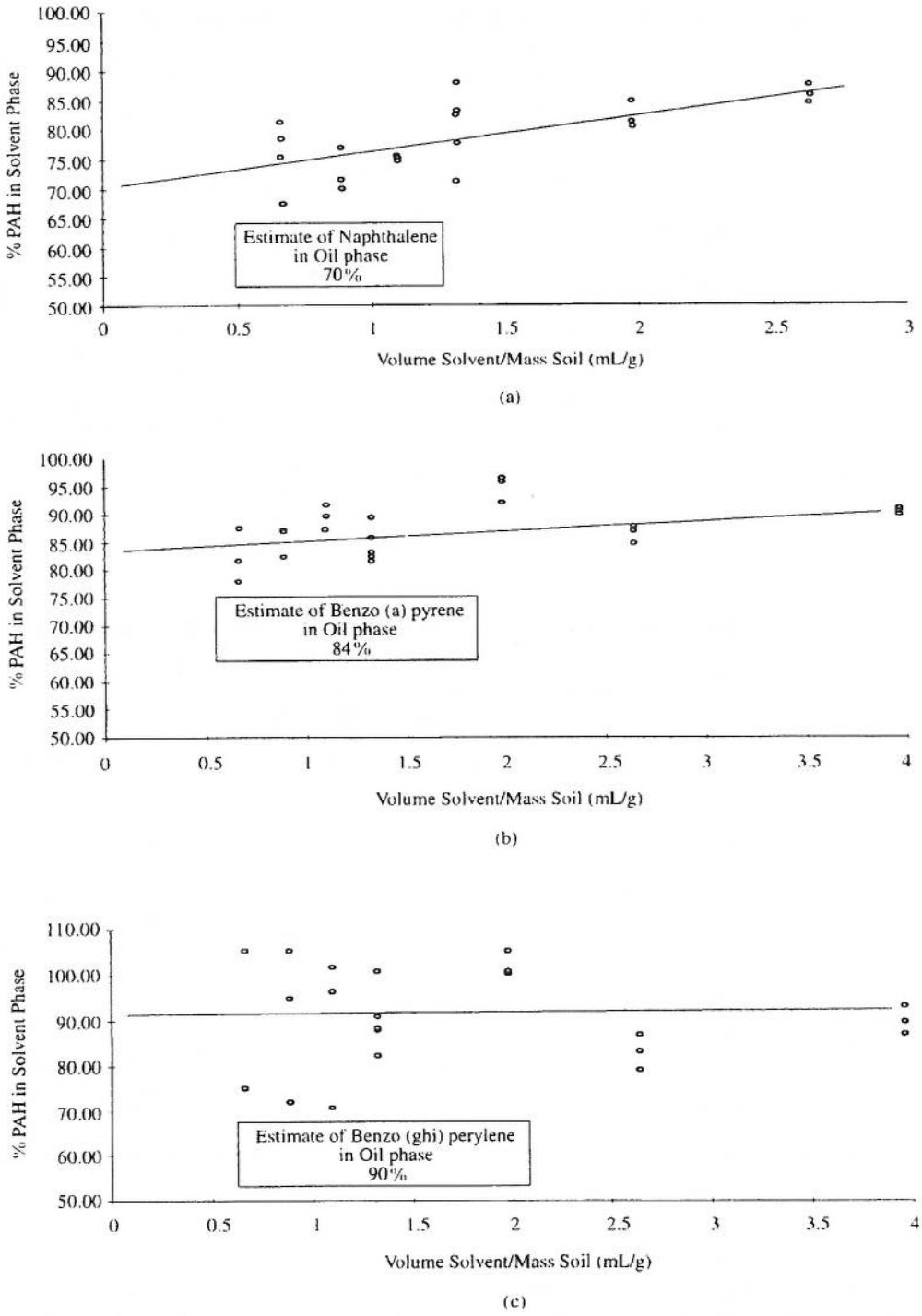


Fig. 1. Initial linear regions of PAH distributions in a soil/solvent equilibrium system: (a) naphthalene; (b) benzo[*a*]pyrene; (c) benzo[*ghi*]perylene.

(DCM) expanded SOM structure. Complete desorption occurs only when the matrix is subjected to Soxhlet extraction for mass balance, rendering the level portion of the batch desorption curve below 100%. Estimation of the PAH solute in the oil phase, however, is not perturbed by organic matter–solvent interaction. The initial linear portion of the desorption curve remains, allowing estimation of the PAH solute in the original oil phase (Fig. 1).

PAH distribution in the water phase

Results from batch equilibration of the CCS with water at the field capacity point are given in Table 5. The percentage of individual PAH in the water phase are low compared to the total PAH in the soil system (Table 6). This verifies that water phase concentrations can be neglected in eqn (8), as they would not significantly change estimated soil adsorbed values. Concentrations of PAH with water solubilities less than

Table 5. Enhanced solubility factors in the water phase of a creosote-contaminated soil

PAH compound	PAH concentration in the water phase Sm (μg ml^{-1})	Total PAH concentration in the soil (μg g^{-1})	Pure aqueous solubility Sw (μg ml^{-1})	Log Sw	Sm/Sw = ESF	log ESF	ESF′	log ESF′
Naphthalene	0.008	24.1	31.7	1.50	0.0003	−3.5894	0.00001	−4.97
Acenaphthylene	0.012	8.2	3.93	0.59	0.0030	−2.5295	0.00036	−3.44
Acenaphthene	0.269	644.5	3.93	0.59	0.0710	−1.1488	0.00011	−3.96
Fluorene	0.047	344.6	1.98	0.30	0.0239	−1.6210	0.00007	−4.16
Phenanthrene	0.026	393.7	1.29	0.11	0.0202	−1.6940	0.00005	−4.29
Anthracene	0.077	735.9	0.073	−1.14	1.0562	0.0237	0.00144	−2.84
Fluoranthene	0.312	1363.7	0.26	−0.59	1.2005	0.0794	0.00088	−3.06
Pyrene	0.243	1088.1	0.135	−0.87	1.7991	0.2550	0.00165	−2.78
Benz[*a*]anthracene	0.034	176.5	0.014	−1.85	2.3979	0.3798	0.01359	−1.87
Chrysene	0.050	251.0	0.002	−2.70	24.8593	1.3955	0.09904	−1.00
Benzo[*b* + *k*]fluoranthene	0.040	225.4	0.001	−3.00	40.0618	1.6027	0.17777	−0.75
Benzo[*a*]pyrene	0.016	96.0	0.0038	−2.42	4.2100	0.6243	0.04387	−1.36
Indeno[1,2,3-*cd*]pyrene	0.010	38.3	0.062	−1.21	0.1689	−0.7724	0.00441	−2.36
Benzo[*ghi*]perylene	0.013	41.0	0.00026	−3.59	50.2760	1.7014	1.22695	0.09

ESF solubility enhancement factor.
ESF′ normalised solubility enhancement factor.

Table 6. Summary of the distribution of selected PAHs in a creosote-contaminated soil

PAH compound	Pure aqueous solubility (μg ml^{-1})	Mass PAH in oil phase per g dry soil (μg g^{-1})	Mass PAH in soil phase per g dry soil (μg g^{-1})	Mass PAH in water phase per g dry soil (μg g^{-1})	Total mass PAH per g dry soil (μg g^{-1})	% PAH in each phase		
						Oil (%)	Soil (%)	Water (%)
Naphthalene	31.7	17.0	7.1	0.003	24.1	70.5	29.5	0.014
Acenaphthylene	3.93	—	—	0.005	8.2	—	—	0.057
Acenaphthene	3.93	565.1	79.2	0.112	644.5	87.7	12.3	0.017
Fluorene	1.98	—	—	0.019	344.6	—	—	0.006
Phenanthrene	1.29	365.7	28.1	0.010	393.7	92.9	7.1	0.003
Anthracene	0.073	643.1	92.8	0.031	735.9	87.4	12.6	0.004
Fluoranthene	0.26	—	—	0.125	1363.7	—	—	0.009
Pyrene	0.135	—	—	0.097	1088.1	—	—	0.009
Benz[*a*]anthracene	0.014	—	—	0.013	176.5	—	—	0.008
Chrysene	0.002	240.3	10.6	0.020	251.0	95.8	4.2	0.008
Benzo[*b* + *k*]fluoranthene	0.001	—	—	0.016	225.4	—	—	0.007
Benzo[*a*]pyrene	0.0038	80.8	15.1	0.006	96.0	84.2	15.8	0.007
Indeno[1.2,3-*cd*]pyrene	0.062	—	—	0.004	38.3	—	—	0.011
Benzo[*ghi*]perylene	0.00026	36.8	4.2	0.005	41.0	89.7	10.3	0.013

Note: PAH masses in all phases are normalized to the weight of dry soil. Water phase masses are given for the field capacity soil water condition.

phenanthrene (i.e. the higher molecular weight PAH) exist at values exceeding their pure aqueous phase solubility, indicating a solubility enhancement phenomenon at work. This is of concern at contaminated sites because water is a medium for migration of PAH and any solubility enhancement will augment contaminant transport. Unification of the individual microprocesses governing enhanced solubility by co-solvents and organic colloids in a genuine waste matrix may provide some insight into the solubility behaviour in the bulk aqueous phase.

The equilibrium partitioning of PAH and other aromatic constituents into water from complex mixtures such as coal tar, diesel fuel and gasoline can be reasonably approximated using a simplified expression of Raoult's law (see, for example, Lee *et al.*, 1992*a*,*b*):

$$C_w = x_o S_1 \tag{9}$$

where C_w is the compound's concentration in the aqueous phase (mol litre^{-1}), x_o, the mole fraction of the chemical in the organic phase (complex organic mixture); and S_1, the compound's aqueous solubility (expressed in mol litre^{-1}). Equation (9) assumes that water phase concentrations of organic compounds exist as a fraction of the aqueous solubility of the pure liquid chemical, but it does not account for co-solvent and colloidal solubility enhancement. An increase in solute solubility in soil water can occur by a change in solvency of the water or by direct partitioning to hydrophobic impurities dispersed in the water phase. The apparent solubility and the physical state of the solute in water is susceptible to modifications by interactions

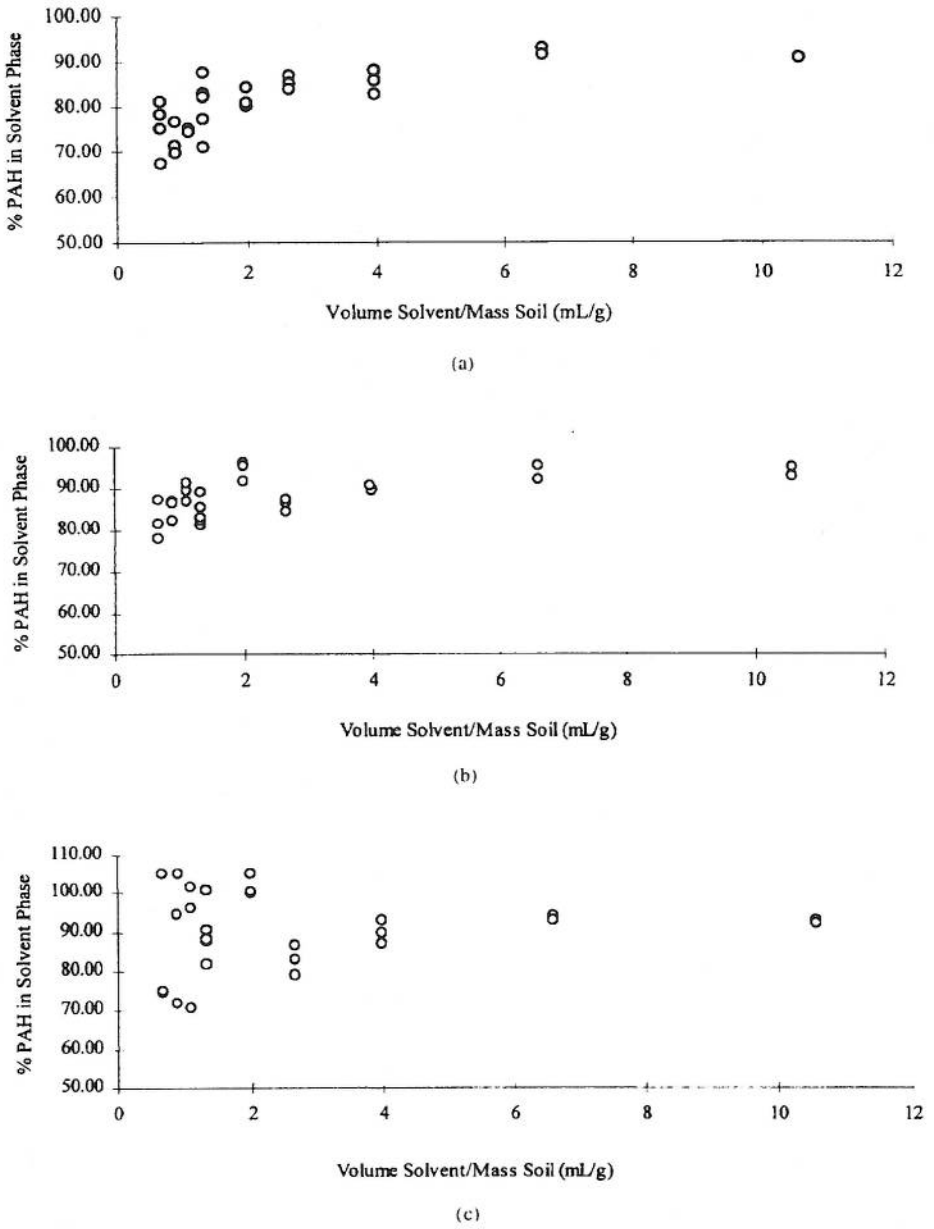


Fig. 2. PAH distributions (% w/w) in a soil/solvent equilibrium system: (a) naphthalene; (b) benzo[*a*]pyrene; (c) benzo[*ghi*]perylene.

with co-solutes such as dissolved humic and fulvic acids (Chiou *et al.*, 1986). Chiou *et al.* (1986) assumed a partition-like interaction occurs between relatively insoluble organic solutes and high molecular weight dissolved organic matter. The increase in solubility of an organic solute can then be described as:

$$S_w* = S_w + Xc_o \tag{10}$$

where S_w* is the apparent solute solubility in water containing dissolved organic matter (mg litre^{-1}); S_w, the compound's aqueous solubility (expressed in mg litre^{-1}); X, the concentration of dissolved organic matter in water (g litre^{-1}); and C_o, the mass of solute partitioned into a unit mass of dissolved organic matter (mg solute g^{-1} dissolved organic matter). Similarly, the enhanced solubility of sparingly soluble organic compounds such as PAH in a water co-solvent mixture can be predicted by a log-linear relationship (Fu and Luthy, 1986*a*,*b*; Rubino and Yalkowsky, 1987):

$$\log S_m = \log S_w + s.f \tag{11}$$

where S_m is the total enhanced solubility of the compound in a water-co-solvent mixture (mol litre^{-1}); S_w, the compound's aqueous solubility (mol litre^{-1}); s, the co-solvency power calculated from the solubilization curve (i.e. slope of log S_m versus f curve which describes the degree of solubility enhancement); and f is the volume fraction of co-solvent.

Generally, the solubility of most hydrophobic organic compounds follow a similar trend of increasing solubility with increasing volume fraction of co-solvent. But the degree of solubility enhancement depends on both the co-solvency power of the solvent(s) and its volume fraction (f) in the aqueous phase. Pinal *et al.* (1990) demonstrated that polar, miscible organic solvents (PMOS), such as *o*-cresol and methanol, significantly enhance organic compound solubility more than non-PMOS. While the non- PMOS dissolve PAH more readily, the PMOS can exist in the aqueous phase at greater concentrations, thereby increasing the volume fraction (f) of co-solvent in solution and enhancing PAH solubility to a greater degree, the resulting effect being a balance between these effects. Soluble phenolic compounds, like *o*-cresol, and heterocyclic compounds typically constitute approximately 15% w/w of creosote (Mueller *et al.*, 1989) and may act as co-solvents in this study. Researchers (Fu and Luthy, 1986*a*,*b*; Rubino *et al.*, 1987) have reported the degree of solubility enhancement observed to be greater for the more hydrophobic solutes.

The capacity of the liquid co-solvent phase to enhance dissolution of the hydrophobic compounds will cause an associated decrease in soil sorption. The partition coefficients of PAH have been shown to be inversely proportional to aqueous solubility in a co-solvent mixture with an increase in the volume fraction of co-solvent (Rao *et al.*, 1985; Fu and Luthy, 1986*b*). The decrease in the partition coefficient is predicted by the relationship:

$$\log K_s = \log K_w - a.s.f \tag{12}$$

where K_s is the solute equilibrium partition coefficient in a soil-co-solvent mixture; K_w, the solute equilibrium partition coefficient in a soil–pure water mixture; where a relates to the dominance of the solute's aqueous activity coefficient in partitioning to soil organic matter; and terms '$s.f$' in eqns (11) and (12) and 'XC_0' in eqn (10) both describe an incremental solubility enhancing effect that a specific solvent-modified water and dissolved organic matter can have on aqueous phase PAH concentrations. Under field conditions, it is difficult to identify and quantify dissolved organic matter and individual co-solvents in the complex waste matrix. The volume fraction of co-solvent (f) and concentrations of dissolved organic matter (X) are typically unknown parameters in complex contaminated matrices, but they remain the same for every individual contaminant in the waste matrix because they are properties of the bulk aqueous phase. Differences in solubility enhancement between individual solutes would then occur by variations in co-solvency power(s) and partitioning to dissolved organic matter (C_0), which are solute specific but also indeterminate in a genuine complex waste matrix. The whole solvating nature of the aqueous phase might be characterised empirically by a comparison of measured individual PAH concentrations in the aqueous phase with concentrations expected if mechanisms of solubility enhancement were not acting (i.e. pure water solubility). An empirical solubility enhancement factor representing the degree of solubility increase above the pure aqueous solubility can be defined by:

$$\mathrm{ESF} = \frac{S_m}{S_w} \tag{13}$$

where *ESF* is the enhanced solubility factor; S_m, the apparent PAH solubility in soil water phase (mg litre^{-1}) (measured); and S_w, the compound's aqueous solubility (mg litre^{-1}). Table 5 shows *ESF* values for 15 PAH quantified in the soil water of a creosote-contaminated soil at field capacity. As expected, solubility enhancement is generally greater in proportion to compound hydrophobicity and inversely proportional to pure aqueous solubility. The general trend (Table 5) demonstrates that solubility enhancement of the higher molecular weight PAH, such as benzo[*a*]pyrene and benzo[*ghi*]perylene, occurs to a greater degree than the more soluble, lower molecular weight compounds, like naphthalene, a behaviour similar to that observed by Fu and Luthy (1986*a*,*b*) and Rubino and Yalkowsky (1987).

The PAH solutes in the creosote-contaminated soil are present in excessive quantities, allowing for saturation of these components in the water phase. Extremely low concentrations of hydrophobic solutes existing in water extracts at other sites may not necessarily indicate that co-solvents are not present, but may signify low quantities available in the oil and soil phases or indicate preferential partitioning to that phase. Solubility enhancement is dependent on the concentrations of solute in the oil phase and the partitioning mechanisms restricting the desorption into the aqueous phase. Therefore, the ESF is limited by the PAH concentrations available in the soil and oil phase as governed by Raoult's law and partition theory. Dividing the ESF by the PAH concentration in the oil and soil phase (Table 5) will 'normalize' the solubility enhancement factor to account for variable individual PAH concentrations available in the waste matrix:

$$\mathrm{ESF}' = \frac{\mathrm{ESF}}{\text{total PAH mass in oil and soil phases per unit mass of soil}} \tag{14}$$

where ESF′ is a normalized enhanced solubility factor. The normalized ESF′ term is an empirical expression of two partitioning mechanisms transpiring in the soil matrix: (1) partitioning of the PAH solute between the soil/oil organic phase and the water phase and (2) enhanced solubility by a solvent/colloid modified water. The ESF' parameter and its logarithm represent a bulk phase 'averaging' of enhanced solubility by various components in the water, and competitive sorption by the soil and oil phase. Neither term differentiates between the mechanisms of enhanced solute solubility by co-solvency, organic colloids or oil micro-emulsions,

but do have use in describing the overall propensity for PAH to exist in the mobile water phase for a particular soil type and contaminant condition. Values of log ESF′ for the PAH examined in this study varied from −4.97 (naphthalene) to 0.09 (benzo[*ghi*]perylene) with the more positive values representing increased solubility enhancement.

CONCLUSIONS

Evaluation of phase partitioning of PAH in creosote-contaminated soil demonstrated that the PAH were predominantly found in the creosote oil phase, with substantially lower proportions found associated with soil organic matter and soil pore water. Substantial solubility enhancement was observed for PAH in the soil pore water with the degree of solubility enhancement substantially more evident for the more hydrophobic PAH. The observed relationship was consistent among the range of PAH studied.

These findings suggest substantial limitations will exist for successful remediation of the PAH contamination in the soils evaluated and the focus of remediation must be on the residual oil phase if total PAH are to be substantially removed.

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The fate of heavy oil wastes in soil microcosms I: a performance assessment of biotransformation indices

S.J.T. Pollard[a,*], M. Whittaker[1,b], G.C. Risden[2,c]

[a] *National Centre for Risk Analysis and Options Appraisal, Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF, UK*
[b] *Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK*
[c] *Geochem Group Ltd., Environmental Analytical Services, Chester Street, Chester, CH4 8RD, UK*

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Abstract

A controlled soil microcosm study was used to evaluate the performance of selected oil biotransformation indices using samples of Nigerian crude, a blended ballast oil and No. 6 fuel oil. Biotic losses were demonstrated through loss of solvent extractable matter (SEM) and changes in class fraction distribution in weathered soil extracts relative to sterilised controls. GC-EI MS peak identification and quantification was achieved for selected (Σ) *n*-alkanes, the isoprenoid alkanes norpristane (iC$_{18}$), pristane (iC$_{19}$) and phytane (iC$_{20}$), combined mono-substituted (1-, 2-, 3- and 9-) methylphenanthrenes (Σmethylphenanthrenes), combined dimethylphenanthrenes (Σdimethylphenanthrenes) and the hopane isomers 17α(H)21β(H)-hopane and 17α(H)21β(H)-30-norhopane. The [Σn-alkanes:17α(H)21β(H)-hopane] index was most sensitive to oil biotransformation and most accurately reflected depletion of oil from contaminated soils in this study. This index was found to be the most reliable for the No. 6 fuel oil saturates, dropping from 81.9 to 18.1 over the course of the 256-day microcosm study. In terms of sensitivity, and taking into account the results of an ANOVA analysis, the biotransformation indices most sensitive to oil biotransformation were (in order of decreasing sensitivity): [ΣC$_{14-28}$:17α(H)21β(H)-hopane] $\gg$ [ΣC$_{14-28}$:Σdimethylphenanthrenes] > [C$_{18}$:phytane]. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Biotransformation; Index; Microcosms; Natural attenuation; Petroleum hydrocarbons

* Corresponding author. Tel.: +44 171 6646832; fax: +44 171 6646836; e-mail: simon.pollard@environment-agency.gov.uk
[1] Present address: Golder Associates, 2180 Meadowvale Boulevard, Missassauga, Ontario, L5N 5S3, Canada.
[2] Present address: TES Bretby, P.O. Box 100, Bretby Business Park, Ashby Road, Burton-on-Trent, DE15 0XD, UK.

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1. Introduction

The ability to detect and monitor the biotransformation of petroleum in soil plays an essential rôle in the effective management of oil-contaminated land because: (a) biotransformation alters the composition of the source term and, consequently, the nature of hazard(s); (b) the fate and transport properties of free product components are altered by biotransformation and this has an impact on the output of exposure and risk assessments; and (c) the appraisal of natural attenuation and bioremediation as treatment options relies on the ability to demonstrate that contaminant biotransformation is in progress.

Chemical techniques for verifying biotransformation in situ are being developed by a number of researchers (Englert et al., 1993; Douglas and McMillen, 1996; Herbert et al., 1996; Voos et al., 1996). One approach involves comparing concentrations of assimilable components relative to 'internally conserved' compounds in the source term. These conserved compounds are usually recognised oil 'biomarkers' that are resistant to microbial attack. A ratio of the assimilable to the conserved compound(s) concentrations can be used as a weathering (or biotransformation) 'index' (Butler et al., 1991; Prince et al., 1994; Croft et al., 1995). For example, the depletion of *n*-alkanes can be monitored through evaluation of a [Σn-alkanes:17α(H),21β(H)-hopane] index, where a decrease in the value of the index over time is presented as evidence of oil biotransformation (Croft et al., 1995). Alternatively, individual compounds may be used for conveying information on the behaviour of the source term. For example, [nC$_{17}$:pristane] and [nC$_{18}$:phytane] ratios have been used as indices for indicating product ageing within contaminated groundwater plumes (Senn and Johnson, 1985; Christensen and Larsen, 1993).

As application of these indices progresses, a number of issues regarding their use is emerging. The assumed microbial recalcitrance of selected conserved internal markers, for example, has been questioned. As petroleum samples become highly weathered, both the isoprenoid biomarkers pristane and phytane, and the cyclic alkane biomarker 17α(H),21β(H)-hopane have been shown to biodegrade (Morris et al., 1996). The use of these indices has also been challenged because individual compounds have differing abundances, solubilities, transport and volatility characteristics across the range of oils released to the environment and because the validity of analytical methods used to determine the compounds of interest are extremely sample dependent (Madsen, 1991; Redican et al., 1996). These issues do not negate the use of biotransformation indices, but they do indicate a need to validate their use and assess their individual performance on a study-specific basis.

Our previous work has involved a performance assessment of some commonly used indices on reference oils (Whittaker and Pollard, 1997), but we now turn to a controlled biotransformation study using an accepted soil microcosm approach that allows verification of index performance under the dynamic conditions of authentic product loss and permits closer analytical scrutiny. Although the microcosm approach cannot reproduce the true subsurface conditions encountered at actual contaminated sites, it nevertheless provides a useful bench-scale means of controlling and studying the myriad of parameters that influence microbial degradation kinetics (e.g. temperature, water content and nutrients) to gain a greater insight into the overall process of oil biotransformation.

The use of biotransformation indices during the natural attenuation or bioremediation of oil-contaminated sites is attractive because of the opportunity to evaluate the 'approach' to, or 'departure' from, steady state conditions with respect to free product depletion. The aim of the work presented here is then twofold: (i) to investigate the extent to which the selected biotransformation indices can be applied to heavy oils in the contaminated soil environment; and (ii) where application proves viable, to evaluate the sensitivity and reliability of selected biotransformation indices. Our study builds on research conducted over a period of 7 years on the chemical characterisation of heavy oil wastes at contaminated sites (Pollard et al., 1992, 1994a,b; Whittaker and Pollard, 1994; Whittaker et al., 1996).

2. Materials and methods

2.1. Experimental rationale

Work was conducted using a 9-month soil microcosm study of heavy and crude oils that made possible a full investigation of the compositional changes occurring during biotransformation. The microcosm study was designed in accordance with British Standard (BS) 7755 (British Standards Institute, 1995). Where experimental details were not provided, guidance was obtained from comparable studies in the literature (notably, Chaineau et al., 1995; Hatzinger and Alexander, 1995; Heusemann, 1995).

Three individual oils were separately mixed with a well-characterised sandy-loam topsoil and incubated for a period of 9 months under optimal biotransformation conditions. Each oil was sampled in triplicate at predetermined intervals and analyzed for selected compound classes and individual components. Control microcosms were prepared in which soils were autoclaved and poisoned with mercuric chloride (Chaineau et al., 1995). A further set of blank microcosms, containing no oil, were prepared to assess the contribution of soil natural organic matter to the solvent extractable matter (SEM) content.

2.2. Soil selection, preparation and characterisation

Sandy clay loam topsoil was sourced from the Scottish Agricultural College (SAC) field station in Auchincruive, Ayrshire, Scotland. Prior to use, the soil was sieved to less than 2 mm to produce a defined particle size distribution that allowed increased oxygen availability. A complete list of the soil's chemical and physical properties is given in Table 1.

2.3. Source terms

Biotransformation of three oils was studied; a Nigerian crude; a mixture of ballast oils originating from the storage tanks of oil transportation vessels; and a No. 6 fuel oil. These oils have been described previously (Whittaker, 1996). The latter two heavy oils were selected because they are representative of the types of heavy oil encountered at many sites. Evaluation of the Nigerian crude during biotransformation provided a useful reference for comparisons with previously reported studies (Whittaker, 1996; Whittaker and Pollard, 1997) and a context for monitoring the loss of the heavy oils.

2.4. Microcosms

Microcosms were prepared in wide-necked, acid-washed 500-ml Erlenmeyer flasks. For the treated and sterilised microcosms, an initial concentration of oil in soil of $2.00 \pm 0.05\%$ w/w was prepared by adding 4.0 ± 0.1 g each oil to 200 ± 0.1 g soil portions via a glass dropping pipette. A similar loading has been used in previous studies (Aprill et al., 1990; Sims, 1990) and is judged to be low enough to avoid toxic inhibition of soil microbial activity, but sufficient to allow compositional changes to be clearly discerned through subsequent analysis. The mixture was homogenised using a blender prior to addition into the flasks. The 27 soils in the sterilised control flasks were first autoclaved at 121°C under a pressure of 103.4 Pa for 15 min and then amended with a 1% w/w solution of $HgCl_2$, to ensure suppression of soil microbial activity. This work was undertaken in a fume cupboard with full face protection, mask and gloves.

Treated, sterilised and blank soils were amended with a nutrient solution of 1.07 g NH_4NO_3 and 0.42 g K_2HPO_4 dissolved in 38 ml of distilled, de-ionised water, sufficient to bring the soil to 50% of its maximum water holding capacity (WHC). This provided a nitrogen and phosphorus input of 1.75 mg g^{-1} soil and 0.35 mg g^{-1} soil, respectively, and an equivalent molar C:N:P ratio of 100:8.75:1.75, comparable with previous studies and considered to be sufficient to support an active hydrocarbon-degrading microbial population (Chaineau et al., 1995; Heusemann, 1995). The water content of the microcosm flasks was monitored throughout the period of study by weighing the control flasks. Any water lost was replaced by an appropriate amount of distilled, de-ionised water, so that the original water content was maintained to within $\pm 5\%$ w/w. pH measurements of a 1:5 (v/v) suspension

Table 1
Chemical and physical properties of soil used in biotransformation study[a]

Soil sampling details		Particle size analysis	(% w/w)	Soil analysis	
Soil texture:	Sandy clay loam	Clay (< 0.002 mm)	21.5	pH (water)	6.0
Sampling date:	17-June-95	Silt (0.002–0.063 mm)	21.2	Available P (mg g^{-1})	10.0
Land use:	Conservation beds in arboretum	Total sand (0.063–2.000 mm)	57.2	Available K (mg g^{-1})	60.0
Sampling depth:	0–26 cm	Very fine sand (0.063–0.125 mm)	16.0	CEC[b] (meq of CEC in 100 g soil)	13.1
Soil type:	Non-calcereous gley	Fine sand (0.125–0.250 mm)	23.6	Nitrogen (mg g^{-1})	4.0
Previous agricultural use:	None for 8 years	Medium sand (0.250–0.500 mm)	12.3	Field capacity moisture content (% at 0.05 bar)	38.7
		Coarse sand (0.500–1.000 mm)	4.7	% Organic matter	5.9
		Very coarse sand (1.000–2.000 mm)	0.7		

[a]Soil characterisation undertaken by Scottish Agricultural College.
[b]Cation exchange capacity.

of soil in water (with KCl buffer) taken at regular intervals using a calibrated laboratory pH meter confirmed that soil pH remained at ~6.5 throughout the study. Microcosms were incubated in a temperature-programmable, fan-assisted oven maintained at 30°C. The range of temperatures to which the flasks were exposed during incubation was within the 2°C drift specified by BS 7755 (British Standards Institute, 1995).

2.5. Sampling and analysis

Microcosms were sampled in triplicate at 0, 2, 4, 8, 16, 32, 64, 128 and 256 days after initial application of the oil, creating a time series data bank. Sacrificial sampling was accomplished by emptying the entire contents of each flask onto clean, labelled aluminium foil and then air-drying under a forced-draught in a fume cupboard in preparation for extraction and analysis.

The SEM content of each microcosm was determined by Soxhlet-extraction of soil sub-samples (~30 g) for 16 h using HPLC grade dichloromethane (DCM) (150 ml). DCM extracts were collected in pre-weighed, acid-washed borosilicate flasks and reduced under a forced stream of air to allow calculation of gravimetric recoveries. The reproducibility of individual SEM values obtained for each microcosm flask was determined by triplicate extraction of randomly selected flasks. Extraction of blank microcosms indicated a mean solvent-extractable natural organic matter content of 0.23 ± 0.04 mg g^{-1}. The values of SEM for the treated and control soils were correspondingly corrected (Table 2).

For the heavy oils, preparative column chromatography was essential for isolating the individual saturate class fractions in which the selected biomarkers report (Pollard and Whittaker, 1997). Prior to column fractionation, the asphaltene fraction was gravimetrically determined by an *n*-pentane precipitation method adapted from Speight et al. (1984). Fractionation was then accomplished using a Quick-Sep™ lateral reservoir flash chromatography column (90 mm × 30 mm) packed with neutral Aldrich STD Grade alumina (80 mm, ~150 mesh, activated overnight at 130°C) and anhydrous Na_2SO_4 (~10 mm, dehydrated by heating at 400°C for 4 h immediately prior to use). A single piston air pump (Fisons, 50 W) was connected to the top of the column and the air pressure adjusted to produce a down-flow elution rate of ~20 ml/min. The column was pre-eluted with 50 ml *n*-pentane prior to the loading of the maltene (*n*-pentane soluble) fraction of each reference oil onto the column by pipette in 2 ml of *n*-pentane. Component classes were obtained using a previously validated elution scheme (Whittaker and Pollard, 1997): 150 ml of *n*-pentane (for elution of saturates), 150 ml of toluene (combined aromatics), 150 ml of a dichloromethane:methanol mixture (50:50) (for polar compounds). All solvents used were HPLC grade. Fractions were collected in pre-weighed, acid-washed borosilicate flasks and reduced under a forced stream of air to allow calculation of gravimetric recoveries.

Analysis of the biomarkers and *n*-alkanes contained within the saturate class fraction extracts (~10 mg ml^{-1} in DCM) from each microcosm flask was accomplished using a Hewlett Packard 5890 series II gas chromatograph (GC) combined with a HP 5972 mass selective (MS) detector. The GC was equipped with a Restek XTI-5 column (equivalent to a standard diphenyl:disiloxane (5%:95%) stationary phase, DB5 column) of length 30 m, diameter 0.25 mm and film thickness 0.25 mm. Two-microliter aliquots were injected in splitless mode. The column temperature was held at 35°C for 1 min following injection, ramped at 6°C min^{-1} to 300°C and then held for a further 15 min at the final temperature. Injector and detector temperatures were set at 300°C and 280°C, respectively. Helium carrier gas was used at a constant flow rate of 7.5 ml min^{-1}.

Electron impact (EI) ion chromatograms were obtained in selective ion monitoring (SIM) mode at a dwell time per ion of 0.1 s and an ion span width of 0.5 a.m.u. The two target ions selected were m/z 85 (for detection of *n*- and isoprenoid alkanes) and m/z 191 (for methylphenanthrenes, dimethylphenanthrenes and pentacyclic terpanes). Biotransformation indices were calculated to single decimal place precision by determining the ratio of the integrated peak areas on single ion chromatograms of the compound(s) featured in

the indices of interest (Wang et al., 1995). Sample blanks, containing neat solvent, and standard mixed *n*-alkane solutions were routinely analyzed to guard against carry-over and to assist with peak identification. Repeat analysis of selected samples indicated that relative standard deviations in biomarker ratio values were up to 10%. Peaks corresponding to the *n*-alkanes and isoprenoids were determined by the use of an analytical standard comprising 5 *n*-alkanes (C_{15}, C_{20}, C_{25}, C_{30} and C_{40}) and a C_{17}/pristane and C_{18}/phytane mixture. ΣMethylphenanthrenes and pentacyclic terpane (hopane) peak identification was possible using the relative retention times of major peaks relative to 17α(H),21β(H)-hopane and by comparison of mass chromatograms at m/z 191 with corresponding reference chromatograms from well-characterised standard crude oils and from the literature (Prince et al., 1994; Wang et al., 1995; Whittaker and Pollard, 1997).[3] Routine analysis of solvent blanks indicated no measurable carry-over between GC-EI MS runs. Values for the precision of each index at each sampling point for the ballast oil, Nigerian crude and No. 6 fuel oil, determined through triplicate analysis of soil microcosms are provided with the index values obtained (Tables 3–5).

3. Results and discussion

3.1. Variations in solvent extractable matter

Variations in corrected SEM concentrations (expressed in mg g^{-1} air-dried soil) recovered from treated and control soils are shown in Table 2. Results indicate significant losses of SEM from the ballast oil and Nigerian crude oil over the course of the experiment. Average SEM concentrations for the ballast oil-treated soils decreased most dramatically, from a maximum of 14.77 ± 0.25 mg g^{-1} at 0 days to 3.18 ± 0.54 mg g^{-1} after 256 days, corresponding to an overall loss of over 80% w/w. SEM concentrations from the ballast oil sterilised control microcosms decreased much less sharply, from an initial 14.98 mg g^{-1} to 12.16 mg g^{-1} after 256 days. Average Nigerian crude oil SEM concentrations decreased significantly over the course of the study, from 17.93 ± 0.44 mg g^{-1} to 6.70 ± 1.47 mg g^{-1}. SEM concentrations from the corresponding sterilised control microcosms decreased by just over 1 mg g^{-1}, from 18.19 mg g^{-1} to 17.17 mg g^{-1}. For the No. 6 fuel oil microcosms, there was little decrease in SEM over time in either the treated or control flasks. The sharp reduction (up to 10% w/w) in SEM at day 16 of the study may be indicative of some biotransformation, but the reproducibility of this data point is poor, and no other flasks supported this reduction.

The loss of each oil due to biotransformation alone, estimated by difference, is provided in Fig. 1a–c. Abiotic losses estimated from the control microcosms are likely to be overestimates of the abiotic losses occurring in treated soils, since in the control microcosms, there is no competition between abiotic and biotic weathering processes. For the blended oil and ballast and Nigerian crude, the abiotic and biotic losses are comparable over the initial period of study. After the 16-day sample for the ballast oil, and 32-day sample for the crude, the control microcosm recoveries become almost constant, and the bulk of the losses observed are attributable to microbial activity. For the No. 6 fuel oil, no such trend is observed.

For both ballast and crude oils, biotransformation reduced the amounts of oil in the microcosms by ~60% w/w in both cases. From an initial soil loading of 20 g of oil per kg dry soil, this represents an overall microbial degradation rate of 0.05 g oil/kg soil/day, assuming first order kinetics, and compares favourably with published degradation rates for heavy oils, sludges and crude oils, which can vary between 0.02 and 0.6 g oil/kg soil/day (Herbes and Schwall, 1978). Importantly, the SEM results indicated that the premise of active microbial transformation of oils within the microcosms was valid.

[3] Previous assignment of peaks at m/z 191 to the tricyclic and tetracyclic terpanes (Whittaker and Pollard, 1997) was, by this work, revealed by more detailed interrogation of the extracted ion chromatogram to be a sum of the 1-, 2-, 3- and 9-methylphenanthrenes and the dimethylphenanthrenes (unassigned) present.

Table 2
Solvent extractable material (SEM) content for each soil/oil microcosm[a]

Time days	Ballast oil					
	Individual SEM values (mg g^{-1})			Mean SEM	S.D.	Control SEM[b]
0	14.82	14.99	14.50	14.77	0.25	14.98
2	14.67	ND	11.63	13.15	2.15	13.94
4	12.68	12.20	10.08	11.65	1.38	13.52
8	11.84	10.36	11.22	11.14	0.74	13.29
16	11.35	9.34	8.66	9.78	1.40	13.06
32	7.14	8.31	8.65	8.03	0.79	13.05
64	5.37	7.12	6.74	6.41	0.92	12.99
128	4.37	6.11	5.25	5.24	0.87	12.50
256	2.56	3.51	3.49	3.18	0.54	12.16
	Crude oil					
	Individual SEM values (mg g^{-1})			Mean SEM[b]	S.D.	Control SEM[b]
0	18.04	17.45	18.30	17.93	0.44	18.19
2	17.97	17.98	16.90	17.62	0.62	18.21
4	16.64	17.60	15.37	16.53	1.12	18.02
8	15.54	14.09	13.66	14.43	0.99	18.09
16	15.31	15.26	16.32	15.63	0.60	17.94
32	13.16	14.73	13.31	13.73	0.87	17.48
64	11.64	12.18	13.50	12.44	0.96	17.44
128	7.23	9.14	10.47	8.95	1.63	17.30
256	8.35	5.54	6.21	6.70	1.47	17.17
	No. 6 fuel oil					
	Individual SEM values (mg g^{-1})			Mean SEM	S.D.	Control SEM[b]
0	19.98	21.75	20.10	20.61	0.99	20.26
2	21.23	21.09	22.19	21.50	0.60	20.91
4	22.15	20.00	22.34	21.50	1.30	20.35
8	20.66	19.74	20.79	20.40	0.57	19.99
16	17.52	22.72	15.57	18.60	3.70	20.07
32	21.75	19.86	20.23	20.61	1.00	21.18
64	18.64	22.96	20.13	20.58	2.19	19.92
128	19.92	21.23	19.40	20.18	0.94	20.14
256	19.14	20.38	20.73	20.08	0.84	19.94

[a]SEM determined gravimetrically using dichloromethane as solvent (blank corrected).
[b]Result of single extraction only.

3.2. Variation in individual class fraction distributions

Characterisation of the bulk compositional changes that take place within the oils, as represented by 'class fraction' (saturates, aromatics, polars and asphaltenes; SAPA) analysis (Voos et al., 1996) allowed a more complete picture of the compositional changes occurring in each oil. Variations in the class fraction abundance in each oil over time are illustrated in Fig. 2a–c. Results show that the saturates class fraction decreased most significantly for all three oils, from 74.6 ±

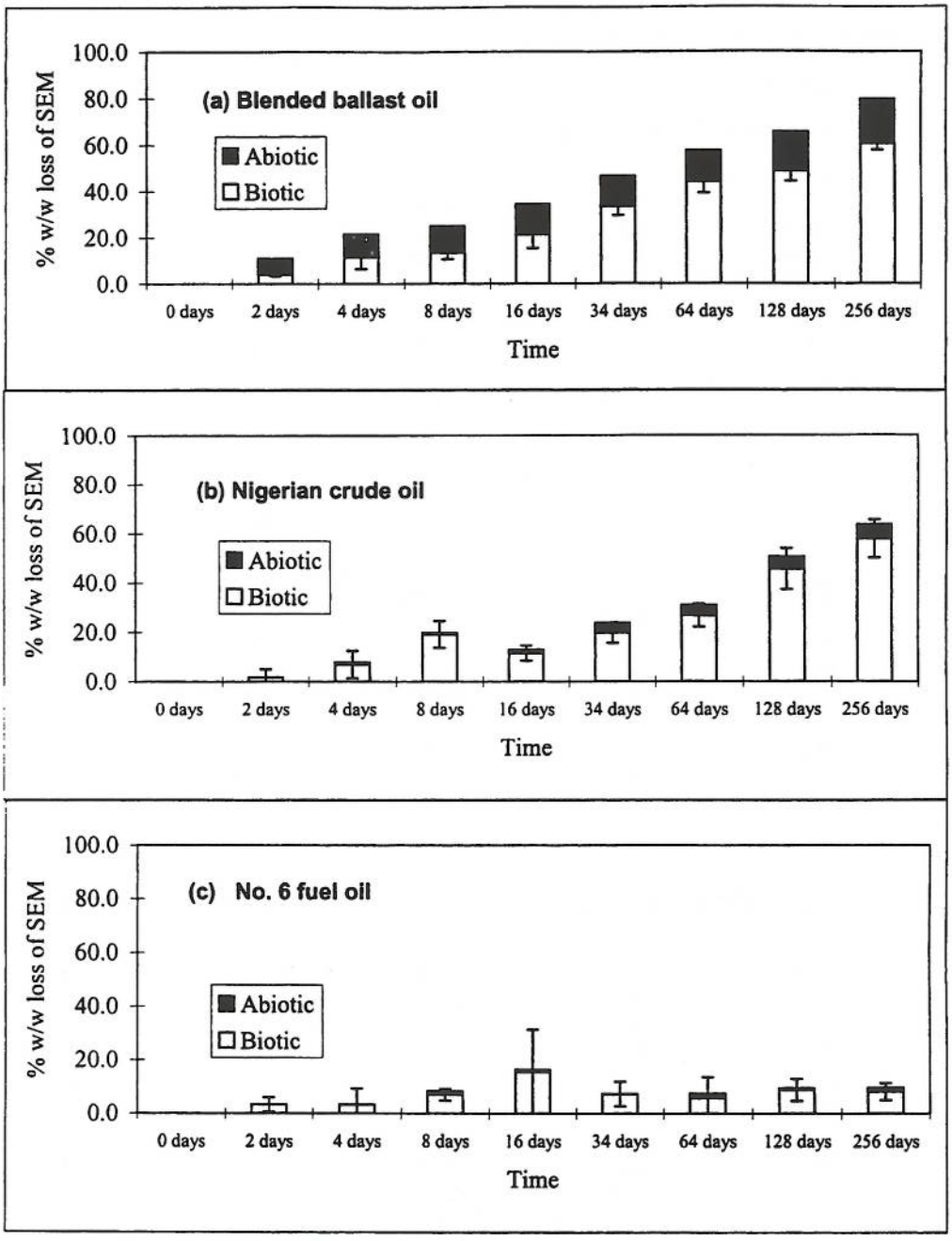


Fig. 1. (a–c) Abiotic and biotic losses of solvent extractable material (SEM) from study oils.

0.9% w/w to 23.2 ± 3.4% w/w for the blended ballast oil; from 91.7 ± 0.8% w/w to 70.1 ± 2.9% w/w for the Nigerian crude; and from 36.9 ± 1.2% w/w to 22.0 ± 2.3% w/w for the No. 6 fuel oil, whilst the average proportions of polars and asphaltenes concomitantly increased. Class fraction distributions in extracts from the control microcosms showed very little variation, with the proportion of class fractions fluctuating by less than 5.0% w/w. An overall mass balance for the four class fractions within each oil is provided in Fig. 3a–f. This clearly illustrates the relative susceptibilities to biotransformation of the respective class fractions. Interestingly, class fraction variations in

the No. 6 fuel oil indicate that despite showing a small overall drop in SEM over 256 days, the saturate fraction abundance declined steadily whilst the amount of asphaltenes recovered almost doubled. One must exercise caution in interpreting such a result because class fractions are always operationally defined by the solvent scheme adopted, but this observation has been previously encountered (Westlake et al., 1974; Gibson, 1984), and been attributed to the production of cross-linked, high molecular weight polymers during biotransformation of lower molecular weight components (Bossert and Bartha, 1984). Other studies have also characterised the microbial recalcitrance of high molecular weight compounds within oil. Heusemann (1995) found that saturates and aromatics of carbon number $> C_{44}$ were less degraded than saturates and aromatics of carbon number $< C_{44}$. For aromatics, the amounts of $> C_{44}$ compounds remaining after a 52-week period of amended were up to 30% w/w greater than the low carbon number equivalents. For saturates, differences remaining over the period of study were much lower ($< 10\%$ w/w), suggesting that the recalcitrance of high carbon number saturate compounds is not substantially lower than the low carbon number saturates. Chaineau et al. (1995) noted a reduction in the concentration of saturated hydrocarbons and aromatics of $\sim 70\%$ w/w and 65% w/w, respectively, during a 250-day soil microcosm biodegradation of fuel oil, whereas the polar class fraction remained almost constant over the period of study. Huddleston and Cresswell (1977) reported in the 22-month land treatment of an oil initially containing 22% w/w saturates, 28% w/w aromatics and 50% w/w combined polars and asphaltenes, an 82% w/w reduction in the saturate fraction, 60% w/w reduction in the aromatic fraction but only a 1% w/w loss of polars and asphaltenes. These patterns of change are generally similar to those observed in our study, although depletions in aromatic class fraction abundance were not as large as previously observed. This may be due to the nature of the heavy oil aromatics, which though not analyzed by detailed component analysis, can be expected to contain a significant portion of polynuclear aromatic hydrocarbons (PAHs) and heterocyclic compounds, not normally so susceptible to biotransformation.

3.3. GC-EI MS biomarker analysis

Reductions in SEM and variations in oil class fraction over the course of the study provide strong evidence that substantial biotransformation of the ballast oil and the Nigerian crude had occurred. Evaluation of selected biotransformation indices for these oils allows the sensitivity (the magnitude of the change in index value) and 'accuracy' (the extent to which the changes in index value match changes in oil SEM) of each index to be assessed, with the overall aim of identifying those indices best able to convey information on oil biotransformation.

Ion chromatograms at m/z 85 and m/z 191 were obtained for oil saturate class fractions at each stage of the biotransformation study. A qualitative, visual examination of the m/z 85 extracted ion traces indicated that, for each oil, weathered samples displayed a much lower abundance of *n*-alkane peaks and a greater proportion of unresolved complex mixture (UCM) than fresh samples. The distribution of mono- and dimethylphenanthrenes, in the m/z 191 extracted ion chromatograms, did not alter significantly over time in the majority of samples, although some depletion was observed in the highly weathered crude oil extracts.

To provide a quantitative analysis of oil biotransformation indices, the following peak areas were determined: Σn-alkanes (principally C_{14}-C_{28}), the isoprenoid alkanes norpristane (iC_{18}), pristane (iC_{19}) and phytane (iC_{20}), Σmethylphenanthrenes, Σdimethylphenanthrenes and the hopane isomers $17\alpha(H)21\beta(H)$-hopane and $17\alpha(H)21\beta(H)$-30-norhopane. In some cases, peaks were not detected for these compounds and no corresponding value obtained for the associated indices and this is denoted by the term N/D. Indices were determined in triplicate at each sample point and for each oil. The results are shown in Tables 3–5. Mean index values for each extract at the successive sampling points are also provided, together with the calculated standard deviations of these measurements and the corresponding results for the control microcosms. To

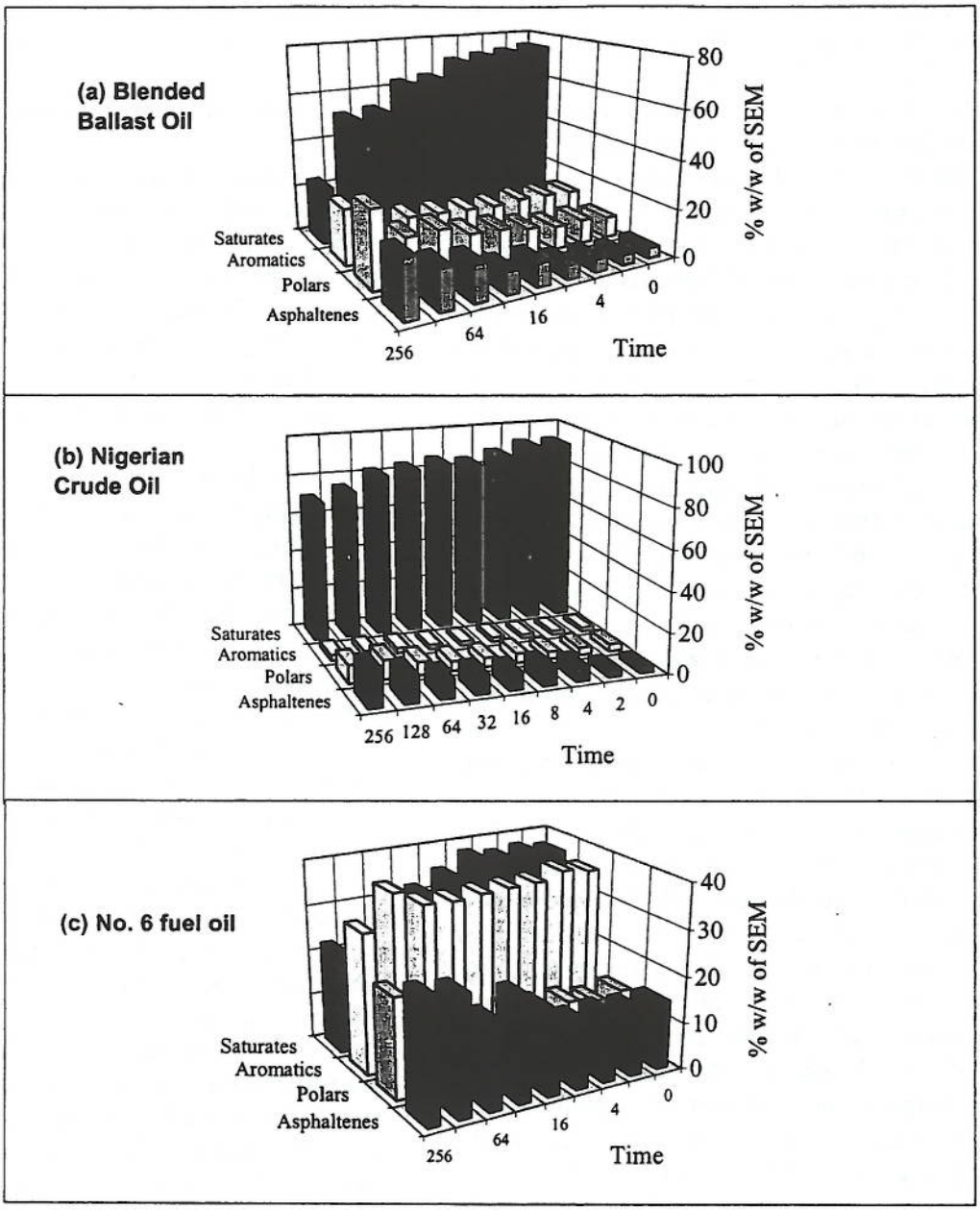


Fig. 2. (a–c) Variations in class fraction abundance in study oils.

test the significance of variations in the indices for each oil an analysis of variance (ANOVA) was conducted (Table 6). The ANOVA test provided a clear statistical argument for assessing the performance of the respective biotransformation indices. For each index, the average 'within-sample' variances of the index values at each of the nine sampling points was compared to the overall 'between-sample' variance of the nine mean index values. Here, the null hypothesis is valid if the nine mean values do not differ significantly. The critical value of F is determined with reference to the appropriate statistical table. To identify the reason for a significant ANOVA result in which the null hypothesis is rejected, the value of the least significant difference (LSD) was also determined.

The results of the ANOVA for each oil are

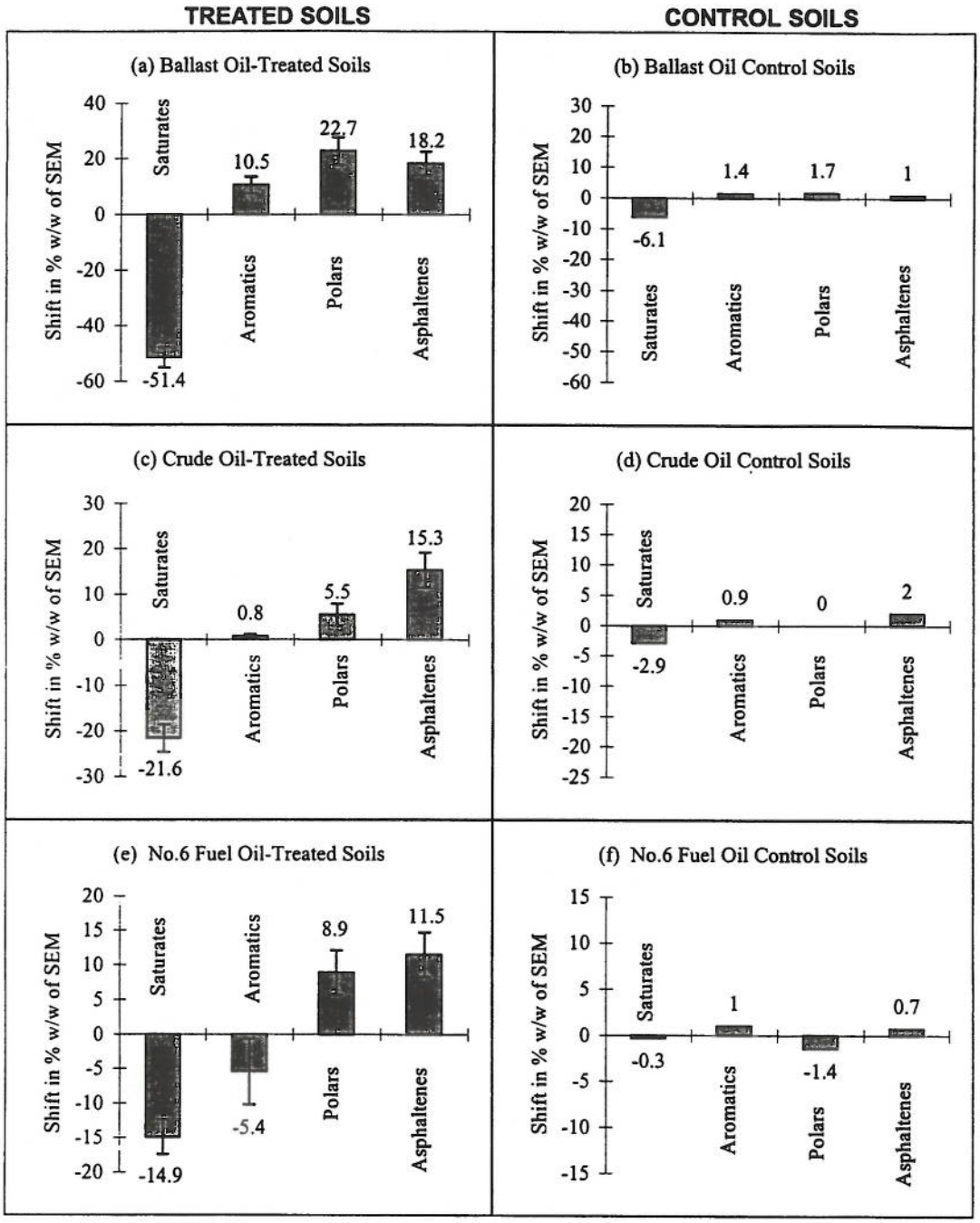


Fig. 3. Overall shift in relative class fraction recoveries (expressed as w/w of SEM) between 0 and 256 days for oil microcosms.

presented in standard format in Table 6. For each biotransformation index, the within-sample and between-sample variance, F_{calc} value, critical F value and LSD are provided. Based on the results obtained, the null hypothesis is either rejected or accepted for each index, depending on whether the mean values did or did not vary significantly over the course of the study. For the ballast oil and crude oil, results indicate that the most sensitive biotransformation index was [ΣC_{14-28}:17α(H)21β(H)-hopane], which for the ballast oil decreased from an initial mean value of 748.9 (37.7) to 8.5 (0.9) and for the crude oil decreased from 15.0 (0.9) to 0.3 (0.2) after 256

Table 3
Variation of biotransformation index values with time for ballast oil-treated and control soils

Biotransformation index		0 days			2 days			4 days			8 days			16 days		
C_{16}:norpristane	*n*1, *n*2, *n*3	4.1	4.5	3.0	2.9	2.5	3.2	3.3	2.8	2.3	3.2	3.4	2.7	2.7	3.6	2.8
	Mean (SD)		3.9 (0.8)			2.8 (0.4)			2.8 (0.5)			3.1 (0.3)			3.0 (0.5)	
	Control[a]					5.4			6.7							
C_{17}:pristane	*n*1, *n*2, *n*3	2.9	3.1	3.1	2.3	2.4	2.4	2.6	2.2	2.6	2.0	2.5	2.5	2.0	2.2	2.0
	Mean (SD)		3.0 (0.1)			2.4 (0.1)			2.4 (0.2)			2.3 (0.3)			2.1 (0.1)	
	Control[a]					2.8			3.1							
C_{18}:phytane	*n*1, *n*2, *n*3	2.0	1.8	1.6	1.6	2.0	1.7	1.5	1.4	1.6	1.5	1.7	1.3	1.5	1.5	1.5
	Mean (SD)		1.8 (0.2)			1.8 (0.2)			1.5 (0.1)			1.5 (0.2)			1.5 (0.0)	
	Control[a]					2.0			1.7							
$C_{14+16+18}$: $C_{24+26+28}$	*n*1, *n*2, *n*3	9.7	11.2	10.2	4.0	3.1	4.3	3.4	3.5	3.9	4.2	4.3	3.4	5.4	6.6	4.7
	Mean (SD)		10.4 (0.7)			3.8 (0.6)			3.6 (0.3)			4.0 (0.5)			5.6 (1.0)	
	Control[a]					10.9			7.7							
ΣC_{14-28}:17α21 β-hopane	*n*1, *n*2, *n*3	709.7	784.8	752.4	N/D	420.9	500.6	N/D	445.9	514.9	586.1	N/D	427.1	627.9	684.9	531.0
	Mean (SD)		748.9 (37.7)			460.8 (56.3)			480.5 (48.8)			506.6 (112.4)			614.6 (77.8)	
	Control[a]					614.3			538.5							
ΣC_{14-28}: Σmethylphen.[b]	*n*1, *n*2, *n*3	13.2	14.7	13.8	13.4	12.4	13.4	14.4	10.5	13.6	13.7	10.3	10.6	10.6	9.5	10.7
	Mean (SD)		13.9 (0.8)			13.1 (0.6)			12.8 (2.1)			11.5 (1.9)			10.3 (0.7)	
	Control[a]					14.9			14.7							
ΣC_{14-28}: Σdimethylphen.[c]	*n*1, *n*2, *n*3	76.1	81.2	69.2	56.6	49.0	56.6	59.3	44.5	60.7	59.1	45.4	44.1	46.1	44.7	44.1
	Mean (SD)		75.5 (6.0)			54.0 (4.4)			54.8 (9.0)			49.5 (8.3)			45.0 (1.1)	
	Control[a]					84.3			81.2							

Table 3 (*Continued*)

Biotransformation index		32 days			64 days			128 days			256 days		
C_{16}:norpristane	*n*1, *n*2, *n*3	N/D	3.0	2.6	N/D	N/D	2.0	N/D	2.1	1.9	2.1	1.8	2.2
	Mean (SD)		2.8 (0.3)			2.0 (N/D)			2.0 (0.1)			2.0 (0.2)	
	Control[a]		5.6			N/D						5.1	
C_{17}:pristane	*n*1, *n*2, *n*3	N/D	2.0	2.1	2.7	2.4	1.9	2.3	2.2	2.4	1.6	1.5	1.4
	Mean (SD)		2.0 (0.0)			2.3 (0.4)			2.3 (0.1)			1.5 (0.1)	
	Control[a]		2.7			3.5						3.1	
C_{18}:phytane	*n*1, *n*2, *n*3	N/D	1.7	1.6	1.9	1.8	1.7	1.9	1.6	1.7	0.9	0.7	0.7
	Mean (SD)		1.6 (0.1)			1.8 (0.1)			1.7 (0.2)			0.7 (0.1)	
	Control[a]		1.6			2.0						2.2	
$C_{14+16+18}$: $C_{24+26+28}$	*n*1, *n*2, *n*3	N/D	4.7	4.1	1.1	1.6	2.3	1.5	3.1	1.1	1.5	1.3	1.6
	Mean (SD)		4.4 (0.5)			1.7 (0.6)			1.9 (1.0)			1.5 (0.2)	
	Control[a]		9.3			5.2						7.3	
ΣC_{14-28}:17α21 β-hopane	*n*1, *n*2, *n*3	N/D	585.8	490.3	N/D	N/D	322.2	N/D	267.3	N/D	9.5	8.2	7.7
	Mean (SD)		538.0 (67.5)			322.2 (N/D)			267.3 (N/D)			8.5 (1.0)	
	Control[a]		552.3			470.5						419.6	
ΣC_{14-28}: Σmethylphen.[b]	*n*1, *n*2, *n*3	N/D	8.2	10.1	12.2	0.3	14.2	0.3	16.7	0.3	1.6	1.5	1.3
	Mean (SD)		9.1 (1.4)			8.9 (7.5)			5.8 (9.5)			1.5 (0.2)	
	Control[a]		12.1			12.7						9.1	
ΣC_{14-28}: Σdimethylphen.[c]	*n*1, *n*2, *n*3	N/D	33.2	40.4	34.1	0.7	43.5	0.9	48.6	0.7	2.4	2.0	1.9
	Mean (SD)		36.8 (5.1)			26.1 (22.5)			16.7 (27.6)			2.1 (0.3)	
	Control[a]		60.2			52.9						41.7	

[a]Control index values determined from single extract only.
[b]Sum of 1-, 2-, 3- and 9-methylphenanthrenes peak areas (m/z 191).
[c]Sum of dimethylphenanthrene peak areas (m/z 191).
N/D not determined.

Table 4
Variation of biotransformation index values with time for crude oil-treated and control soils

Biotransformation index		0 days			2 days			4 days			8 days			16 days			
C_{16}:norpristane	*n*1, *n*2, *n*3	2.3	2.2	2.1	N/D	1.7	1.8	2.0	1.8	2.0	2.0	1.8	2.0	N/D	2.2	N/D
	Mean (SD)		2.2 (0.1)			1.7 (0.1)			1.9 (0.1)			1.9 (0.1)			2.2 (N/D)	
	Control[a]					2.2			2.1							
C_{17}:pristane	*n*1, *n*2, *n*3	1.8	1.6	1.3	N/D	1.1	1.2	1.3	1.9	1.5	1.1	0.9	0.9	0.9	0.9	N/D
	Mean (SD)		1.6 (0.2)			1.1 (0.1)			1.5 (0.3)			1.0 (0.1)			0.9 (0.0)	
	Control[a]					0.9			1.2							
C_{18}:phytane	*n*1, *n*2, *n*3	2.1	1.6	2.1	N/D	1.4	1.6	2.0	2.2	2.0	2.3	1.7	1.6	1.4	1.4	N/D
	Mean (SD)		1.9 (0.3)			1.5 (0.1)			2.1 (0.1)			1.9 (0.4)			1.4 (0.0)	
	Control[a]					1.6			1.6							
$C_{14+16+18}$: $C_{24+26+28}$	*n*1, *n*2, *n*3	1.0	0.9	1.0	N/D	1.1	1.0	0.6	0.7	0.6	0.5	0.6	0.6	0.6	0.5	N/D
	Mean (SD)		1.0 (0.1)			1.1 (0.0)			0.7 (0.1)			0.6 (0.0)			0.6 (0.0)	
	Control[a]					0.9			1.2							
ΣC_{14-28}:17α21 β-hopane	*n*1, *n*2, *n*3	16.0	14.5	14.5	N/D	15.4	16.7	15.4	13.7	13.7	14.7	15.8	18.4	14.2	15.6	N/D
	Mean (SD)		15.0 (0.9)			16.1 (0.9)			14.3 (1.0)			16.3 (1.9)			14.9 (1.0)	
	Control[a]					16.2			17.9							
ΣC_{14-28}: Σmethylphen.[b]	*n*1, *n*2, *n*3	19.1	16.2	17.1	N/D	14.7	15.2	19.0	19.9	19.5	19.9	20.6	22.9	20.6	20.6	N/D
	Mean (SD)		17.5 (1.5)			15.0 (0.4)			19.5 (0.4)			21.1 (1.6)			20.6 (0.0)	
	Control[a]					18.0			18.5							
ΣC_{14-28}: Σdimethylphen.[c]	*n*1, *n*2, *n*3	53.6	44.9	59.5	N/D	39.9	39.8	56.8	48.4	59.4	52.4	60.1	61.4	59.7	66.1	N/D
	Mean (SD)		52.7 (7.3)			39.8 (0.0)			54.9 (5.8)			57.9 (4.9)			62.9 (4.5)	
	Control[a]					49.2			47.5							

Table 4 (*Continued*)

Biotransformation index		32 days			64 days			128 days			256 days		
C_{16}:norpristane	*n*1, *n*2, *n*3	2.6	N/D	1.9	1.5	1.8	N/D	0.5	1.5	N/D	N/D	N/D	N/D
	Mean (SD)		2.2 (0.5)			1.6 (0.2)			1.0 (0.7)				
	Control[a]		2.1			2.1						2.6	
C_{17}:pristane	*n*1, *n*2, *n*3	0.9	1.3	1.1	2.1	1.6	0.9	0.9	0.7	N/D	1.3	0.5	0.9
	Mean (SD)		1.1 (0.2)			1.5 (0.6)			0.8 (0.2)			0.9 (0.4)	
	Control[a]		1.3			1.6						1.3	
C_{18}:phytane	*n*1, *n*2, *n*3	1.5	1.6	1.5	2.1	2.3	1.9	0.9	0.9	N/D	1.0	0.4	1.0
	Mean (SD)		1.5 (0.1)			2.1 (0.2)			0.9 (0.0)			0.8 (0.3)	
	Control[a]		1.3			1.2						2.2	
$C_{14+16+18}$: $C_{24+26+28}$	*n*1, *n*2, *n*3	0.5	0.4	0.4	0.3	0.4	0.3	0.5	0.5	N/D	0.2	0.5	0.3
	Mean (SD)		0.4 (0.1)			0.3 (0.1)			0.5 (0.0)			0.3 (0.2)	
	Control[a]		0.9			1.1						1.0	
ΣC_{14-28}:17α21 β-hopane	*n*1, *n*2, *n*3	12.8	11.8	13.4	9.9	10.1	10.5	2.7	0.9	N/D	0.5	0.2	0.3
	Mean (SD)		12.7 (0.8)			10.2 (0.3)			1.8 (1.3)			0.3 (0.2)	
	Control[a]		14.9			14.3						14.3	
ΣC_{14-28}: Σmethylphen.[b]	*n*1, *n*2, *n*3	25.1	21.5	27.5	57.3	26.9	27.5	N/D	15.6	0.3	0.0	0.0	0.0
	Mean (SD)		24.7 (3.0)			37.2 (17.4)			8.0 (10.8)			0.0	
	Control[a]		15.5			15.5						17.4	
ΣC_{14-28}: Σdimethylphen.[c]	*n*1, *n*2, *n*3	70.4	57.2	70.2	78.3	58.0	60.5	N/D	19.7	N/D	9.4	5.3	N/D
	Mean (SD)		65.9 (7.6)			65.6 (11.1)			19.7 (N/D)			7.4 (2.9)	
	Control[a]		40.1			42.3						45.9	

[a] Control index values determined from single extract only.
[b] Sum of 1-, 2-, 3- and 9-methylphenanthrenes peak areas (m/z 191).
[c] Sum of dimethylphenanthrene peak areas (m/z 191).
N/D not determined.

Table 5
Variation of biotransformation index values with time for No. 6 fuel oil-treated and control soils

Biotransformation index		0 days			2 days			4 days			8 days			16 days			
C_{16}:norpristane	*n*1, *n*2, *n*3	N/D	N/D	N/D	6.0	N/D	N/D	N/D	2.7	2.9	N/D	2.7	1.9	N/D	N/D	N/D	
	Mean (SD)		N/D			6.0 (N/D)			2.8 (0.1)			2.3 (0.6)					
	Control[a]					N/D			N/D								
C_{17}:pristane	*n*1, *n*2, *n*3	10.6	N/D	N/D	10.8	6.9	N/D	N/D	7.8	7.0	N/D	N/D	6.7	9.7	7.3	N/D	
	Mean (SD)		10.6 (N/D)			8.9 (2.8)			7.4 (0.6)			6.7 (N/D)			8.5 (1.7)		
	Control[a]					11.6			11.0								
C_{18}:phytane	*n*1, *n*2, *n*3	2.7	N/D	N/D	3.1	3.4	3.0	N/D	2.9	2.4	3.7	2.0	2.3	3.5	3.4	N/D	
	Mean (SD)		2.7 (N/D)			3.2 (0.2)			2.7 (0.3)			2.7 (0.9)			3.5 (0.1)		
	Control[a]					2.5			3.9								
$C_{16+18+20}$: $C_{26+28+30}$	*n*1, *n*2, *n*3	2.0	N/D	N/D	1.9	1.8	1.9	N/D	1.7	1.7	1.7	1.8	1.8	2.1	2.3	N/D	
	Mean (SD)		2.0 (N/D)			1.9 (0.1)			1.7 (0.0)			1.8 (0.0)			2.2 (0.2)		
	Control[a]					3.4			2.2								
ΣC_{14-30}:17α21 β-hopane	*n*1, *n*2, *n*3	81.9	N/D	N/D	86.6	92.9	N/D	N/D	82.9	85.2	70.4	N/D	80.6	85.2	N/D	N/D	
	Mean (SD)		81.9 (N/D)			89.8 (4.5)			84.1 (1.7)			75.5 (7.2)			85.2 (N/D)		
	Control[a]					108.6			94.4								
ΣC_{14-30}: Σmethylphen.[b]	*n*1, *n*2, *n*3	2.9	N/D	N/D	2.3	2.4	2.4	N/D	2.1	2.1	2.2	2.4	1.8	1.3	1.7	N/D	
	Mean (SD)		2.9 (N/D)			2.4 (0.0)			2.1 (0.1)			2.1 (0.3)			1.5 (0.3)		
	Control[a]					2.6			2.1								
ΣC_{14-30}: Σdimethylphen.[c]	*n*1, *n*2, *n*3	12.2	N/D	N/D	8.3	8.4	8.4	N/D	8.0	8.7	7.4	6.7	7.1	5.8	4.9	N/D	
	Mean (SD)		12.9 (N/D)			8.4 (0.1)			8.3 (0.5)			7.1 (0.4)			5.4 (0.7)		
	Control[a]					9.3			7.4								

Table 5 (*Continued*)

Biotransformation index		32 days			64 days			128 days			256 days		
C_{16}:norpristane	*n*1, *n*2, *n*3 Mean (SD) Control[a]	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	6.6 6.6 (N/D) N/D	N/D
C_{17}:pristane	*n*1, *n*2, *n*3 Mean (SD) Control[a]	9.8	6.2 8.0 (2.5) N/D	N/D	10.0	N/D 8.4 (2.4) 6.2	6.7	4.9	N/D 4.9 (N/D)	N/D	1.6	4.2 2.6 (1.4) N/D	2.1
C_{18}:phytane	*n*1, *n*2, *n*3 Mean (SD) Control[a]	3.2	5.8 4.5 (1.9) N/D	N/D	2.9	N/D 2.7 (0.4) 3.6	2.4	1.8	2.7 2.6 (0.8)	3.4	0.6	2.3 1.7 (1.0) 5.0	2.2
$C_{16+18+20}$: $C_{26+28+30}$	*n*1, *n*2, *n*3 Mean (SD) Control[a]	1.8	2.0 2.6 (1.2) 1.7	4.0	2.3	N/D 1.8 (0.6) 3.1	1.4	1.3	1.9 1.6 (0.3)	1.7	1.0	2.2 1.7 (0.6) 1.4	1.8
ΣC_{14-30}:17α21 β-hopane	*n*1, *n*2, *n*3 Mean (SD) Control[a]	83.6	83.3 83.5 (0.2) 93.4	N/D	83	N/D 82.5 (N/D) 107	N/D	37.3	54.3 49.3 (10.4)	56.2	1.7	25.2 18.1 (14.2) 125.1	27.2
ΣC_{14-30}: Σmethylphen.[b]	*n*1, *n*2, *n*3 Mean (SD) Control[a]	1.7	1.6 1.1 (0.9) 2.1	0.1	2.4	N/D 1.3 (1.5) 3.0	0.2	1.5	2.3 2.1 (0.6)	2.5	0.1	2.8 1.8 (1.5) 3.7	2.6
ΣC_{14-30}: Σdimethylphen.[c]	*n*1, *n*2, *n*3 Mean (SD) Control[a]	5.5	5.9 3.8 (3.2) 7.8	0.1	8.0	N/D 4.2 (5.3) 10.9	0.5	3.6	6.6 5.1 (1.5)	5.0	0.2	3.2 2.4 (1.9) 9.5	3.8

[a] Control index values determined from single extract only.
[b] Sum of 1-, 2-, 3- and 9-methylphenanthrenes peak areas (m/z 191).
[c] Sum of dimethylphenanthrene peak areas (m/z 191).
N/D not determined.

Table 6
Analysis of variance (ANOVA) of biotransformation indices from soil microcosms

Biotransformation ratios	Ballast oil					
	Mean individ. variance[a] (S_1^2) (F_{calc})	Overall variance[b] (S_2^2)	D of F[c]	F_{test}^{d}	Significant variation?	LSD[e]
C_{16}: norpristane	2.51		8,14	2.69	NO	0.49
C_{17}: pristane	4.18		8,17	2.55	YES	0.24
C_{18}: phytane	5.40		8,17	2.55	YES	0.17
$C_{14+16+18}$: $C_{24+26+28}$	17.30		8,17	2.55	YES	0.80
ΣC_{14-28}: 17α21β-hopane	13.84		8,10	3.07	YES	70.60
ΣC_{14-28}: Σmethylphen	0.91		8,17	2.55	NO	5.09
ΣC_{14-28}: Σdimethylphen	2.98		8,17	2.55	YES	15.72
	Crude oil					
	Mean individ. variance[a] (S_1^2) (F_{calc})	Overall variance[b] (S_2^2)	D of F[c]	F_{test}^{d}	Significant variation?	LSD[e]
C_{16}: norpristane	1.80		7,13	2.83	NO	0.37
C_{17}: pristane	1.22		8,15	2.64	NO	0.33
C_{18}: phytane	5.34		8,15	2.64	YES	0.25
$C_{14+16+18}$: $C_{24+26+28}$	15.26		8,15	2.64	YES	0.08
ΣC_{14-28}: 17α21β-hopane	34.72		8,15	2.64	YES	1.26
ΣC_{14-28}: Σmethylphen	2.24		7,16	2.66	NO	8.49
ΣC_{14-28}: Σdimethylphen	9.30		8,14	2.70	YES	9.33
	No. 6 fuel oil					
	Mean individ. variance[a] (S_1^2) (F_{calc})	Overall variance[b] (S_2^2)	D of F[c]	F_{test}^{d}	Significant variation?	LSD[e]
C_{16}: norpristane	0.95		2,3	9.55	NO	2.46
C_{17}: pristane	2.04		8,7	3.73	NO	2.01
C_{18}: phytane	0.86		8,12	2.85	NO	1.00
$C_{14+16+18}$: $C_{24+26+28}$	0.33		7,14	2.76	NO	0.63
ΣC_{14-30}: 17α21β-hopane	12.88		8,8	3.44	YES	7.98
ΣC_{14-30}: Σmethylphen	0.50		8,13	2.77	NO	0.99
ΣC_{14-30}: Σdimethylphen	1.76		8,13	2.77	NO	2.74

[a]Mean variance of index values at each sampling point.
[b]Overall variance between sampling points.
[c]Number of degrees of freedom S_1^2 and S_2^2, respectively.
[d]Critical F value from statistical tables.
[e]Least significant difference between index values.

days. The magnitude of these changes is considered to be due to the discrepancy between the biotransformation susceptibility of the *n*-alkanes with that of the hopane (Prince et al., 1994). ANOVA of the values of [Σ*n*-alkanes: 17α(H)21β(H)-hopane] over the 256 days indicated that the variation was statistically significant for all three test oils. The use of this index in a similar context was reported by Butler et al. (1991), who used this ratio to demonstrate the 80% w/w depletion in crude oil in contaminated beaches over a 6-month period, although Croft et al. (1995) observed the value of this index decreased by only a small margin, from 551 to 518, during a 45-day biodegradation of oil-contaminated sand. These results provide evidence

that the [Σn-alkanes:17α(H)21β(H)-hopane] index is a highly sensitive means of determining oil depletion during biotransformation activities.

Of the other biotransformation indices examined, the [C_{16}:norpristane], [C_{17}:pristane] and [C_{18}:phytane] ratios also reduced in value over the period of study, but to a lesser degree and in a manner that did not follow an easily predictable trend. For the ballast oil, for example, the overall changes in these indices were 1.9, 1.5 and 1.1, respectively, a variation similar to that observed by previous authors (Christensen and Larsen, 1993; Croft et al., 1995). In particular, Davis and Tibbets (1997) found that for crude oil in submerged sediments [C_{18}:phytane] decreased slightly from 1.3 to 1.1 after 106 days and to 0.4 after 437 days, and Christensen and Larsen (1993) observed a decrease in [C_{17}:pristane] of 2.0, from 2.2 to 0.2, between fresh diesel and diesel that had been in the soil subsurface for an estimated 20 years. ANOVA of these indices indicated that for the ballast oil, the variations of both [C_{17}:pristane] and [C_{18}:phytane] were significant, whereas for the crude oil, only the [C_{18}:phytane] index produced a significant variation between microcosm samples.

Many authors have documented the susceptibility of phytane to microbial attack (Butler et al., 1991; Prince et al., 1994; Madsen, 1991) and here this is demonstrated by the decrease in value of the [phytane:17α(H)21β(H)-hopane] ratio for the ballast and crude oils. This provides clear evidence that phytane becomes depleted in heavily biotransformed oils, and suggests that the biotransformation index [C_{18}:phytane] may be used to monitor oil biotransformation reliably only in light-to-moderately weathered samples. Of the remaining biotransformation indices, the [ΣC_{14-28}:Σdimethylphenanthrenes] and [ΣC_{14-28}:Σmethylphenanthrenes] indices both decreased steadily in value during the study, although only the latter index was found by ANOVA to produce significant variations between the respective ballast oil and crude oil samples. The reason for this may be the disparities in variance of the values at each sampling point, which in ANOVA tests are usually assumed to be similar. Finally, the ratio of low-to-high carbon number n-alkanes, [$C_{14+16+18}$:$C_{24+26+28}$] also produced lower values as the microcosm study proceeded, decreasing from 10.4 ± 0.7 to 1.5 ± 0.2 in the ballast oil and from 1.0 (0.1) to 0.3 (0.2) in the crude oil. ANOVA of these indices produced a significant variation, suggesting that this index is sensitive to oil weathering. Wang et al. (1995) evaluated a similar index ([C_{8-12}:C_{16-20}]) to determine the weathered state of fuel oil spilled on an Arctic beach, and found that from a value in fresh oil 2.3, the index lowered to between 0.2 and 0.6 for 'less weathered' samples and to between zero and 0.007 for 'highly weathered' samples. Based on these criteria, the crude oil would not be judged to be weathered significantly whilst the ballast oil would be weathered only moderately. Recently published results by Hatzinger and Alexander (1995), which suggest that higher number ($> C_{44}$) n-alkanes are not significantly more resistant to microbial activity than n-alkanes of carbon number $< C_{44}$, indicate that the use of this index may not be applicable in circumstances where substantial oil biotransformation has taken place. Thus for confirmation of oil biotransformation, this index should not be relied upon to provide accurate information as both index numerator and denominator would be expected to decrease in value.

To further characterise the indices in terms of their capacity to accurately reflect changes in oil composition, the relationship between the 'recorded' decrease in oil saturate abundance (mg g^{-1} soil) and the decrease in saturate abundance 'predicted' by each index was evaluated, using the actual initial abundance as a starting point. This was calculated by determining the equivalent decrease in mg g^{-1} abundance that would produce the observed decrease in index value. The results of this calculation, shown in Fig. 4a,b, indicate that [ΣC_{14-28}:Σdimethylphenanthrenes] and, to a slightly lesser degree, [ΣC_{14-28}:17α(H)21β(H)-hopane] produced ballast oil saturate class fraction concentrations that most closely matched the actual abundances in the ballast oil samples determined by gravimetric column fractionation. For the [ΣC_{14-28}:Σdimethylphenanthrenes] index, the calculated and actual abundances were generally within 0.5 mg g^{-1}, whereas for [ΣC_{14-28}:17α(H)21β(H)-hopane], the difference between the two values was found to be up to

approximately 3 mg g^{-1}. For the crude oil, the index that most closely matched the actual loss in saturates was the [ΣC_{14-28}:17α(H)21β(H)-hopane] index, although discrepancies in value of up to approximately 5 mg g^{-1} were observed. Here, the [ΣC_{14-28}:Σdimethylphenanthrenes] index produced calculated saturate abundances of up to 10 mg g^{-1} apart from the actual amounts determined.

In summary, the [Σn-alkanes:17α(H)21β(H)-hopane] index was most sensitive to oil biotransformation and most accurately reflected the actual depletion of oil from the contaminated soil. This index was also found to be the most reliable for the No. 6 fuel oil saturates, which though not as depleted over the microcosm study as either the ballast oil or crude oil saturates, caused the index to fall from 81.9 to 18.1 over 256 days. Notwithstanding these findings, some authors have suggested that there may be practical limitations to the utility of this index. For example, Morris et al. (1996) found that hopane concentration in fuel oil dropped over a 30-day period from 436 μg g^{-1} to 96 μg g^{-1} in one incubated oil-soil

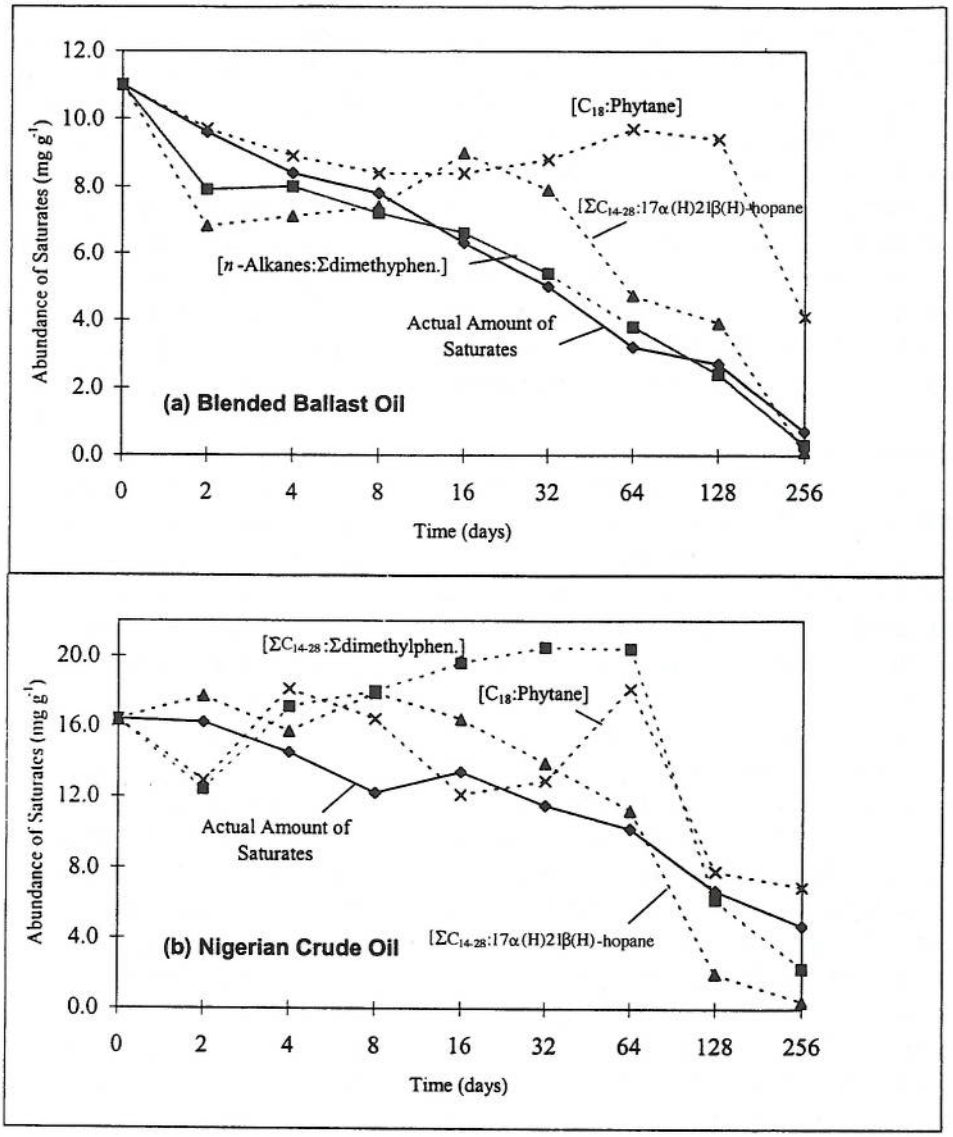


Fig. 4. Comparison of actual abundance of saturates in two study oils with amounts predicted by selected biotransformation indices (mg/g).

sample. As the actual abundance of the hopane in the soil microcosms was not determined in this study, it is not possible to state whether this compound was or was not completely conserved over the course of the experiment. If hopane is slightly depleted during biotransformation, then the estimates of oil depletion produced by the [Σn-alkanes:17α(H)21β(H)-hopane] index will be underestimates of the actual amount of oil depleted.

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The fate of heavy oil wastes in soil microcosms II: a performance assessment of source correlation indices

M. Whittaker[1,a], S.J.T. Pollard[b,*], G. Risden[2,c]

[a] *Environmental Chemistry Unit, Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK*

[b] *National Centre for Risk Analysis and Options Appraisal, Environment Agency, Steel House, 11 Tothill Street, London, SW1H 9NF, UK*

[c] *Geochem Group Ltd., Environmental Analytical Services, Chester Street, Chester, CH4 8RD, UK*

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Abstract

Chemical fingerprinting is commonly undertaken to assist in the resolution of multi-party liability disputes, particularly when contaminants have migrated beyond property boundaries, in litigation-driven environmental assessments related to oil spills, and in assessing potential environmental impacts following releases of petroleum products into the environment. In this paper, we present data relating to the performance of source correlation indices for selected heavy oils over the course of a 9-month microcosm study. The results obtained in this study demonstrated that hopane pair indices varied little in magnitude, and may therefore be considered reliable source correlation indices. Over the course of the 9-month microcosm study [17α(H)21β(H)-norhopane: 17α(H)21β(H)-hopane] exhibited mean values of 0.7 ± 0.1 for a heavy ballast oil, and mean values that varied between 0.6 and 0.7 (± 0.05) for a crude oil. Similarly [(17α(H)21β(H)-homohopane (22S): 17α(H)21β(H)-homohopane (22R)] gave a mean value of 1.3 (precisions less than 0.05) and [17α(H)21β(H)-bishomohopane: 17α(H)21β(H)-methylhopane] varied between 1.3 and 1.6 (precision up to 0.1) for the same crude oil. These source correlation indices may be used to support a correlation between fresh and weathered oil samples for source identification purposes involving heavy and crude oil contamination of the terrestrial environment. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Chemical fingerprinting; Microcosms; Biotransformation; Biomarkers; Petroleum hydrocarbons; Natural attenuation

* Corresponding author. Tel.: +44 171 6646832; fax: +44 171 6646836; e-mail: simon.pollard@environment-agency.gov.uk

[1] Golder Associates, 2180 Meadowvale Boulevard, Missassauga, Ontario, L5N 5S3.

[2] TES Bretby, PO Box 100, Bretby Business Park, Ashby Road, Burton-on-Trent, DE15 0XD, UK.

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1. Introduction

Chemical fingerprinting is commonly undertaken to help discern the character and assess potential sources of petroleum contaminants in the environment. Information of this kind can assist in the resolution of multi-party liability disputes, particularly when contaminants have migrated beyond property boundaries, in litigation-driven environmental assessments related to oil spills, and in assessing potential environmental impacts following releases of petroleum products into the environment (Nyer and Skladeny, 1989; Douglas et al., 1992; Boehm et al., 1995).

The chemical analytical techniques used in oil 'fingerprinting' are similar to those used in verifying oil biotransformation, in that they involve non-routine GC/MS methods to measure the characteristic distribution of target biomarker compounds within the contaminant matrix, which, in turn, allows a comparison to be made between two or more contaminant samples (for distinguishing between oils) (e.g. Hostettler and Kvenvolden, 1994) or between a contaminant sample and a suspected source (for source correlation) (Volkman et al., 1992). The general usefulness of chemical biomarkers in source correlation stems from two key characteristics: firstly, their distribution within oils has been shown to represent a type of chemical fingerprint that varies uniquely between different oil types (Philp, 1985; Douglas et al., 1996), and secondly, they are generally regarded as resistant to oil weathering processes, particularly biotransformation, relative to most other oil components (Prince et al., 1994). Hopane biomarkers are generally accepted as being the most reliable conserved internal markers within oils, being neither produced nor destroyed over considerable periods of oil weathering (Butler et al., 1991), although PAHs have also been demonstrated to be useful fingerprinting target compounds in certain situations (Wang et al., 1994a).

Source correlation using biomarkers is achieved either by making a qualitative comparison of individual biomarker mass fragmentogram patterns (obtained by El GC-MS) (Volkman et al., 1992) or, more quantitatively, through calculation of the ratio of one biomarker to another (Wang et al., 1994b). The latter approach, with which we are concerned in this paper, leads to the formation of oil (or source) correlation indices whose values remain consistent between related oils and unaltered by oil weathering. A positive or negative contaminant identification is achieved through a comparison of the contaminant source ratio value with that of a candidate source product.

Recently, source correlation indices have been used to: (1) suggest that certain Alaskan shoreline oil residues originated from pre-1970 industrial oil usage rather than as a direct result of the *Exxon Valdez* oil spill (Kvenvolden et al., 1995); (2) confirm the source of highly weathered No. 6 fuel oil released onto Nova Scotian beaches over 22 years ago from the oil tanker *Arrow* (Wang et al., 1994b); and (3) monitor chemical compositional changes and the fate of weathered crude oil residues from an Arctic beach (Wang et al., 1995).

As the wider application of biomarkers in source correlation studies has evolved, increasing effort has been directed towards evaluating and assessing their true integrity under varying environmental conditions. These studies have raised a number of issues. For example, the assumed microbial recalcitrance of selected conserved internal markers has recently been questioned (Madsen, 1991; Voos et al., 1996). These concerns should be addressed, partly because of the general need to validate the utility of biomarker indices, but also because of the tremendous potential that exists for the wider application of chemical fingerprinting techniques within the contaminated land industry. Application of source correlation indices to medium- and heavy oil-contaminated sites is particularly attractive because of the prevalence of such wastes at former industrial contaminated sites and the significant liability issues arising as a consequence. Moreover, chemical fingerprinting may provide a means of addressing some of the analytical constraints that have hampered the chemical characterisation of such wastes (Pollard et al., 1992, 1994a,b; Whittaker and Pollard, 1994; Whittaker, 1996; Whittaker et al., 1996).

In a companion paper (Pollard et al., 1999), we describe a controlled soil microcosm study in

which selected medium and heavy oils underwent significant biotransformation under controlled conditions over a period of 9 months. In that paper, details are provided on the performance of biotransformation indices used for evaluating hydrocarbon depletion due to microbially-mediated processes over time. Here, we present data relating to the performance of source correlation indices for the respective oils over the course of the study. The aim of the work presented here is twofold: (1) to investigate the extent to which oil correlation indices can be applied to heavier oils that have undergone significant biotransformation in the contaminated soil environment; and (2) to evaluate and compare the sensitivity and reliability of several currently accepted source correlation indices.

2. Materials and methods

2.1. Experimental rationale

The performance of source correlation indices was evaluated by determining and comparing index values for selected oils during a 9-month soil microcosm study. Details on the design specifications and conditions of the microcosm study, including soil selection and sampling protocol, the nature of the oil source terms used in the study and the analytical procedures used to determine index values are provided in a companion paper (Pollard et al., 1999). The microcosm study was designed in accordance with British Standard (BS) 7755 guidelines on the selection and conduct of tests for determining the biodegradation of organic chemicals in soil under aerobic conditions (British Standards Institute, 1995). Where experimental details were not provided in the standard, guidance was obtained from comparable studies in the literature (notably, Chaineau et al., 1995; Heusemann, 1995; Hatzinger and Alexander, 1995).

GC-El MS peak identification and quantification was achieved for selected (Σ) *n*-alkanes, the isoprenoid alkanes norpristane (iC$_{18}$), pristane (iC$_{19}$) and phytane (iC$_{20}$), combined mono-substituted (1-, 2-, 3- and 9-) methylphenanthrenes (Σmethylphenanthrenes), unassigned dimethylphenanthrenes (Σdimethylphenanthrenes), and the hopane isomer pairs 17α(H)21β(H)-norhopane and 17α(H)21β(H)-hopane, 17α(H)21β(H)-homohopane (22S) and 17α(H)21β(H)-homohopane (22R), and 17α(H)21β(H)-bishomohopane and 17α(H)21β(H)-methyl hopane, by obtaining target ion chromatograms at m/z 85 and m/z 191.[3]

To test the significance of the variations in the source correlation indices for each oil over the entire biotransformation study, an analysis of variance (ANOVA) was conducted. The results of the ANOVA for each oil are presented in standard format in Table 1. For each source correlation index, the within-sample and between-sample variance, F_{calc} value, critical F-value and LSD are provided. Based on the results obtained, the null hypothesis is either rejected or accepted for each index, depending on whether the mean values did or did not vary significantly over the course of the study.

3. Results and discussion

3.1. Confirmation of oil biotransformation

A prerequisite to studying the performance of the oil correlation indices was the need to verify that the subject oils had undergone significant biotransformation over the course of this study. This was verified by monitoring the bulk oil loadings and the changes in oil chemical composition in the soil microcosms with time, and through the use of oil biotransformation indices (Pollard et al., 1999). The results of these investigations, presented in the accompanying paper, confirm that for both ballast and crude oils, biotransformation reduced the amounts of oil in the microcosms by approximately 60% w/w in both cases. From an initial soil loading of 20 g of oil per kilogram of dry soil, this represents an overall microbial

[3] Previous assignment of peaks at m/z 191 to the tricyclic and tetracyclic terpanes (Whittaker and Pollard, 1997) was revealed through this work to be a sum of the 1-, 2-, 3- and 9-methylphenanthrenes and the Σdimethylphenanthrenes (unassigned), respectively.

Table 1
Analysis of variance (ANOVA) of source correlation indices from soil microcosms

Source indices	Mean individ. variance[a] (σ_1^2) / Overall variance[b] (σ_1^2) (F_{calc})	D of F[c]	F_{test}^{d}	Significant variation?	LSD[e]
Ballast oil					
Pristane:phytane	1.18	8,17	2.55	No	0.15
Phytane:17α21β-hopane	8.53	8,10	3.07	Yes	6.88
17α21β-Norhopane:17α21β-hopane	3.86	8,10	3.07	Yes	0.03
ΣMethylphenanthrenes:Σdimethylphenanthrenes	18.91	8,17	2.55	Yes	0.05
17α21β-Homohop. (22S):17α21β-Homohop. (22R)	0.65	5,5	5.05	No	0.10
17α21β-Bishomohop. (22S):17α21β-Bishomohop. (22R)	–	–	–	–	–
Crude oil					
Pristane:phytane	2.07	8,15	2.64	No	0.24
Phytane:17σ21β-hopane	15.91	8,15	2.64	Yes	0.08
17α21β-Norhopane:17α21β-hopane	2.07	8,15	2.64	No	0.03
ΣMethylphenanthrenes:Σdimethylphenanthrenes	20.11	7,15	2.70	Yes	0.12
17α21β-Homohop. (22S):17α21β-homohop. (22R)	0.62	8,15	2.64	No	0.04
17α21β-Bishomohop. (22S):17α21β-bishomohop. (22R)	0.54	8,15	2.64	No	0.16
No. 6 fuel oil					
Pristane:phytane	0.47	8,7	3.73	No	0.15
Phytane:17σ21β-hopane	2.47	8,8	3.44	No	0.68
17α21β-Norhopane:17α21β-hopane	0.78	7,7	3.77	No	0.05
ΣMethylphenanthrenes:Σdimethylphenanthrenes	0.95	8,14	2.70	No	0.44
17α21β-Homohop. (22S):17α21β-homohop. (22R)	–	–	–	–	–

[a] Mean variance of index values at each sampling point.
[b] Overall variance between sampling points.
[c] Number of degrees of freedom σ_1^2 and σ_2^2, respectively.
[d] Critical F-value from statistical tables.
[e] Least significant difference between index values.

degradation rate of 0.05 g oil/kg soil/day, and compares favourably with published data on degradation rates for heavy oils, sludges and crude oils, which vary between 0.02 and 0.6 g oil/kg soil/day (Herbes and Schwall, 1978).

Source correlation index reliability is assessed according to the constancy of the value of the index during oil weathering. Indices that remain constant are useful because they allow the source of an oil to be determined, providing a sample of the fresh source candidate is available for comparison.

Source correlation index values were evaluated in this study for each of the oils under examination at each sampling point over the 256 days. Clearly, the most useful results are those obtained for the ballast oil and crude oil, because of the extent to which these oils were depleted over the study. Results are provided in Table 2 (a) and (b) (for the ballast oil and crude oil, respectively).

3.2. Ballast oil source correlation indices

The most reliable source indices were [17α(H)21β(H)-norhopane: 17α(H)21β(H)-hopane] and the ratio of 17α(H)21β(H)-homohopane (22S) and 17α(H)21β(H)-homohopane (22R) isomers [22S:22R], which did not vary by greater than 0.2 over the entire study period. The values for [pristane:phytane] and [Σmethylphenanthrenes: Σdimethylphenanthrenes] were found to remain steady over the initial period of

Table 2
(a) Variation of source correlation index values with time for ballast oil treated and control soils

Source index		0 days	2 days	4 days	8 days	16 days	32 days	64 days	128 days	256 days
Pristane: Phytane	n1,n2,n3	0.9, 0.9, 0.9	0.7, 0.9, 0.8	0.6, 0.7, 0.7	0.9, 0.8, 0.7	0.8, 0.8, 0.8	N/D, 0.8, 0.8	0.2, 0.4, 0.8	0.4, 0.7, 0.4	0.6, 0.6, 0.6
	Mean (S.D.)	0.9 (0.0)	0.8 (0.1)	0.7 (0.1)	0.8 (0.1)	0.8 (0.0)	0.8 (0.0)	0.5 (0.3)	0.5 (0.2)	0.6 (0.0)
	Control[a]		0.9	0.7			0.9	0.7		0.9
Phytane: 17α21β-Hopane	n1,n2,n3	41.4, 43.1, 41.0	N/D, 26.3, 39.7	N/D, 37.4, 41.1	48.8 N/D 37.3	51.5, 54.2, 47.9	N/D, 49.9, 39.3	N/D, N/D, 25.6	N/D, 23.8, N/D	1.1, 1.2, 1.2
	Mean (S.D.)	41.9 (1.1)	33.0 (9.5)	39.2 (2.6)	43.1 (8.1)	51.2 (3.2)	44.6 (7.5)	25.6 (N/D)	23.8 (N/D)	1.2 (0.1)
	Control[a]		43.1	31.5			30.8	37.1		42.3
17α21β-Norhopane: 17α21β-Hopane	n1,n2,n3	0.7, 0.8, 0.8	N/D, 0.8, 0.8	N/D, 0.7, 0.7	0.8 N/D 0.9	0.7, 0.7, 0.7	N/D, 0.7, 0.8	N/D, N/D, 0.7	N/D, 0.8, N/D	0.7, 0.7, 0.7
	Mean (S.D.)	0.7 (0.0)	0.8 (0.1)	0.7 (0.0)	0.9 (0.0)	0.7 (0.0)	0.8 (0.0)	0.7 (N/D)	0.8 (N/D)	0.7 (0.0)
	Control[a]		0.8	0.7			0.7	0.8		0.8
Σmethyl-phenanthrenes:[a] Σdimethy-phenanthrenes	n1,n2,n3	1.1, 1.2, 1.1	1.0, 0.9, 1.0	1.0, 0.9, 1.0	1.0 1.0 1.0	1.0, 1.0, 0.9	N/D, 0.9, 0.9	0.7, 0.7, 0.8	0.7, 0.8, 0.7	0.6, 0.6, 0.6
	Mean (S.D.)	1.1 (0.0)	1.0 (0.1)	0.9 (0.1)	1.0 (0.0)	1.0 (0.0)	0.9 (0.0)	0.7 (0.1)	0.7 (0.1)	0.6 (0.0)
	Control[a]		1.0	0.8			1.0	1.2		1.2
17α21β-Homohop. (22S):[c]	n1,n2,n3	1.5, 1.2, 1.5	N/D, 1.3, N/D	N/D, 1.3, 1.4	N/D, N/D, N/D	N/D, N/D, N/D	N/D, N/D, N/D	N/D, N/D, 1.3	N/D, 1.3, N/D	1.2, 1.3, 1.3
17α21β-Homohop. (22R)	Mean (S.D.)	1.4 (0.2)	1.3 (N/D)	1.4 (0.1)				1.3 (N/D)	1.3 (N/D)	1.3 (0.0)
	Control[a]		1.2	N/D				1.2		1.4

Table 2
(b) Variation of source correlation index values with time for crude oil treated and control soils

Source index		0 days	2 days	4 days	8 days	16 days	32 days	64 days	128 days	256 days
Pristane: phytane	n1,n2,n3	2.0, 2.0, 1.9	N/D, 1.4, 1.6	2.1, 1.7, 1.8	2.1, 2.1, 2.0	1.8, 1.7, N/D	1.8, 1.9, 1.6	1.3. 1.5, 1.6	1.6, 1.1, N/D	1.7, 0.9, 1.3
	Mean (S.D.)	2.0 (0.1)	1.5 (0.0)	1.9 (0.2)	2.1 (0.1)	1.8 (0.1)	1.8 (0.2)	1.5 (0.1)	1.3 (0.3)	1.3 (0.4)
	Control[a]		1.8	1.8			1.9	1.8		2.1
Phytane: 17α21β-Hopane	n1,n2,n3	0.6, 0.5, 0.6	N/D, 0.9, 1.0	0.6, 0.5, 0.5	0.5, 0.7, 0.8	0.6, 0.7, N/D	0.5, 0.4, 0.5	0.3, 0.3, 0.4	0.2, 0.1, N/D	0.0, 0.0, 0.0
	Mean (S.D.)	0.6 (0.0)	0.9 (0.0)	0.6 (0.0)	0.7 (0.2)	0.6 (0.0)	0.5 (0.1)	0.3 (0.0)	0.2 (0.1)	0.0
	Control[a]		0.8	0.8			0.6	0.6		0.6
17α21β-Norhopane: 17α21β-Hopane	n1,n2,n3	0.7, 0.8, 0.7	N/D, 0.7, 0.7	0.7, 0.7, 0.8	0.6, 0.7, 0.6	0.7, 0.7, N/D	0.7, 0.7, 0.7	0.6, 0.6, 0.7	0.7, 0.7, N/D	0.7, 0.7, 0.7
	Mean (S.D.)	0.7 (0.0)	0.7 (0.0)	0.7 (0.0)	0.6 (0.0)	0.7 (0.0)	0.7 (0.0)	0.6 (0.0)	0.7 (0.0)	0.7 (0.0)
	Control[a]		0.7	0.7			0.7	0.8		0.6
Σmethyl-phenanthrenes:[b]	n1,n2,n3	1.3, 1.2, 1.3	N/D, 1.2, 1.2	1.3, 1.4, 1.4	1.3, 1.2, 1.3	1.6, 1.4, N/D	1.7, 1.4, 1.5	1.1, 1.3, 1.3	N/D, 2.5, N/D	0.0, 0.0, 0.0
Σdimethy-phenanthrenes	Mean (S.D.)	1.3 (0.1)	1.2 (0.0)	1.4 (0.1)	1.3 (0.1)	1.5 (0.2)	1.5 (0.2)	1.2 (0.1)	2.5 (N/D)	0.0
	Control[a]		1.3	1.1			1.3	1.8		1.4
17α21β-Homohop. (22S)[c]	n1,n2,n3	1.3, 1.3, 1.3	N/D, 1.3, 1.3	1.3, 1.4, 1.3	1.3, 1.3, 1.2	1.3, 1.3, N/D	1.3, 1.3, 1.2	1.3, 1.3, 1.3	1.3, 1.3, N/D	1.3, 1.3, 1.2
17α21β-Homohop. (22R)	Mean (S.D.)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)	1.3 (0.0)
	Control[a]		1.2	1.3			1.3	1.3		1.3
17α21β-Bishomohop. (22S):[d]	n1,n2,n3	1.3, 1.2, 1.3	N/D, 1.4, 1.3	1.5, 1.4, 1.3	1.5, 1.6, 1.4	1.3, 1.7, N/D	1.6, 1.3, 1.7	1.4, 1.5, 1.5	1.4, 1.3. N/D	1.4, 1.4, 1.3
17α21β-Bishomohop. (22R)	Mean (S.D.)	1.3 (0.0)	1.3 (0.1)	1.4 (0.1)	1.5 (0.1)	1.5 (0.3)	1.6 (0.2)	1.5 (0.1)	1.3 (0.0)	1.3 (0.0)
	Control[a]		1.3	1.3			1.1	1.4		1.4

[a]Control index values based on single extraction only.
[b]Combined mono-substituted (1-, 2-, 3- and 9-) methylphenanthrene peak areas.
[c]Ratio of 17α21β-homohopanes (22S) and (22R).
[d]Ratio of 17α21β-bishomohopanes (22S) and (22R).
N/D not determined.

study, at 0.8 and 1.0 (precisions up to 0.1), respectively, until the 64 day samples, whereupon their values began to decrease, by approximately 0.3 in both cases. Changes in the values of [phytane: 17α(H)21β(H)-hopane] were observed to be largest, decreasing from 41.9 ± 1.1 to 1.2 ± 0.1 as the proportion of phytane in the extracts diminished.

Source correlation indices in the ballast oil control microcosms also remained largely constant, varying by between 0.2 and 0.4 in most cases. The exception to this was the [phytane: 17α(H)21β(H)-hopane] index, which decreased in value slightly over the latter period of biotransformation to produce a maximum shift in index of 12.3.

3.3. Crude oil source correlation indices

The source correlation indices for the crude oil treated soils displaying the highest level of consistency throughout the study were also the hopane isomer pairs [17α(H)21β(H) norhopane: 17α(H)21β(H)-hopane], with mean values that varied between 0.6 and 0.7 (precisions less than 0.05), the ratio of 17α(H)21β(H)-homohopane (22S) and 17α(H)21β(H)-homohopane (22R) isomers [22S:22R], which gave a mean value of 1.3 (precisions less than 0.05) at every sampling point, and [17α(H)21β(H) bishomohopane: 17α(H)21β(H)-methylhopane], which varied between 1.3 and 1.6 (precision up to 0.1). The [pristane:phytane] and [phytane:17α(H)21β(H)-hopane] ratios showed moderate variations over the first five sampling points (i.e. until day 32), but significantly decreased in value for the samples taken after 64, 128 and 256 days. Similarly, the values of [Σmethylphenanthrenes: Σdimethylphenanthrenes] were consistently between 1.2 and 1.5 between 0 and 64 days (precision up to 0.1),

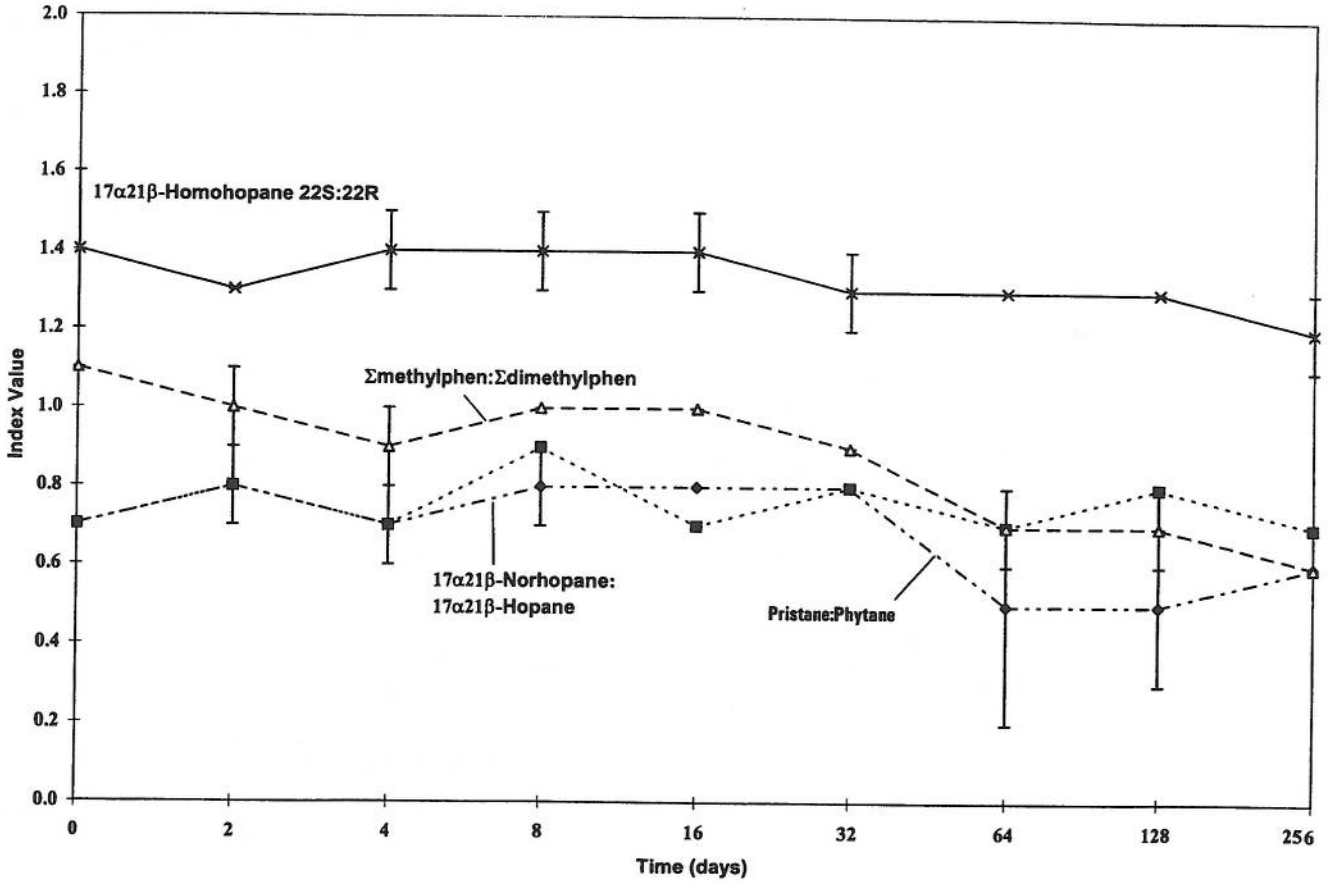


Fig. 1. Variation of selected source correlation index values for ballast oil-treated soils.

but increased to 2.5 (single measurement) after 128 days and finally dropped to 0 (undetected) for the final set of samples at 256 days. In the control microcosms, the source correlation indices were found to remain almost constant over the study, with the notable exception of the [pristane: phytane] value at 256 days, which was elevated by 0.3 in relation to previous values.

3.4. No. 6 Fuel oil source correlation indices

Because of the low abundance of the higher carbon number hopanes (i.e. the homohopanes, bishomohopanes and methylhopanes) in these samples, only four source correlation indices were determined for the extracts from the No. 6 Fuel oil microcosms. Of these [pristane: phytane] and [17α(H)21β(H)-norhopane: 17α(H)21β(H)-hopane] changed least over time, the former varying between 0.3 and 0.6, and the latter between 0.7 and 0.8. The [Σ-methylphenanthrenes: Σdimethylphenanthrenes] also remained largely the same between 0 and 32 days, at approximately 2.3, but then decreased over the final three sample points to 1.5 ± 0.4 after 256 days. The [phytane:17α(H)21β(H)-hopane] index varied more erratically during the study, increasing from $2.5 \pm n/d$ initially to a maximum of $4.0 \pm n/d$ before decreasing to 1.2 ± 0.9 after 256 days. Results from the control microcosms were very similar to these, in that none of the indices registered significant changes with time. The most consistent indices were [Σmethylphenanthrenes: Σdimethylphenanthrenes] and [17α(H)21β(H) norhopane:17α(H)21β(H)-hopane], which varied between 2.4 and 1.8, and 0.7 and 1.2, respectively. The [phytane: 17α(H)21β(H)-hopane] again varied most erratically during the study, between 4.6 (2 days) and 1.9 (256 days). Only two values of [pristane:phytane] could be determined, at 2 and 4 days, and these were 0.3 and 0.4, respectively, in close agreement with the values obtained for this index in the treated soils.

Plots comparing the changes in the mean val-

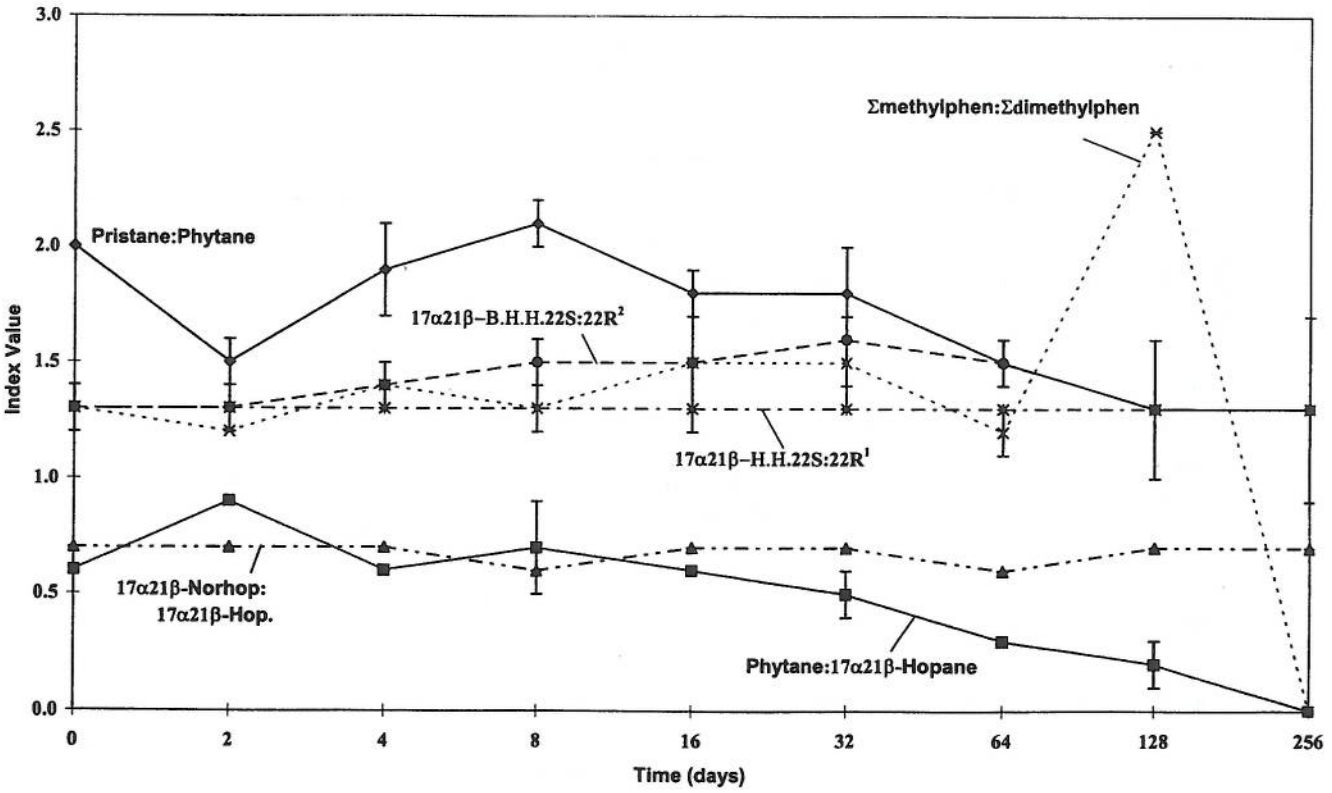


Fig. 2. Variation of selected source correlation index values for crude oil-treated soils.

ues of ballast, crude and No. 6 fuel oil source indices in the treated soils and control soils are shown in Fig. 1, Fig. 2 and Fig. 3, respectively. The relative sensitivities of the source indices are shown in summarised form in Fig. 4(a)–(c) which depicts the overall change in value of each and source index.

These results indicate that the most reliable source indices are those comprising ratios of hopane isomers, specifically:

1. the [17α(H)21β(H)-norhopane: 17α(H) 21β(H)-hopane] for the ballast oil and crude oil, which exhibited mean values of approximately 0.7 ± 0.1 for the ballast oil, and mean values that varied between 0.6 and 0.7 (precisions less than 0.05) for the crude oil;
2. the ratio of 17α(H)21β(H)-homohopane (22S) and 17α(H)21β(H)-homohopane (22R) isomers [22S:22R], which gave a mean value of 1.3 (precisions less than 0.05) at every sampling point for the crude oil microcosms, and;
3. [17α(H)21β(H)-bishomohopane: 17α(H) 21β(H)-methylhopane], which varied between 1.3 and 1.6 (precision up to 0.1) for the crude oil microcosms.

Other studies have also demonstrated the utility of the hopane isomer indicators in discriminating between heavily biotransformed oil samples. Hostettler and Kvenvolden (1994), for example, found that [17α(H)21β(H)-norhopane: 17α(H)21β(H)-hopane] varied by 1.4 ± 0.2 between fresh crude oil spilled from the *Exxon Valdez* oil tanker and oily residues taken from beaches in the vicinity of the spill site several years after the incident.

Similarly, Pande et al. (1994) found that this index ranged from 1.2 to 1.7 for five crude oils

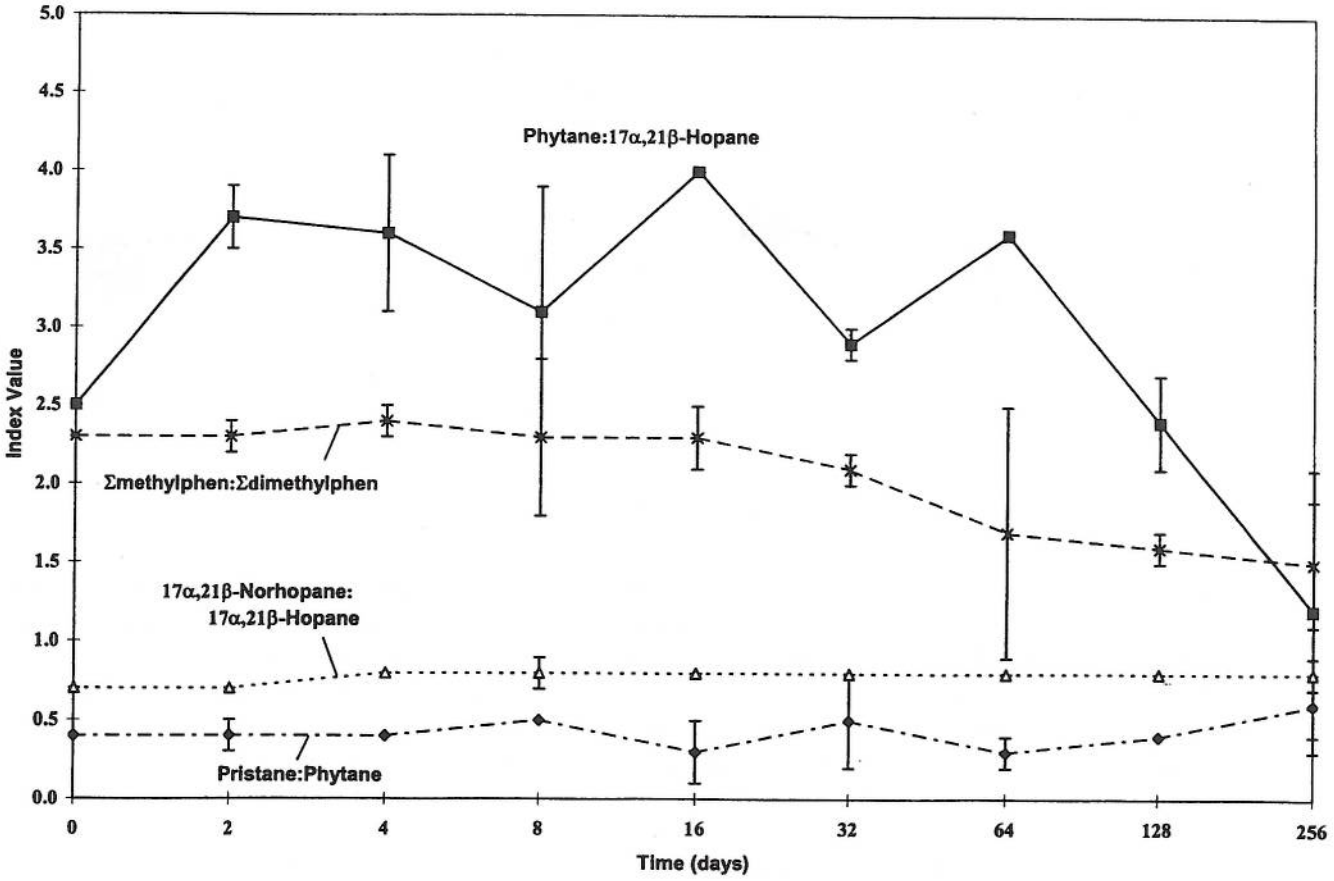


Fig. 3. Variation of selected source correlation index values for No. 6 fuel oil-treated soils.

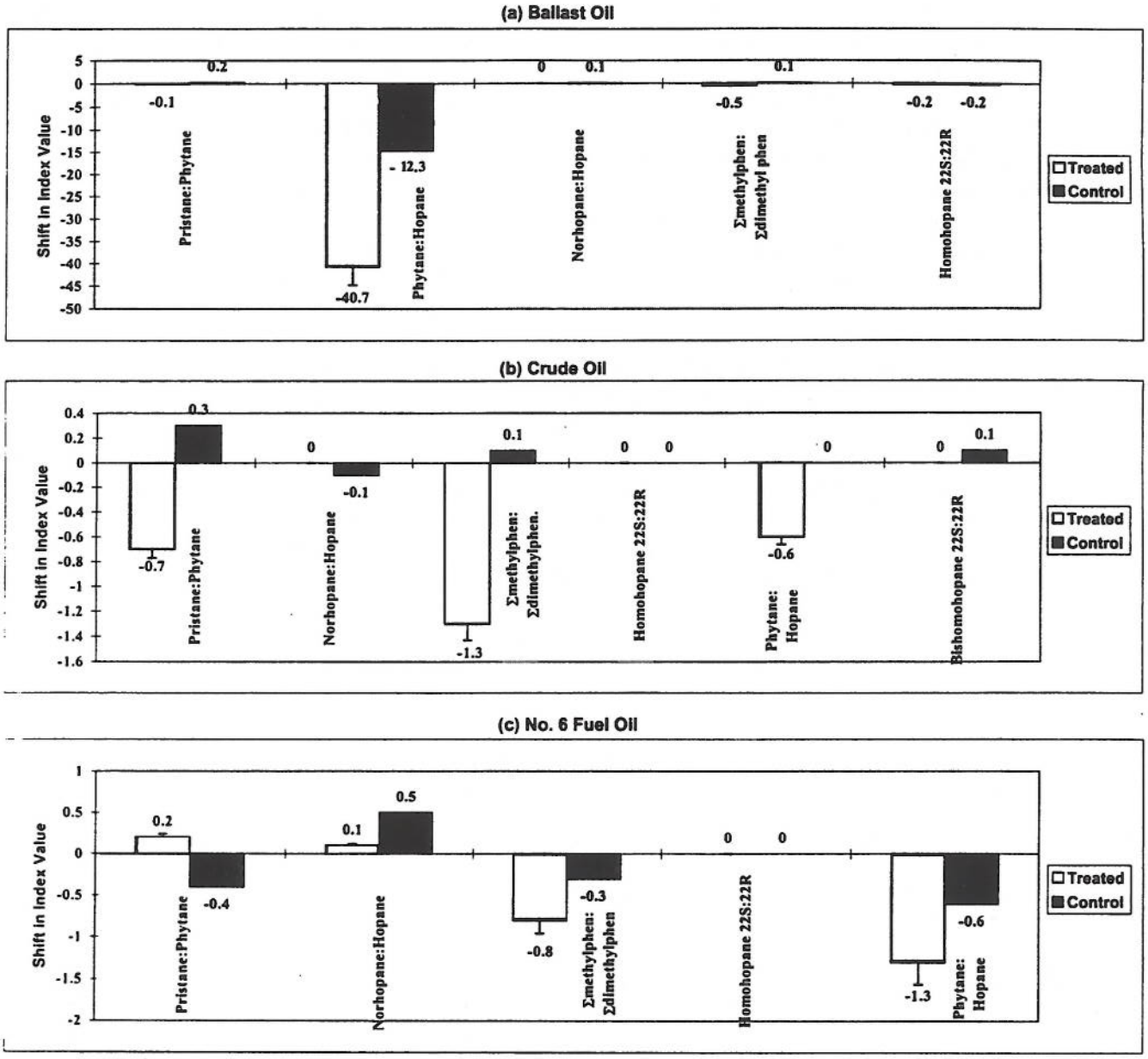


Fig. 4. Relative sensitivities of source correlation indices for (a) ballast oil (b) crude oil and (c) No. 6 fuel oil.

from the same geochemical family, but at different stages of natural biodegradation, and Davis and Tibbets (1987) observed that this index varied by only 0.04 from an initial value of 0.6 over the 437 day biodegradation of crude oil in submerged marine sediments. Sauer et al. (1993) calculated the ratio of [18α(H)21β(H)-trisnorhopane: 17α(H)21β(H)-trisnorhopane], two C_{27} hopanes, to be within the range 2.6–3.3 for beached oil in the Arabian Gulf to make a positive correlation with a Kuwait crude oil (index value = 2.7) believed to be the source of the contamination. However, Wang et al. (1995) have suggested that this index becomes altered in heavily weathered samples and may be unreliable in such circumstances as a source correlation index. In their study, the authors found that [17α(H)21β(H)-norhopane: 17α(H)21β(H)-hopane] was the most reliable of the paired hopane source indices, as this maintained a value of 0.95 ± 0.2 between

fresh crude oil and 13-year-old residues of the oil spilled on an Arctic Beach in a controlled oil spill environment.

The results presented here also show that the [pristane:phytane], [phytane: 17α(H)21β(H)-hopane] and [Σmethylphenanthrenes:Σdimethylphenanthrenes] indices remained fairly constant over the initial stages of oil biotransformation (up to approx., day 32), but then decreased significantly in value. ANOVA calculations for each of the source correlation indices suggest that [phytane: 17α(H)21β(H)-hopane] and [Σmethylphenanthrenes:Σdimethylphenanthrenes] varied significantly between samples over the course of the study (Table 1), which indicates that these indices are not useful for source correlation purposes. Swannel et al. (1995) also noted a decrease in the former index of 0.19 (from 0.44 to 0.25) during the nutrient-enhanced biodegradation of crude oil in contaminated sediments over 600 h. Pande et al. (1994) also noted that [phytane:17α(H)21β(H)-hopane] decreased in increasingly biodegraded crude oil samples, in this instance from 200 in fresh crude oil to 4.3 in the most degraded sample. These results suggest that these indices may be useful as source diagnostic parameters in light to moderately degraded oils, but are unreliable when prolonged weathering has been in effect.

In summary, the results obtained in this study provide evidence that hopane pair indices, specifically [17α(H)21β(H)-norhopane: 17α(H)21β(H)-hopane] [17α(H)21β(H) homohopane (22S): 17α(H)21β(H)-homohopane (22R)] and [17α(H)21β(H)- bishomohopane: 17α(H)21β(H)-methylhopane], may be used to support a correlation between fresh and weathered oil samples for source identification purposes not just in the crude oil-contaminated marine environment, but also for heavy and crude oil contamination of the terrestrial environment. This may be of major utility in helping to locate the source of petroleum products that have spread in the subsurface, either through lateral soil migration or carried by groundwater, to contaminated areas away from the original spill site. In particular, where liability for a contaminant site is disputed, for example, when the source of residual contamination cannot be identified, GC-El MS fingerprinting may be used to establish a match between the contaminant and a possible source candidate, even if it is highly weathered. This has significant legal implications, as well as assisting in a more general sense with contaminant treatment and risk assessment.

Acknowledgements

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5

Linking Pollutant Transport, Environmental Forecasting and Risk Assessment: Case Studies from the Geosphere

SIMON J. T. POLLARD AND RAQUEL DUARTE-DAVIDSON

Environment Agency National Centre for Risk Analysis and Options Appraisal, London, UK

5.1 INTRODUCTION

The study of the geosphere, and in particular of the soil matrix, has played a key role in improving our understanding of the behaviour of pollutants in the total environment. For example, advances in the understanding of metal and organic partitioning in soils have made important contributions towards advancing the analytical sciences and chemical risk-assessment methodologies. They have also helped to advance our understanding of pollutant treatment technologies and the environmental regulations that seek to control direct and indirect releases to the geosphere.

Environmental risk assessment has emerged over recent years as a widely accepted tool for environmental management in business, regulation and research (Calow 1998, European Environment Agency 1998). In many instances, the value of this activity has been in formalising existing judgements within an overall decision-making framework for the purpose of effectively managing risk. In this chapter, we present and examine the role of environmental fate and transport processes within the wider context of environmental risk assessment. Pollutant transport processes are viewed afresh as components of exposure assessment, set between the hazard identification and risk estimation stages within a classical risk-assessment structure. Case studies from the geosphere are used to illustrate the role of pollutant transport processes in informing regulatory decisions about the management of environmental risk.

5.2 POLLUTANT TRANSPORT PROCESSES

The law of the conservation of mass allows us to follow the fate and transport of pollutants by virtue of a simple mass balance. Within a system boundary (or

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between boundaries), whether at the global or field scale, the flow of pollutants can be expressed simply as

$$\text{Input rate} = \text{output rate} + (\text{decay rate}) + (\text{accumulation rate}) \quad (1)$$

The assumption of steady state (equilibrium) allows the accumulation rate to be set to zero. The conservative assumption of setting the decay rate (biotransformation or radioactive decay) to zero allows the input rate to be equated to the output rate. Finally, the assumption of homogeneity (i.e. that the distribution of pollutants throughout the system volume is uniform) completes the simplest view of the environment; that of the homogenous, 'complete mix box' or 'continuously stirred tank' (Masters 1991, Alloway and Ayers 1993).

This has been the starting-point for many approaches to the modelling of pollutant transport processes, (Schnoor 1996) and, as needs have dictated, progressive layers of complexity have been incorporated into environmental models. Examples include the inclusion of **storage** terms (lake phosphorus), **decay** terms (groundwater modelling of mineralizable organics, radionuclide decay) and the additional complexities with respect to mixing, including **advection** (riverine and free product flow), **diffusion** (bottom sediments) and **dispersion** (air quality modelling). These processes have been widely used to assess how, once released, pollutants are disseminated in the wider environment and, in particular, how they reach a point of **exposure**, be it a public supply borehole, point of inhalation downwind of a stack, or the site of inadvertent ingestion for a soil particle. Several texts have described pollutant fate and transport processes and modelling approaches in detail (Mackay 1991, Schnoor 1996).

5.3 ENVIRONMENTAL RISK ASSESSMENT

5.3.1 WHAT IS ENVIRONMENTAL RISK?

'Risk' is a term used to denote the probability of suffering harm from a hazard and embodies both likelihood and consequence. The hazard with which we are concerned, refers to the potential adverse effect posed by a source—a toxic substance or hazardous situation—and the effect represents the potential to cause harm. The actual harm that results from a risk relates to the **observable damage** that occurs once the hazard is realized and which is also referred to as the detriment, impact or response. Hazard, risk and harm are discrete terms and their interchangeable use is to be avoided. Environmental risk assessment is concerned with risks to and from the environment. Pollutant transport has most to do with the likelihood of environmental exposures from a chemical hazard.

As an illustrative example, consider one of the risks from methane gas emanating from an active landfill site. Methane gas represents an explosion (effect) hazard at certain concentrations in confined spaces. Methane poses a high risk where the likelihood of concentrations building up to the lower

explosive limit are high (high probability, due to sufficient gas pressure, permeable strata, building ingress, etc.) and where there are occupied buildings in the vicinity (high consequences). The damage that can result from explosion risks includes loss of life, property and structural damage (harm).

5.3.2 ENVIRONMENTAL RISK ASSESSMENT

Risk assessment is a process for combining what is known, and what can be reasonably inferred about an exposure situation for the purpose of managing risk (Department of the Environment 1995, Calow 1998, Douben 1998, Hester and Harrison 1998). It typically involves answering the following questions which have become grouped into the classical stages of risk assessment (Box 5.1; Figure 5.1).

Box 5.1 Essential questions in environmental risk assessment

Question	Stage and definition
1. What hazards are present and what are their properties?	**Hazard identification**: Identification of the sources of the hazard and assessment of the consequences of the hazard if realised, including the identification of dose-response relationships, where appropriate
2. How might the receptors become exposed to the hazards and what is the probability and scale of exposure?	**Exposure assessment**: Evaluating the plausibility of the hazard being realized at the target, and by which mechanisms, allowing an assessment of the probability, magnitude and duration of exposure
3. Given exposure occurs at the above probability and magnitude, what is the probability and scale of harm?	**Risk estimation**: Consideration of the consequences of exposure with reference to effects and dose, expressed as a likelihood or probability of the hazardous effects of exposure being realized; and expressed over a range of spatial and temporal fields
4. How significant is the risk and what are the uncertainties?	**Risk characterization**: Evaluating the acceptability and significance of risk with reference to standards, targets, background risks, cost–benefit criteria or risk 'acceptability' and 'tolerability' criteria, and commenting on the uncertainties associated with the assessment

Figure 5.1 A framework for environmental risk assessment.

As a management tool, risk assessment can be conducted at various levels or tiers (Pollard *et al.* 1995, Environment Agency 1997). This can start with an initial screening of risk using a 'source-pathway-receptor' approach (Figure 5.1), and can increase in complexity through the use of risk ranking systems to a detailed analysis of complex risks using quantitative techniques to assess and express consequence and probability in numerical terms. Risk assessment is iterative and informs the appraisal of risk management options within a wider decision-making context.

Exposure assessment (Box 5.1) is an important stage of the risk-assessment process, as risks cannot occur without the exposure of a target or receptor to the source of the hazard. For chemical exposure, this principle is encapsulated within the phrase 'the dose makes the poison'; that is, it is the amount of a hazardous substance (either as a one-off dose or as incremental doses over time) that reaches a receptor that is important in determining the risk, along with the dose–response function. This reference to exposure provides us with a broader context for a discussion of pollutant transport processes, in that these processes inform exposure assessment — they represent the pathway(s) between the source of the hazard and the receptor and their characteristics determine the amount of pollutant to which the receptor is exposed.

5.3.3 FORECASTING THE FUTURE STATE OF THE ENVIRONMENT

Risk assessment has become an important tool in moving environmental regulation from a reactive to a more proactive activity. This is because risk can also be concerned with what may happen at some point in the future, should exposure to a particular hazard result in an anticipated exposure. Estimating, or forecasting what may happen as opposed to making decisions about the future based solely on the current state of the environment is, by definition more defensible. It may also prove to be more economical. Notwithstanding the above, forecasting the future state of our environment, through an understanding of the risks that may occur, is a complex area. The environment is a dynamic system, and about which comparatively little is known. As a consequence, accurate forecasts of the future state of the environment will not be possible. However, it is clear that, by looking for possible future scenarios, such as the need to regenerate brownfield sites for future house building, regulation and environmental protection effort can be focused appropriately.

Given our knowledge of how industry and other pressures such as the disposal of waste, private transport and energy usage will change in the future, we can make reasonable assumptions about the future. In addition, in some areas we can predict how the environment may respond to such changes in inputs. A considerable constraint, however, is the paucity of risk-based environmental standards. The Royal Commission on Environmental Pollution has recently expressed concern in this area (Royal Commission on Environmental Pollution 1998). In the absence of standards with an acceptable probability component,

regulatory action can only be taken on when damage occurs, as opposed to when the likelihood of damage exceeds a predetermined acceptable level. The paucity of such standards will constrain our ability to forecast the severity of future environmental damage.

The needs of future generations are a particular consideration when it comes to long-term environmental management and protection. Increasingly, it will be possible to identify risks to future generations and the environment in which they may live. However, placing a value on that environment, in order to balance the costs of risk mitigation today is much more difficult, and will require some important assumptions. While our knowledge of pollutants, transport processes and their short-term effects has increased, gaps in our longer-term understanding and of the socio-economic implications of the effects warrant attention.

5.4 POLLUTANT TRANSPORT PROCESSES AND EXPOSURE ASSESSMENT IN A REGULATORY CONTEXT

5.4.1 CONTEXT

The Environment Agency of England and Wales was established on 1 April 1996. It has statutory responsibilities for water resources, pollution prevention and control, flood defence, fisheries, conservation, navigation and recreation across England and Wales. For the Environment Agency, environmental exposure assessment (Pollard *et al.* 1999) is concerned with evaluating the mechanisms, probability, duration and magnitude of exposure to a hazard. It is principally concerned with the 'pathways' by which exposure may take place. Hazard sources of interest may be **physical** (e.g. flood waters), **chemical** (e.g. oestrogenic substances) or **biological** (e.g. algal blooms) in nature, and the receptors of interest may include humankind, buildings and infrastructure, ecosystems and environmental capital (air quality, aquifers).

The study boundaries for environmental exposure assessment are potentially from the initiation of the hazard (whether intentional or accidental, natural or anthropogenic) to the point where harm is manifest and, therefore, may include:

1. Direct release from the source term to the recipient environmental medium (e.g. stack emissions to the atmospheric environment).
2. Advective transport and distribution within a recipient medium to an exposure point (e.g. transport of a point-source discharge via surface water flow).
3. Multimedia fate processes between recipient media and other indirect media, for example, the partitioning of organic compounds between recipient soil and groundwater or soil and plants (Wilson *et al.* 1996, Duarte-Davidson and Jones 1996).
4. Transport mechanisms to points of exposure (advection, diffusion and dispersion of landfill leachate or groundwater pollutants to public supply boreholes).
5. 'Dose' estimation (via direct and indirect pathways), with reference to factors influencing exposure to the hazard, ultimately as the 'effective' dose.

In practice, the detail of dose estimation, beyond consideration of an exposure point concentration (for example as an actual or predicted environmental concentration), is encapsulated during the derivation of an environmental quality standard.

5.4.2 CURRENT PRACTICE IN THE APPLICATION OF POLLUTANT TRANSPORT MODELS

Most pollutant concentrations can be estimated through monitoring or modelling. At present, environmental modelling effort focuses on the use of **environmental distribution models** concerned with the transport, degradation or multiphase partitioning of contaminants in the environment in space and time. In practice, **dose determination modelling** for the evaluation of exposure intakes is not widely applied with the exception of product licensing and radioactive waste disposal. In the future, however, this will become a wider feature of the Agency's new duties and powers on contaminated land, for example. **Pharmacokinetic modelling** for the determination of effective doses at the target organ from exposure point 'intakes' is not in routine practical use at present.

Increasingly, environmental distribution models can incorporate contaminant removal processes such as biotransformation, decay or hydrolysis; processes themselves that might be incorporated within bulk transport models. For rivers, groundwater and air, finite element dispersion modelling is used to determine concentration distributions within a medium, usually as a function of space and/or time (Douben 1998). Many models of pollution dispersion in environmental media are based on simplified parameterizations of ensemble-average conditions. This is particularly true of air dispersion models, for example, which for many years have focused on ensemble-mean dispersion rather than on trying to include the detailed (in time and space) fluctuations occurring around the ensemble mean on specific occasions (i.e. realizations). The advent of shorter-term and higher-percentile air quality standards has made it necessary to develop models that can predict the probability of such fluctuations. Generic multiphase partitioning models (e.g. USES and EUSES) are applied in chemical product licensing for predicting equilibrium distributions of contaminants across air, water, soil and biota and invoke Mackay fugacity modelling for these purposes (van Leeuwen 1995).

5.5 CASE STUDIES FROM THE GEOSPHERE

For the modelling of pollutant transport processes and the execution of exposure assessment, the geosphere presents the particular challenges of:

- extreme system heterogeneity
- multiple phases (pore fluids, mineral and organic matter, biota and often 'free product') in intimate contact and

- analytical difficulties that often hinder model validation (Hrudey and Pollard 1993).

All models in this context become a gross simplification of the field situation. Nevertheless, transport processes must sometimes be simplified for the purposes of informing regulatory decisions on the management of risk. Three case studies of regulatory exposure assessment are presented below that illustrate the role of pollutant transport processes in this regard.

5.5.1 SOIL VAPOUR INTRUSION INTO BUILDINGS FROM CONTAMINATED LAND

The increased use of brownfield sites for housing, and the concerns expressed regarding the movement of pollutants from contaminated sites into adjacent buildings has emphasized the need for the rigorous assessment of human health risks from soil pollutants. In deriving guideline values to protect against unacceptable risks to human health from land contamination, the Department of the Environment, Transport and the Regions has developed an exposure assessment model (Contaminated Land and Exposure Assessment (CLEA) model) that incorporates a number of exposure routes. For volatile substances,

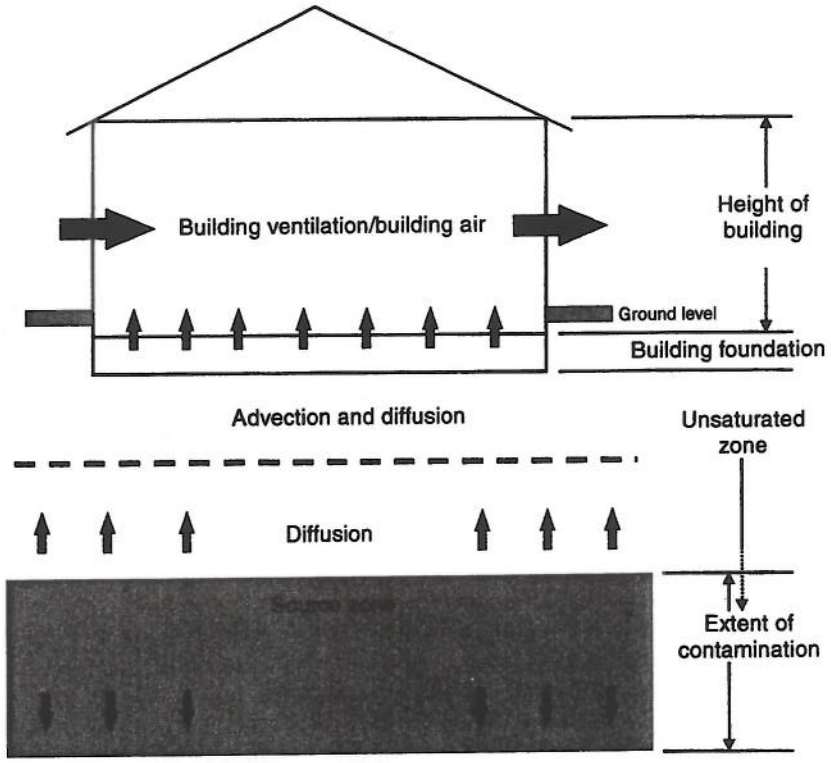


Figure 5.2 Soil vapour intrusion into buildings from contaminated land.

soil vapour intrusion from surface or subsurface contamination in the geosphere can be an important route of exposure.

A wide variety of models have been developed to predict soil vapour concentrations based on pollutant concentrations measured in soils, building design and the most likely migration routes (see for example Johnson and Ettinger 1991, Ferguson *et al.* 1995, Hers *et al.* 1997, Johnson *et al.* 1998). Figure 5.2 is an illustrative example of such models and shows a one-dimensional steady-state transport model based on a multi-compartment framework is presented, where the relevant compartments are the source of the pollution, the unsaturated soil zone and the building foundation. Models like this can be used to estimate contaminant levels inside buildings from the soil vapour concentration based on the equilibrium partitioning between the absorbed, aqueous and vapour phases, and are based on octanol–water partition coefficient, organic carbon content and effective diffusivity.

The complexity in the estimates produced by individual models can vary considerably, reflecting the purpose for which the model is being developed. Generally, models incorporate the fate and transport processes in the unsaturated zone and transport through the building foundation, taking into account the foundation construction, building ventilation rates, enclosure height and estimated flux from subsurface sources. More complex models may consider degradation rates and fate and transport processes in the source zone.

5.5.2 NEW SUBSTANCES REGULATION

European Union (EU) legislation requires that, to comply with the 'new substances' regulations, the appropriate authorities, including the Environment Agency, need to collect relevant documentation to assess the intrinsic hazardous properties of substances prior to agreements on product licensing. Regulatory authorities conduct a preliminary evaluation of human health risks, using the limited information normally supplied regarding exposure. All risk assessments of new chemicals must be conducted in accordance with guidelines set out in the European Commission's *Technical Guidance Document (TGD) on Risk Assessment of New and Existing Chemicals* (European Commission 1996). The guidance documents are used by the Environment Agency to assess the intrinsic hazardous properties of these substances before, for example, introduction into the market. The *TGD* document provides guidance on the assessment of risks from chemicals to humans and the environment and uses simple compartmental models for surface water, groundwater, soil and air and a multimedia approach for estimating exposure to humans.

Exposure assessment for the soil compartment is important with respect to terrestrial organisms. Contaminated soil may also lead to indirect human exposure via the consumption of crops grown on agricultural soils or cattle grazing on contaminated grassland. Figure 5.3 shows the key fate-determining processes of chemicals in soil. When considering exposure of contaminants in

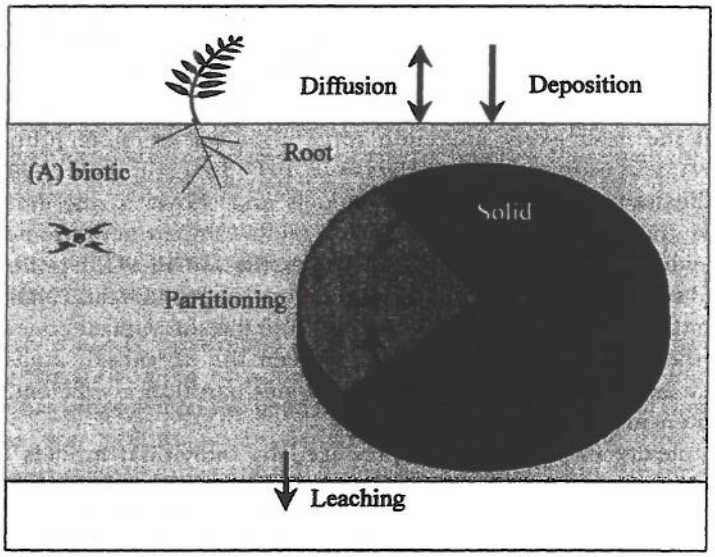


Figure 5.3 Possible fate processes of chemicals in the soil compartment (adapted from van de Meent *et al.* 1995).

the soil environment, the *TGD* considers the exposure from sludge-amended soils and from dry and wet deposition from the atmosphere. The mobility of chemicals in the soil is largely determined by the partitioning between the solids, air and pore water in soil, which can be estimated from the adsorption/desorption rate constants and the Henry's law constant. Soil sorption influences migration of chemicals down the soil profile and volatilization from the soil surface. In addition, the bioavailability to, and biotransformation by soil micro-organisms is dependent on the fraction of the chemical not adsorbed to the solid fraction of the soil.

5.5.3 PROTECTION OF WATER RESOURCES FROM SOIL-BORNE POLLUTANTS

The Environment Agency's Groundwater Protection Policy (for context and explanation, see United Kingdom Groundwater Forum 1998) sets out a framework of guidance to ensure that groundwater resources are safeguarded from pollution. A serious risk to groundwater quality can arise from accidental spills or leaks from tanks and pipelines of petroleum products and solvents. Where only sparingly soluble, the bulk or 'free products' (that is, liquid solvents), are referred to as non-aqueous phase liquids (or NAPLs). They can be further subdivided into light (L) and dense (D) NAPLs, according to whether they are lighter or denser than water. The presence of NAPLs in the unsaturated and saturated zones of subsurface soils offers a potential source of ongoing pollution

to ground and surface waters. Because of the nature of these compounds, they present a formidable multiphase problem with respect to their remediation (Figure 5.4). Following a spillage, LNAPLs will percolate through the unsaturated zone of the soil. Once they reach the surface of the groundwater table, they form a floating pool of material; the soluble constituents then dissolving into the groundwater and migrating in the direction of groundwater flow. If a significant portion of the LNAPL is retained in the unsaturated zone, volatilization can become an important pathway. Dense DNAPLs are transported by gravity through the unsaturated zone, and once it reaches the saturated zone a plume can develop of dissolved chemical. Ultimately, the sinking free product can descend to the bedrock, forming a pool of free product that is almost unrecoverable.

The derivation of remediation objectives for soils posing a threat to water resources relies on a back-extrapolation of water quality standards at the receptor to the soil or groundwater concentration at the source: an exposure assessment operating in 'reverse'. A tiered approach (Figure 5.5) has been developed by the Environment Agency that involves structured decision-making, cost–benefit analysis and progressive data collection and analysis (Environment Agency 1999). At each tier, a remediation objective is derived that can form the starting-point for regulatory decisions on the standard of remediation. With successive tiers the data requirements and sophistication of the analysis increases, with a corresponding reduction in the uncertainty of the predicted impact (Figure 5.5). The increase potentially allows for a relaxation in the remedial requirements, if the risk assessment is favourable. Tier 1 considers whether the concentration in pore water in polluted soil below the site is sufficient to impact on the receptor, ignoring dilution, dispersion and attenuation processes. Tier 2 takes into account the dilution effect in the receiving groundwater or surface water body and whether this is sufficient to reduce the pollutant concentration to acceptable levels. Tiers 3 and 4 consider whether natural attenuation of the pollutant, as it moves through the unsaturated and saturated zones to the receptor, are sufficient to reduce contaminant concentrations to acceptable levels. The difference between Tiers 3 and 4 is that Tier 4 uses more sophisticated numerical models and predictive processes to calculate the significance of the attenuation. For each tier, the pore water concentration determined for the soil zone is compared to a remedial objective to determine the need for remedial action.

These case studies illustrate the link between pollutant fate and transport, environmental forecasting in the context of predictive modelling and environmental exposure assessment within the broader context of risk assessment. After the uncertainties associated with the baseline toxicology, it is often the exposure assessment that harbours the greatest source of uncertainty for risk assessors. From a regulatory perspective, decisions must be based on sound science, but they will also often be made in the face of considerable conceptual and data uncertainty. This dilemma can be addressed in part by risk assessors ensuring:

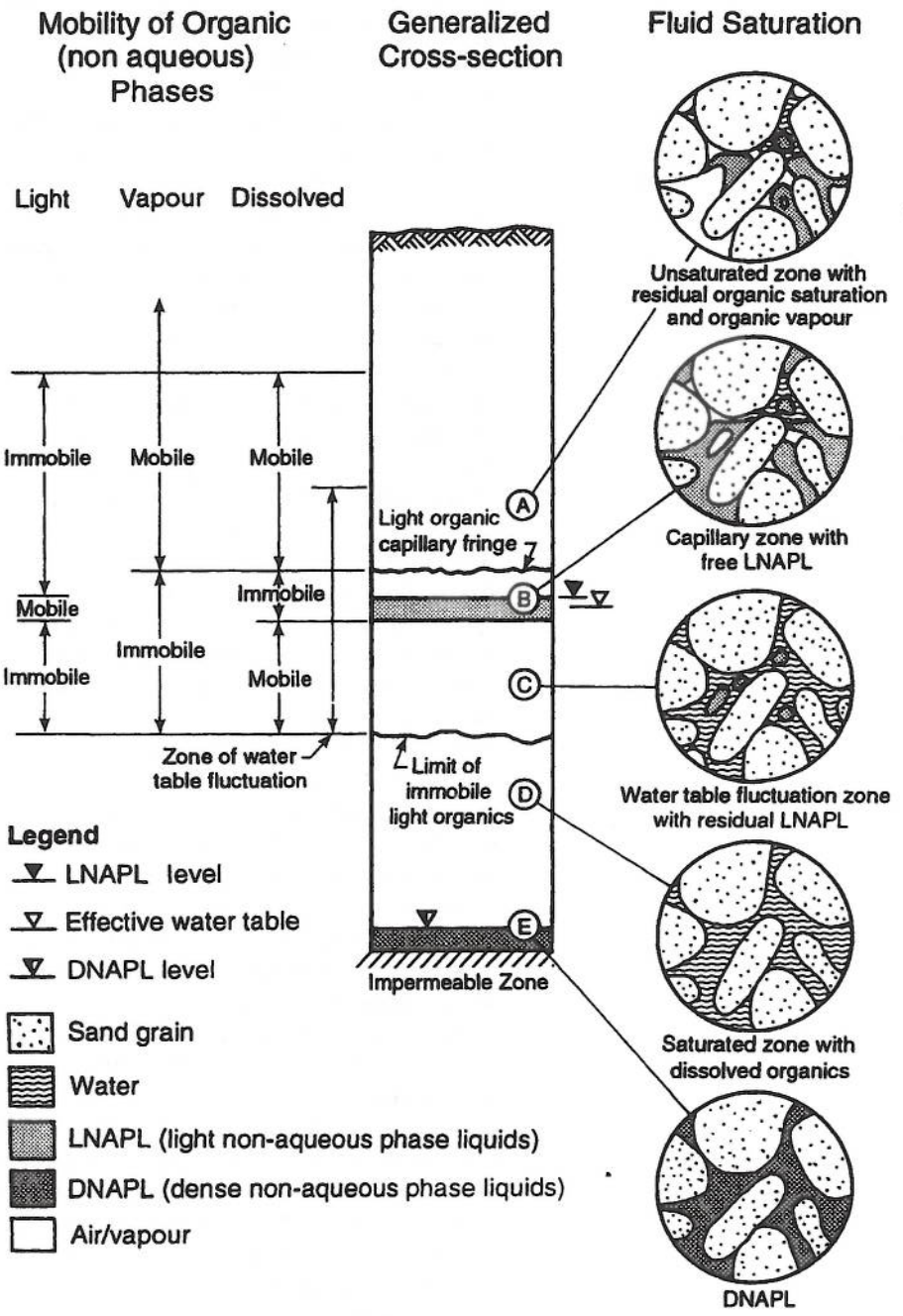


Figure 5.4 Multiphase pollution of non-aqueous phase liquids in the subsurface (after Hrudey and Pollard, 1993).

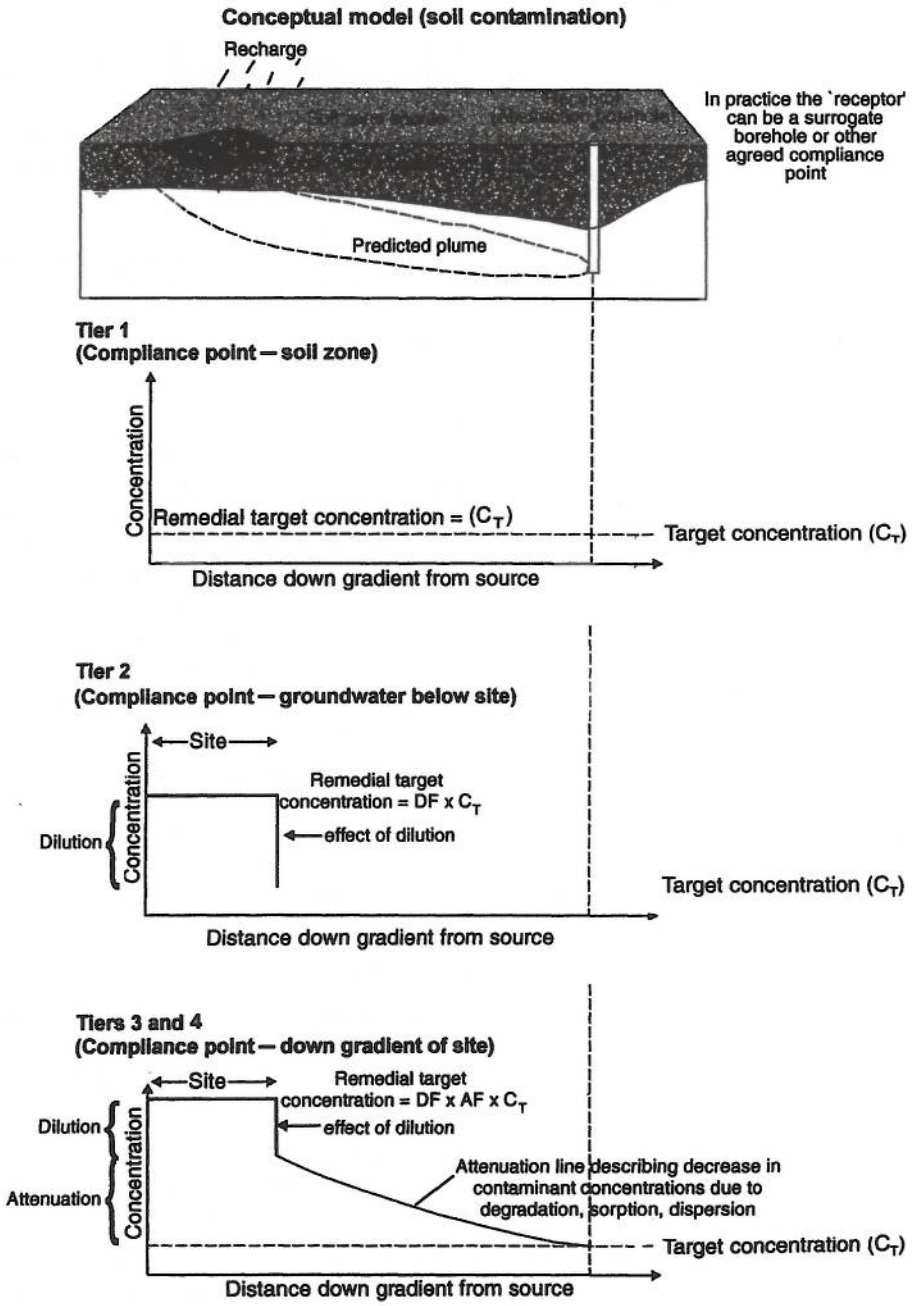


Figure 5.5 Summary of tiered approach for the derivation of remedial objectives to protect water resources from land contamination (Environment Agency 1999).

1. The conceptual model of exposure is bounded and agreed by all parties early on.
2. A clear, unambiguous guiding rationale to the exposure assessment is presented prior to detailed analysis.
3. Uncertainties in the exposure assessment are recognized and prioritized.
4. Input data is of a high quality and validated.
5. The level of analysis in the exposure assessment is proportionate to the problem and input data quality.
6. Assumptions are clearly justified and referenced.

5.6 CONCLUSIONS

1. Forty years of research in pollutant transport processes has enlightened the environmental science and engineering community as to the fate and behaviour of pollutants in the environment.
2. Many of these processes have been modelled for use in compliance assessments in regulation, starting first with the aquatic and air environments where homogeneity has often been assumed, but moving beyond to the geosphere.
3. The development of environmental risk assessment as a management tool for assessing the risks of pollutants to humans and the environment embraces pollutant transport as a component of the exposure assessment.
4. Environmental legislation and regulatory guidance is now actively adopting the outputs of the research community to better inform regulatory decision-making.

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CHAPTER 4

Soils and Land Contamination

S.J.T. POLLARD AND M.G. KIBBLEWHITE

Cranfield University, UK

4.1 INTRODUCTION

4.1.1 Soil as a Living System

Soil, with air and water, is one of the three key compartments of the terrestrial environment.[1] It is a living system made up of complex communities of organisms that use carbon from plants as substrate. Soil organisms process approximately 60×10^{18} tonnes of plant carbon globally per year.[2] It is the presence of organic matter and biological activity that distinguishes soil from the regolith (weathered rock).

4.1.2 The Soil Habitat

The biomass in most soils is greater than that in the corresponding above ground habitat. It is of the order of 3 tonnes ha^{-1} in temperate agricultural soils (Table 1). Moreover, it is characterised by extreme diversity, which increases with decreasing spatial scale: at the cm scale, there are only a few mammals; at the mm scale, there are hundreds of larger invertebrates; while at a microscopic scale, there are many tens of thousands of species of microbe.

Table 1 *Abundance of microorganisms and fauna in soil*

Organism	*Abundance*
Algae	10^4 cells g^{-1}
Fungi	10^6 cells g^{-1}
Nematodes	$10–10^2$ g^{-1}
Protozoa	$10^5–10^6$ cells g^{-1}
Actinomycetes	10^7 cells g^{-1}
Bacteria	10^9 cells g^{-1}

This diversity underpins the multifunctionality of the soil system and its capacity to deliver a wide range of ecosystem services (*e.g.* food and fibre production, the retention of water in catchments) upon which humankind relies.

The "architecture" of the soil, in terms of the physical network and size distribution of pores and the associated behaviour of water and dissolved solutes, has been proposed as a key factor controlling the type and extent of life in soil.[3] The physical and chemical nature of the soil habitat determines the types and condition of biological communities and so the health or quality of the soil system. The spaces between particles and aggregates form a system of pores, which are filled with aqueous soil solution and gases. The extent and size distribution of these pores is critical (Figure 1). In general, a soil that has an open structure that allows a free movement of water, solutes and gases into and out of it will support a richer biological community than one with a massive structure.

Soils are continually subject to physical and chemical stresses. How a soil reacts to stress can be described in terms of response and resilience[5] (Figure 2). Resistance is the change in state for a given level of perturbation, for example, a reduction in the respiration rate arising from compaction. Resilience describes how far the system is able to return to it original state. Restoration of the physical and chemical condition of degraded soil habitats is a pre-requisite for biological recovery, but even with active management, return to fully functioning soil systems may take many years. Methods for assessing the biological health of soil are not yet agreed, although basic measurements of soil biomass and respiration rates are useful, if not always easily interpreted.

4.1.3 Soil Functions

Soil supports a range of ecosystem services that are critical to the quality of human life and the conservation of biodiversity.[6] Soil resources represent

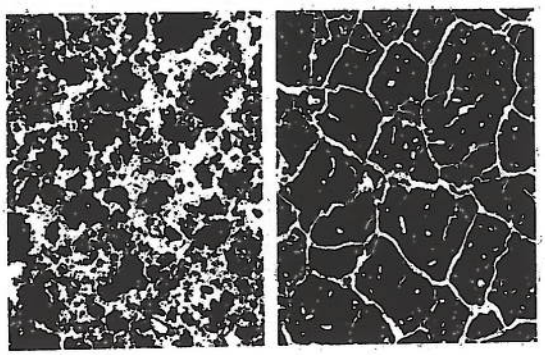


Figure 1 *Soil pore networks*
(Reproduced from Crawford, Ritz and Young (1993))[4]

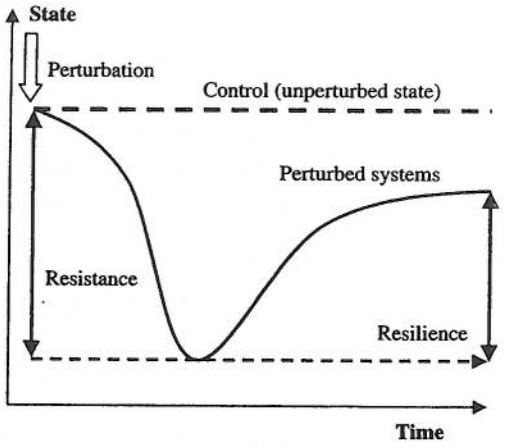


Figure 2 *Graphical representation of trajectory of resistance and resilience to perturbed system* (After Ritz *et al.* (2003)[5])

'natural capital' for current and future generations. Starting from the agricultural revolution of the early nineteenth century, scientific interest in soil has focused on its role as a medium for plant growth and the production of food and fibre. This remains an important focus. Increasingly however, other soil-based services are recognised as being of equal or even more importance.[7] Soil links the atmosphere to surface as well as groundwaters, attenuating and degrading pollutants as well as moderating the hydrology of river basins. Soil conserves biodiversity, both directly below the ground and indirectly above the ground. Soil is a platform for the natural as well as the built terrestrial environment, providing physical foundations for buildings and anchorage for plants and trees. The role of soil in the formation and maintenance of landscapes, urban as well as rural, is critical to our sense of place and community, while soil is often an artefact itself as well as a medium for archaeological conservation.

4.1.4 Soil Protection

Maintenance of the capacity of soil to deliver this wide range of services requires that the soil system remains intact and its performance is not compromised by imposed stresses. Particular threats to soil include surface sealing by construction, erosion, contamination and loss of organic matter. Figure 3 shows the range of soil organic carbon across Europe. Other threats that are important in some regions and with particular land uses include increased salinity and compaction.

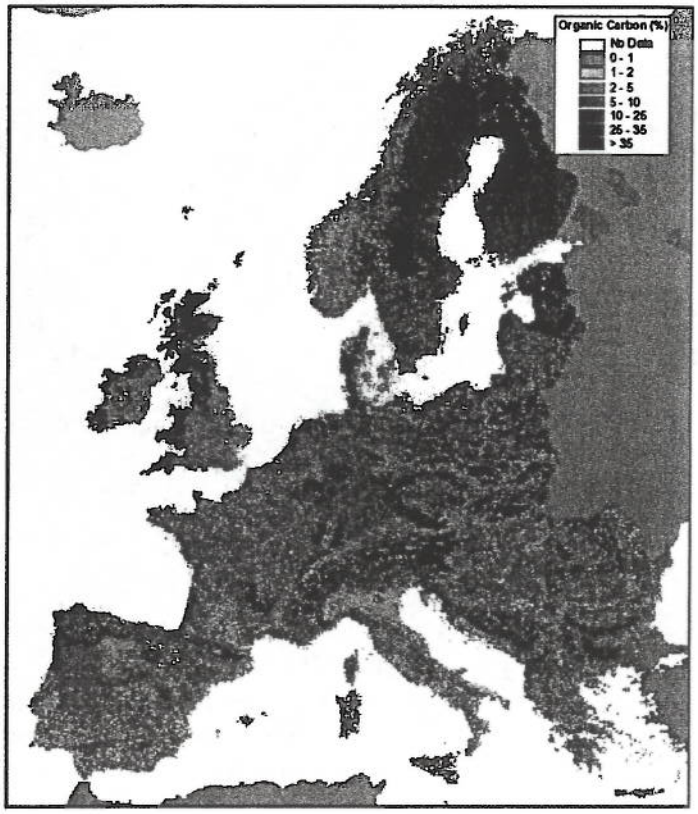


Figure 3 *Organic carbon content (%) in the surface horizon of soils in Europe* (European Soil Bureau Network)

4.2 SOIL RESOURCES

4.2.1 Soil Formation

There is a great variety of soil types. Different soils form depending on a range of factors, including the available parent material (which may be hard rock but is often superficial deposits), the climate, the landscape topography, the past and present land use and the time over which soil formation has occurred. The result is a three-dimensional continuum of soil properties,[8] with different types of soil prevailing in different locations, each with a set of distinct horizontal layers (horizons) that make up a characteristic soil profile (Figure 4). The process of soil formation is called pedogenesis and combines physical, physicochemical and biological processes.

The soil water regime has a profound influence on soil formation, properties and behaviour. Where precipitation exceeds evapotranspiration (the combined evaporation losses from plants and the soil surface), the tendency

taken in a spatially representative manner. Similarly, estimating the background distribution of an element in a region may require a complex pattern of sampling so that different populations of soil types are represented adequately. More complex still are sampling designs that are capable of measuring change in soils, which is also subject to spatial and temporal variation.

4.3 SOIL CONSTITUENTS[10]

4.3.1 The Mineral Fraction

4.3.1.1 Texture. The particle size distribution of mineral components in a soil is described by its texture. Three main size fractions are recognised in the international classification scheme; namely sand (particle diameter 0.02–2.00 mm), silt (0.002–0.02 mm) and clay (<0.002 mm). Textural classes are defined as in Figure 6. Silica is the main component of the sand fraction.

4.3.1.2 Clay Minerals. The clay fraction contains a variety of clay minerals, depending on parent material and the strength and length of time of weathering. These aluminosilicates are secondary minerals produced by weathering of primary minerals in rocks. They are sheet silicates formed from two basic components: tetrahedral silica and octahedral alumina. Isomorphous substitution, of either Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+} in the structural sheets, generates

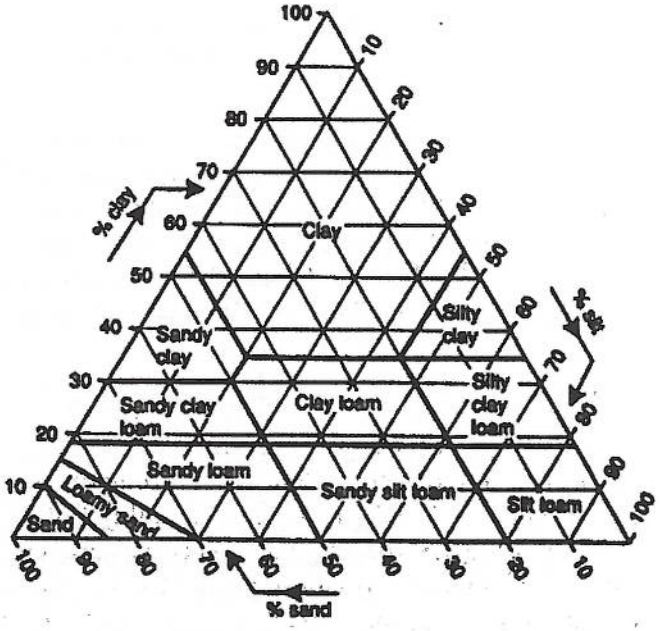


Figure 6 *Soil texture classes*

negative charges on the clay surface. This permanent excess negative charge is independent of the soil pH and contributes to the cation exchange capacity (CEC) of a soil.

Some clay minerals are non-expansive while others shrink and swell with varying soil moisture. This shrinking and swelling has a strong influence on the formation of soil aggregates and structure. The predominant non-expansive clay mineral is kaolinite, which has silica and alumina in a ratio of 1:1 and a relatively low surface area (up to $100\,m^2\,g^{-1}$) and a CEC of $2–20\,cmol\,g^{-1}$. Smectites are a group of expansive clay minerals with silica and alumina in a ratio of 2:1. They have a large surface area ($700–800\,m^2\,g^{-1}$) with access to interlamellar surfaces, which, together with isomorphous substitution, leads to their high CEC ($80–120\,cmol\,g^{-1}$). Montmorillonite and bentonite are important smectitic clay minerals. Illites have properties which are intermediate between kaolinite and the smectites, while vermiculite has extensive isomorphous substitution of Mg^{2+} for Al^{3+} leading to a high CEC ($100–150\,cmol\,g^{-1}$).

4.3.1.3 Metal Oxides. Oxides of Fe and Al are ubiquitous in soil and are the ultimate residual weathering products of rocks. The quantities in soil depend on the mineralogy of the soil parent material, the extent of secondary weathering and the prevailing oxidation–reduction (redox) conditions. The prevalence of Fe in its various forms can be presented in a *pe*-pH diagram (Figure 7). Here, the chemical form of Fe is presented by reference to the soil pH and the soil oxidisability (its redox status) represented here by *pe*, the negative common log of the free electron activity. Larger *pe* values favour oxidised species and smaller *pe* values favour reduced species.

The pH-dependent solubility of both Fe and Al leads to their dissolution and precipitation with varying pH. Co-precipitated hydrous oxides of Al and Fe have an amorphous structure. The behaviour of Fe is also controlled by redox conditions, with reducing conditions generating soluble Fe(II) and oxidising ones Fe(III), which is precipitated at higher pH. The ferromagnesian minerals, such as olivine, augite and biotite mica that are found in igneous rocks are a particularly rich source of Fe. Under the oxidising conditions found in freely draining soil environments, Fe(III) oxides are highly stable and give rise to the characteristic brown colouration of many soils. The main forms of Fe oxide are ferrihydrite ($5Fe_2O_3 \cdot 9\,H_2O$), goethite (alpha-FeOOH) and in warmer soils, haematite (alpha-Fe_2O_3). In poorly drained and waterlogged soils, reducing conditions produce more soluble Fe(II). Commonly, such conditions exist within the core of larger peds (aggregates) even when the overall soil condition is not reducing. Manganese oxide is precipitated as MnO_2 when Mn(II) is oxidised to Mn(IV). If reducing conditions are restored, the reverse reaction is slowed by the solubility of MnO_2.

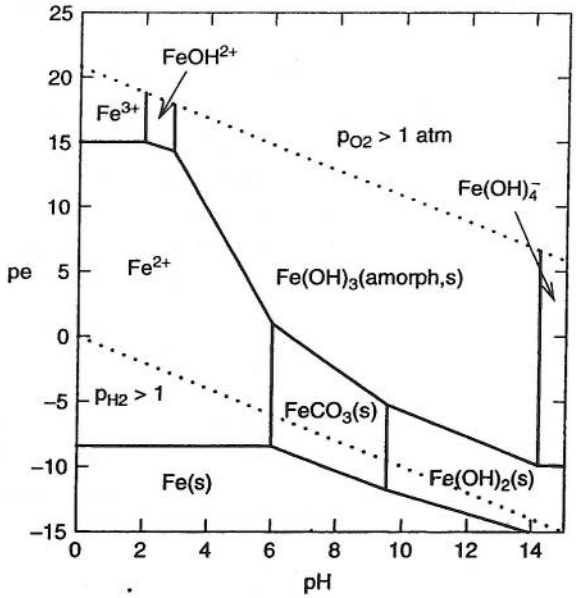


Figure 7 *Phase diagram for the Fe–CO_2–H_2O system in soils*
(G.J.D. Kirk, *The Biogeochemistry of Submerged Soils.* Wiley, Chichester, 2004)

4.3.1.4 Carbonates. Calcium carbonate or calcite ($CaCO_3$) occurs in soils with chalk- or limestone- containing parent material but is also formed by chemical reactions in the soil profile, for example in semi-arid soils. Where free calcite is naturally present in soil, this ensures a soil pH above 7.0. Calcite also contributes to the chemisorptive properties of soil. Liming of soil to modify its pH is a well-established practice in agriculture for controlling soil fertility; it is also used to control the solubility of contaminants that are precipitated at higher pH and would otherwise be phytotoxic or be a source of wider environmental contamination.

4.3.1.5 Sulfides and Sulfates. The forms of sulfur (and also selenium) change with varying redox condition, a process that is mediated biologically. Sulfides occur in anaerobic soils and in soils that are periodically anaerobic due to waterlogging (gley soils). Sulfate moves down or up the soil profile, depending on net water movements. Calcium sulfate (gypsum) is found in the surface horizon of semi-arid and arid soils and in the lower horizons of some temperate soils where groundwater is saturated with calcium.

4.3.1.6 Trace elements. Depending on parent material, past land-use and atmospheric deposition, soil contains varying quantities of a wide range of trace elements. Urban soil often contains much higher concentrations of metals from anthropogenic sources (see Table 2).

Table 2 *Ranges of heavy metal concentrations (mg kg^{-1}) in grassland soils of Austria as compared to public greens and parks in Vienna*[11]

Metal	*Grassland soils (mg kg^{-1})*	*Soils in urban parks*
Cd	0.14–0.59	0.33–0.88
Cr	19.8–66.6	16.4–40.3
Cu	11.2–43.2	22.6–81.1
Hg	Upto 0.33	0.14–0.96
Ni	9.1–46.2	22.2–34.5
Pb	12.3–55.7	37.2–143.7
Zn	52.6–145.0	84.2–269.6

4.3.2 Organic Matter

Plant residues and products of their microbial decomposition contribute to the formation of soil organic matter (SOM), which has a highly heterogeneous composition. The levels of organic matter in wetter and colder soils tend to be higher than those in drier and warmer ones. Soils in arid environments typically contain only small amounts of organic matter (<1%), whereas those in humid temperate regions have greater contents (*e.g.* 1–10%). Within a climatic region, soil wetness influences organic matter levels. There is evidence that minimum levels of organic matter, at least in temperate soils, increase with higher clay contents[12], possibly because a combination of strong absorption and occlusion reduces microbial degradation.

Globally, there is much more carbon in soil than in either the atmosphere or above the ground biota, so understanding the dynamics of soil organic carbon is important for modelling of global carbon cycles. The overall dynamics of soil organic carbon reflect changes in different carbon pools that turn over at widely varying rates[13]. Relatively, fresh plant material including roots is quickly colonised by microbes and a small proportion of this is incorporated into SOM (most is respired to the atmosphere). Polysaccharides and other extra-cellular material from microbes are released into soil pores where they may become inaccessible and combined with metal oxides. More recalcitrant plant material such as lignin is degraded more slowly. Except in cold and wet soils, where peat forms, carbon in plant material is either respired to the atmosphere or incorporated into SOM within a few seasons. This newly formed SOM is then repeatedly cycled through the soil biota over lengthening periods, with each cycle releasing carbon to the atmosphere. The most aged soil carbon has half-lives measured in hundreds of years and is in forms that appear to be resistant to biological degradation. This stability may arise from a combination of molecular heterogeneity and strong adsorption within and on clay minerals.

Extensive structural investigation of SOM, lasting more than a century, has provided only incomplete information on its chemical nature. Classical

investigations were based on extraction of soil with alkali, followed by acidification of the extract to separate an acid-soluble fulvic acid fraction from an acid insoluble humic fraction. Organic matter that could not be extracted from soil by alkali was termed as humin. Attempts to assign formal structures to fulvic and humic acids are probably misleading. These are colloidal materials of indeterminate composition and a wide range of molecular weights, containing varying quantities of co-extracted Al and Fe. Studies of carbon in whole soil using techniques such as ^{13}C NMR and pyrolysis GC–MS have revealed information about the relative proportions of carbon forms in SOM, including the prevalence of aromatic structures[14]. Characterisation of soil extracts has revealed that soil contains most classes of natural organic molecules, including lipids, polysaccharides and polyuronic acids, polyphenols and polycarboxylic acids. The overall nature of SOM can be summarised as being polymeric, heterogeneous and colloidal, with a predominance of carboxylic acid and phenolic groups, which support a high, pH-dependent, CEC (up to 200 cmol kg^{-1}).

Typically, the nitrogen content of SOM is about one-tenth to one-twentieth of the carbon content. This nitrogen, together with soil phosphate, strongly influences the natural fertility of soil and forms the main reservoir of nitrogen in the terrestrial environment. Surprisingly, given its importance to agriculture and ecosystems in general, the form of this nitrogen is not known completely. About half of it can be accounted for by amino acids, amino sugars, nucleic acids and other identifiable structural components. In some circumstances, a further significant component is adsorbed ammonium.

4.4 SOIL PROPERTIES

4.4.1 Water Retention and Drainage

4.4.1.1 The Soil Pore System. The voids between soil particles and aggregates form a continuous system of pores within the soil profile. The complexity of this labyrinthine system reflects the wide range of particle and aggregate sizes and shapes. It is a highly important feature of soil, because it controls the movement of water and air into and from the soil profile, which in turn controls the mass transfer of gases, liquids, sediment and other particles, and dissolved substances.

4.4.1.2 Soil Water. Experimentally, water-retention curves can be determined for soils by applying progressively higher tensions using a porous plate or pressure membrane apparatus and measuring the resulting equilibrium water contents. Water contents are then plotted against applied pressure on a logarithmic scale (pF) as in Figure 8. The form of the retention curve depends on the distribution of pore sizes, because fine pores hold water more strongly against

an applied pressure than do the coarse ones. Figure 8 illustrates retention curves for a clay loam and a fine sandy loam and their relationship to pore size. Pores with diameter greater than 30 μm tend to drain under gravity while water in smaller ones is held by capillary action. When a saturated soil is allowed to drain fully, its water content reduces to "field capacity" and is then largely held in pores of less than 30 μm diameter. The precise water content at which field capacity is reached is not easily determined because the pore structure in soil is not uniform and, within the bulk soil, different volumes have different capacities to hold water.

In addition to the inter-particle pores, larger ones (macropores) are normally present in soil as worm burrows, root channels and cracks opened by shrinking and swelling during seasonal wetting and drying cycles. If the soil is cultivated, macropores may have been introduced by tillage, including sub-soiling. These larger pores allow bulk drainage of water through the soil profile to groundwater, or to field drains.

When a surface load is applied to soil by, for example, vehicles, animals or storage of bulk materials, the soil may become compacted, especially if it is wet and above its plastic limit, which is lower for finer textured soils. Compaction can also be caused by the shear forces set up by the interaction of wet soil and implements during tillage and excavation operations. Soil compaction disrupts

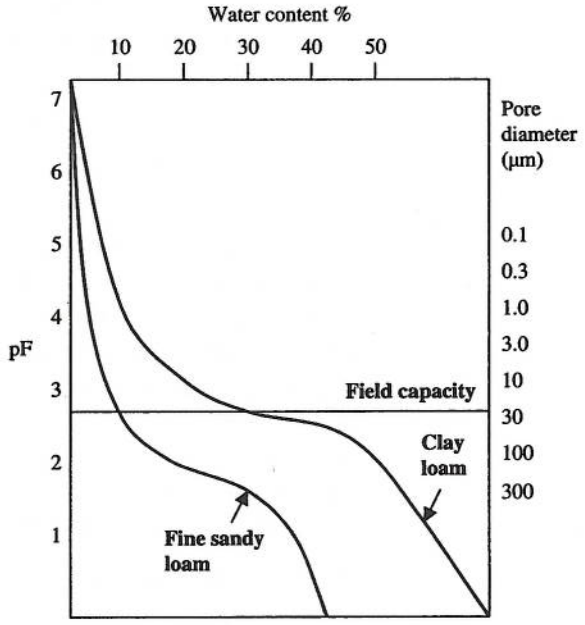


Figure 8 *Moisture retention curves for contrasting soils. Moisture content is plotted against applied pressure on a logarithmic scale (pF)*

the pore system and so water movement. It can lead to surface or lower horizons remaining saturated or at least wetter than soil that is deeper in the profile.

4.4.2 Soil pH and Redox

4.4.2.1 Soil pH. Soil pH is a measurement of the concentration of H^+ ions in the soil solution that are in equilibrium with the negatively charged surfaces of soil particles. Normally, soil pH is measured by equilibrating soil with de-ionised water, although under many field conditions the bulk soil solution contains cations such as Ca^{2+} and, in semi-arid and saline conditions, Na^+.

Soil pH is the most important physico-chemical characteristic of soil because it strongly influences the chemistry of the soil solution, affecting plant growth, microbial ecology and activity and contaminant chemistry. Soil pHs are normally in the range 4–9, although more extreme values occur exceptionally. In general, non-limed soils in humid regions tend to have pH values between 5 and 7 and those in arid regions between 7 and 9. In temperate regions, such as the UK, the optimum pH for arable soils is 6.5 and for grassland it is 6.0 and these values are maintained by liming of non-calcareous soils.

4.4.2.2 Redox Potential. Generally, a high oxygen demand in soil is maintained by aerobic organisms and plant root respiration. Rates of gaseous exchange with the atmosphere depend on the pore structure and its water content. Saturated soil containing fresh organic material will quickly become reducing. A fully drained, sandy soil that contains little fresh organic matter will remain mostly aerobic.

4.4.3 Adsorptive Properties

4.4.3.1 Soil Surfaces. The surface area within all soils is large and is greatest in fine textured clays. Many different types of surface are present and are heterogeneous. The surfaces of clay minerals are charged and therefore provide sites for physical adsorption of solutes. Clay and also sand particles are generally coated to varying degrees with organic matter and hydrous oxides of Al and Fe that carry a surface charge and sites for physical adsorption. Some surfaces are occluded within inaccessible pores, while fluctuating soil water fills and drains the soil solution to and away from surfaces. SOM has a higher CEC at pH 7 than other soil colloids, and therefore plays a very important part in the adsorption reactions of soils.

4.4.3.2 Physical (Non-Specific) Adsorption. Ion exchange (or non-specific adsorption) refers to the exchange between counter-ions balancing the surface charge on the soil colloids and the ions in the soil solution. Generally CEC increases with increase in soil pH, at least up to pH 7. It is the negative

charge on soil colloids that is mainly responsible for cation absorption. This negative charge arises in three ways: (a) permanent charges from isomorphous substitution in clay minerals; (b) dissociation of carboxylic and phenolic groups on organic matter; and (c) the pH-dependent charge on oxides of Fe, Al, Mn and Si. Hydrous Fe and Al oxides have relatively high isoelectric points (pH 8) *in vitro* but lower values in the soil system (c. pH 7) and so tend to be positively charged in most soils in which they occur.

A double diffuse layer exists in the volume of soil solution close to a charged soil surface. In the solution volume close to the charged surface, a net opposite charge forms from hydrated counter ions that have diffused a short distance into the soil solution. The thickness of this diffuse double layer depends on both the surface charge density and the soil solution (electrolyte) concentration and composition. The layer contracts with increasing charge density on the surface or in the soil solution. An important consequence of the diffuse double layer is that it acts as a partial barrier to the exchange of ions between the charged surface and the bulk soil solution. When the soil solution is a weak electrolyte the diffuse double layer is thicker and exchange of ions between the surface and the bulk solution requires more energy. In the case of H^+, this means that when the soil solution is saturated with Ca^{2+} as compared to Na^+, the diffuse double layer is more compressed and the effective pool of H^+ available by exchange from the soil surface is greater, and so the apparent pH of the soil solution is decreased. More energy is required to remove an ion with a large hydrated radius from the charged surface and the diffuse double layer, than one with a smaller hydrated radius. Thus cation adsorption strength increases with oxidation state and with increasing ratio of ion charge to radius. For example, although K^+ and Na^+ carry the same charge, Na^+ has a smaller ionic radius and so an increased hydrated radius and will displace K^+. The commonly quoted relative order of replacement of metal ions one by another to a cation exchange surface is as follows:

$$Li^+ = Na^+ > K^+ = NH_4^+ > Mg^{2+} > Ba^{2+} > La^{3+} = H^+$$

The anion adsorption capacity of soils is much less than their CEC. Below pH 7 or 8, Fe and Al hydrous oxides are positively charged and positive charges also occur on 'broken edges' of clay minerals. Simple ions, such as chloride or nitrate are only weakly absorbed by soil. Other ions, such as phosphate and arsenate, are absorbed more strongly, but in these cases the absorption is not purely ionic and non-specific.

4.4.3.3 Chemical (Specific Adsorption) of Metals. Specific adsorption occurs when a chemical bond is formed and therefore it is stronger than non-specific ion exchange. The main sites for specific adsorption are on Al, Fe and Mn oxides and organic matter.

Some oxyanions, such as phosphate and arsenate form strong and insoluble complexes with Al and Fe oxides, effectively removing them from the soil solution. Metals that form hydroxy complexes may also be adsorbed specifically to hydrous metal oxides. The order for increasing strength of specific adsorption is as follows:

$$Cd > Ni > Co > Zn > Cu > Pb > Hg$$

SOM carries a wide range of functional groups that are able to complex metal ions, in particular, carboxylic acid and hydroxyl ones. Normally, a large proportion of the available sites for complex formation are likely to be occupied by Fe and Al. The general pattern of stability of complex formation with SOM might be expected to reflect the order for the replacement of water from aqueous complexes, as follows:

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

In fact, the general order of stability for complexes of metals is as follows:

$$Cu > Fe = Al > Mn = Co > Zn$$

The strong adsorption of Cu may be enhanced by the presence of amine and other functional groups that adsorb this metal strongly, and the order is also affected by the potentially stronger adsorption when the oxidation state is higher than +2. These relationships and their pH-dependencies are also strongly influenced by the propensities of the different metal ions to form complexes with dissolved organic ligands.

4.4.3.4 Adsorption of Organic Compounds. Organic contaminants that form anions (*e.g.* the phenoxyalkanoic herbicide, MCPA) are less strongly bound to soil than those that are non-ionic (*e.g.* polyaromatic hydrocarbons (PAH)) or cationic (*e.g.* the bipyridal herbicides, paraquat and diquat). The adsorption to soil of non-ionic and non-polar anthropogenic organic contaminants, which includes many pesticides and persistent organic pollutants (POPs), occurs mainly but not exclusively on organic matter. The mechanisms for adsorption to organic matter are largely non-specific as evidenced by the ability of non-aqueous solvents to quite efficiently extract many of these molecules from soil. Adsorption to clay minerals is similarly non-specific. The strength of adsorption of non-polar organic contaminants by organic matter can be predicted by determining their octanol–water distribution coefficients (K_{ow}). Substances with low K_{ow} values tend to be more hydrophilic, whereas those with higher values are more hydrophobic and adsorbed more strongly by organic matter. For example, the herbicide 2,4-D (2,4-dichloro-phenoxyacetic acid) is relatively soluble in water (900 mg L^{-1}) and has a low K_{ow} ($\log K_{ow} = 1.57$), whereas the insecticide DDT has a low water solubility (0.002 mg L^{-1}), a high K_{ow} ($\log K_{ow} = 5.98$) and accumulates in SOM.

Case Study 1: Using Partition Coefficients for Soils and Groundwater

Estimate the dimensionless soil/water partition coefficient for 1,1,1-trichloroethane (log K_{ow} = 2.49) in (i) a silty loam soil (density ρ = 2.66 Mg m^{-3}) containing 19 g SOM per kg and (ii) a peat surface soil (ρ = 0.44 Mg m^{-3}) containing 650 g SOM per kg.

Here we assume that organic matter is 56% w/w organic carbon. We also estimate the organic carbon partition coefficient first knowing the Karickhoff (1981) correlation, which relates K_{oc} to K_{ow}:

The fraction of organic carbon in the soil, $f_{oc} = 19/1000 \times 0.56$
$= 0.01064$

From the Karickhoff correlation, $K_{oc} \approx 0.41\, K_{ow}$
$K_{oc} = 0.41\,(10^{2.49})$
$= 126.7\,\text{L kg}^{-1}$

Assuming for non-polar organics that hydrophobic interaction dominates the soil water partition coefficient (K_d)

$$K_d = f_{oc} K_{oc}$$
$$= 1.351\,\text{L kg}^{-1}$$

For a dimensionless quantity, we multiply by the density of the soil, remembering that the units Mg m^{-3} are equivalent to kg L^{-1}.

dimensionless K_d = 1.35 L kg^{-1} × 2.66 kg L^{-1}
= 3.59 for the silty loam, and
= 20.29 for the peat

Assuming a dimensionless K_d for the silty loam of 3.6, estimate the aqueous phase concentration (μg L^{-1}) of 1,1,1-trichloroethane in the soil solution, assuming the surficial soil is contaminated with 380 ppb 1,1,1-trichloroethane. Compare the result with a drinking water regulation limit of 30 μg L^{-1} for trichloroethane.

The soil/water partition coefficient is the ratio of the equilibrium concentrations of the chemical in these two media:

$$K_d = C_s/C_w$$

Rearranging, $C_s = K_d C_w$

$$380\,\mu\text{g kg}^{-1} = 3.6\, C_w$$

Multiply C_w by soil density:

$$380\,\mu\text{g kg}^{-1} \times 2.66\,\text{kg L}^{-1} = 3.6\, C_w\ \mu\text{g L}^{-1}$$
$$1010.8 = 3.6\, C_w$$

From which $C_w = 280.8\,\mu\text{g L}^{-1}$

This compared to a drinking water criterion of 30 μg L^{-1} for trichloroethane.

4.5 CONTAMINATION THREATS TO SOIL

In their role as a medium for food and fibre production and as an engineering platform for development, soils have been subjected to a number of contamination threats before and since industrialisation.[15] Soil scientists and land managers are faced with a wide range of threats to soil quality, including those from

- potentially toxic elements (pte) and pathogens in sewage sludge applied to agricultural land and forestry;
- industrial sludges (*e.g.* pulp and paper mill wastewater treatment, saline process residues) and canal dredgings applied to land as a means of waste disposal;
- radioactive isotopes released following industrial accidents or from wastes disposal;
- POPs deposited on soils following their aerial release from industrial processes;
- residues from production chemicals used in agriculture (pesticides, fungicides, herbicides);
- spent munitions and explosives following demilitarisation;
- heavy metals (Pb, Hg, As) and organic contaminants (petroleum hydrocarbons, polynuclear aromatic hydrocarbons (PAH)) from historic land contamination, discovered during redevelopment or factory decommissioning;
- nitrogen-rich organic manures and wastes applied to soils in nitrogen vulnerable zones;
- prion materials from wastes removed from the food chain to control bovine spongiform encalopathy (BSE) in cattle; and
- considerable quantities of animal carcass material released to soils during foot and mouth disease (FMD) outbreaks and similar emergencies involving animals reared for human consumption.

While our understanding of how to manage these threats has grown considerably, new threats continue to emerge; for example, those from the application of waste pre-treatment residues and low-grade composts to land, from the disposal of nuclear decommissioning residues to nuclear waste repositories, from new generation agricultural chemicals and from genetically modified organisms (GMOs) released to the soil environment.

The general scientific approach to managing these threats promotes the application of risk assessment and risk management[16] (Figure 9). This is being underpinned by an improved understanding of the environmental capacity of soils and the impacts of hazardous agents (physical, chemical and biological) on soil function.

Central to the management of risk is an understanding of "what specifically is at risk" (the soil function, the soil microbiota, crops, humans) and "what it is at risk from" (loss of buffering capacity, loss of soil structure, reduction in soil quality, loss of future use). Environmental risk assessment has become a discipline in its own right. A straightforward description of risk assessment is provided by considering it as answering four essential questions (Figure 9; Table 3).

Being composed of pore water, pore gas, biota, mineral and organic matter, the soil environment is susceptible to harm from contaminants that might arrive through water, air and direct application routes. For contaminants for which soil is an 'environmental sink', this is of particular concern. Furthermore, with water passing down through soils to groundwaters, laterally through soils to surface waters and with gases rising up from soils to buildings above, contaminated soils can act as sources of contamination for other environmental compartments. More so than any other medium, soils are multifunctional and may act as a *source* of contamination, as the *pathway* by which contamination reaches other environmental compartments and as the *receptor* of contamination in its own right. This complexity can cloud the objectives of soil-quality management.

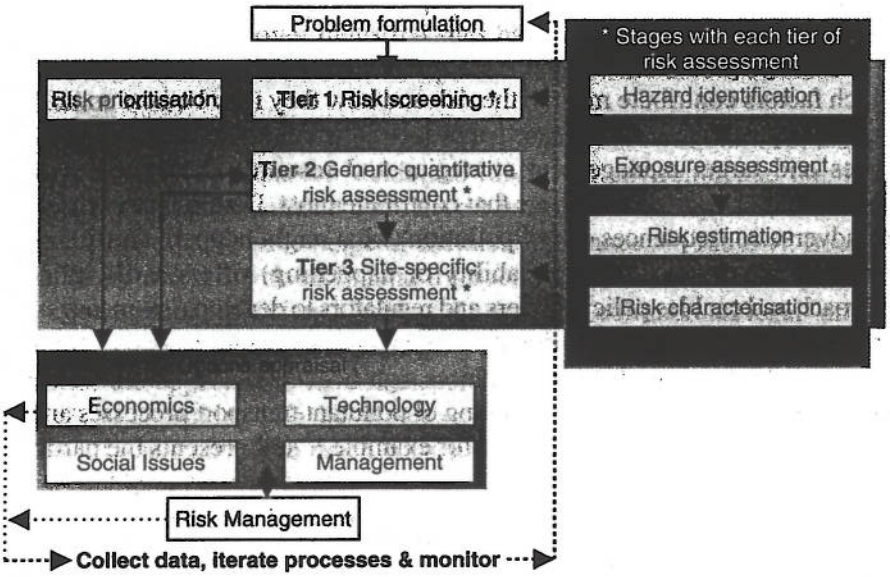


Figure 9 *This framework shows the relationship between good problem definition and a staged approach to risk assessment. Once risks have been assessed, options for the management of risk can be identified and consideration given to the economics, technology required, the social implications and management arrangements*

Table 3 *Essential questions for risk assessment*

Risk assessment question	*Stage and description*
(1) What hazards are present and what are their properties?	Hazard identification: Identification of the sources of the hazard and assessment of the consequences of the hazard if realised, including the identification of dose–response relationships, where appropriate
(2) How might the receptors become exposed to the hazards and what is the probability and scale of exposure?	Exposure assessment: Evaluating the plausibility of the hazard being realised at the target, and by which mechanisms, allowing an assessment of the probability, magnitude and duration of exposure
(3) Given exposure occurs at the above probability and magnitude, what is the probability and scale of harm?	Risk estimation: Consideration of the consequences of exposure with reference to effects and dose, expressed as a likelihood or probability of the hazardous effects of exposure being realised; and expressed over a range of spatial and temporal fields
(4) How significant is the risk and what are the uncertainties?	Risk characterisation: Evaluating the acceptability and significance of risk with reference to standards, targets, background risks, cost-benefit criteria or risk 'acceptability' and 'tolerability' criteria and commenting on the uncertainties associated with the assessment

In managing risks to or from the soil environment, it is critical to understand which factors contribute most to the risk and how they may be best controlled. The principal value of a risk-based approach is the ability to prioritise between issues and target management strategies and resources towards the more significant risks and those factors that contribute most. Distinguishing between the adverse consequences of soil pollution (what might happen) and their likelihood of occurrence (the probability of happening) offers a discipline of approach and enables policy-makers and regulators to develop risk-management strategies suitable and proportionate to the nature and significance of the risk. However, the risk-based approach places significant demands on our scientific understanding of soils. In the modelling of pollutant transport processes and the application of exposure assessment, for example,[17] soil presents the particular challenges of

- extreme system heterogeneity;
- multiple phases (pore fluids, mineral and organic matter, biota and often 'free product') in intimate contact; and
- analytical difficulties that often hinder exposure model validation.

Risk assessment approaches are proving particularly important where direct exposures are considered and expensive management decisions are being made, for example

- in estimating the likely in-building concentrations of and inhalation exposures from volatile compounds released from soils contaminated with organic compounds;
- in estimating the potential pathogenic load to commercial crops grown where organic wastes have been applied to agricultural land;
- in protecting groundwater resources affected by land contamination; and
- in regulating new substances released to environment at the end of their product cycle.

4.6 LAND CONTAMINATION AND REGENERATION

Soil contamination has been of special concern to developed nations seeking to manage the problems of historic industrialisation. Movement to a post-industrialised society, together with the globalisation of many national companies, has meant that portfolios of former industrial sites have been made available for redevelopment and new uses for the land, such as housing and light industrial use. As companies acquire and divest themselves of their land holdings, former industrial sites have changed hands with the need for liability assessments as new companies acquire the assets of those they have taken over.

House builders developing new homes on former brownfield land, and the more progressive companies seeking to limit their environmental liabilities by cleaning up their own land bank have been faced with land contamination problems involving a wide range of chemical substances[18] (Table 4). Because of the many actors involved in land transactions, the scientific complexities and uncertainties associated with soil and the commercial/legal drivers involved, those involved with managing land contamination have sought to formalise the approach to land management in order to improve clarity and ease decision-making. To be effective, these multiple parties must work together (Case study 2) to reach consensus on how to manage soil contamination problems best.

To help decision-makers navigate the complexities of site investigation, risk assessment and remediation, a number of decision-making frameworks have been developed. This has coincided with an increased research interest in the fate of contaminants in soils, in methods for their analysis and in technologies for their remediation.

Case Study 2: The Importance of Partnerships to Site Regeneration[19]

An example of the value of consensus decisions on historically contaminated land is provided by Pollard and Herbert.[19] The site described was the centre for Scotland's oil shale refining industry at the end of the past century. Initially, shale was subject to distillation at or near the mines to produce crude "retort oil". As shallow mines became exhausted, deep mining of the shale was undertaken and refining was performed at one of three sites. Viscous tarry residues from the refining process were usually disposed of in hollows or ponds near to the sites. From 1948 onwards, the site was also used for detergent manufacture with oil refining eventually ceasing in 1962. The detergent works closed in 1993 when the majority of plant and buildings were demolished.

Post-closure site investigations revealed two principal contaminant groups at the site – surfactants from detergent manufacture and hydrocarbons from oil refining – both with further implications for land and groundwater contamination. Several remedial options were examined including: (i) incineration, (ii) cement kiln, (iii) specialised recycling, (iv) stabilisation, (v) bioremediation (*i.e.* biological removal of contamination), and (vi) land-fill. Of these, only bioremediation and cement grout stabilisation (mixing contaminated material into a cement-based matrix) were shown to be effective.

Tar residues form the oil refining process classed as 'soft' tars and having a relatively low PAH content, were easy to work with and become mobile when warm. These tars were suitable for biological treatment. Trials showed an initial 50–60% w/w reduction in most contaminants due to the 'bulking' process, rising to an 85–95% w/w reduction within 8 weeks of biological treatment. A staged risk assessment, including the derivation of site-specific health-based remediation criteria, was conducted in consultation with the regulator to determine acceptable final concentrations of the key contaminants, most notably the more carcinogenic PAHs, commensurate with the intended use for the site as an extension to an adjacent golf course ("suitable for use"). From the bioremediation trials, it was estimated that all target concentrations would be achieved in 3–4 months of full-scale treatment.

The hard tars from the refining process, tars form the detergent sulfonation process and high phenol tars from an adjacent site were not suitable for bioremediation. These materials were treated using *ex-situ* stabilisation. The site was restored to a level suitable for use as a golf course with the bioremediation residues and imported topsoil used as cover for the existing land. Close working in partnership with the regulator throughout proved vital to the successful regeneration of this site.

Table 4 *A prioritised list of 25 chemicals encountered at national priorities list (NPL) sites in the United States Superfund programme, based on a combination of frequency, toxicity and potential for human exposure (after Agency for Toxic Substances and Disease Registry (ATSDR), 2004)*

Chemical substance	*Chemical abstracts service (CAS) registry no.*
Arsenic	007440-38-2
Lead	007439-92-1
Mercury	007439-97-6
Vinyl chloride	000075-01-4
Polychlorinated biphenyls	001336-36-3
Benzene	000071-43-2
Cadmium	007440-43-9
Polynuclear aromatic hydrocarbons	130498-29-2
Benzo(*a*)pyrene	000050-32-8
Benzo(*b*)fluoranthene	000205-99-2
Chloroform	000067-66-3
DDT, P,P′-	000050-29-3
Aroclor 1254	011097-69-1
Aroclor 1260	011096-82-5
Dibenzo(*a*,*h*)anthracene	000053-70-3
Trichloroethyelene	000079-01-6
Hexavalent chromium	018540-29-9
Dieldrin	000060-57-1
Phosphorus, white	007723-14-0
Chlordane	000057-74-9
DDE, P,P′-	000072-55-9
Hexachlorobutadiene	000087-68-3
Coal tar creosote	008001-58-9
DDD, P,P′-	000072-54-8
Benzidine	000092-87-5

4.6.1 Risk-Based Land Management

Mindful of the potential impacts of soil pollution, governments across the world have sought to intervene at sites that pose the most significant harm to public and environmental health. Since the early 1980s, industrialised nations have progressed national legislation on the assessment and management of land contamination. For many countries and jurisdictions, this has been a 'Pandora's box' and they have uncovered many more historic sites than were initially imagined. With the costs of site assessment and remediation high, policy-makers and regulators have to focus their efforts on the most serious sites, using risk assessment as the means of setting national priorities and informing management activities at the site level.

4.6.1.1 Environmental Fate and Transport Properties. The pollution science supporting the risk-based management of contaminated land is founded on the basic physicochemical properties of environmental pollutants in soils.

These properties, shown in Table 5 for priority organic pollutants at sites contaminated with wood-preserving chemicals,[20] determine the propensity of individual compounds to associate with, or partition between the organic matter, mineral matter, the pore gas, the pore water and the wastes itself within a waste-soil matrix. These properties should be used to (i) direct site investigation techniques and the selection of analytical methods by identifying the key

Table 5 *Physicochemical properties of wood-preserving chemicals. Shading indicates physico-chemical properties that dominate the environmental fate of these compounds in soil-water systems (after Pollard et al., 1993)*

Compound	*MW* ($g\,mol^{-1}$)	*Aqueous solubility* ($g\,m^{-3}$)	*Vapour pressure* (*Pa*)	K_{oc} (*unitless*)	*Half-life* (*d*)
benzene	78.1	1780	[illegible]	65	69
toluene	92.1	515	3800	257	37
phenol	94.1	[illegible]	71	14	1
p-cresol	108.1	[illegible]	15	19	1
2,4,6-trichlorophenol	197.5	900	1	[illegible]	5.3
pentachlorophenol	266.4	14	0.2	[illegible]	20
naphthalene	128.2	32	10	1290	10
benzo(*a*)pyrene	252.3	3.8×10^{-3}	0.73×10^{-6}	[illegible]	450
carbazole	167.2	1	0.093	1300	0.6
hexachlorodibenzo(*p*)dioxin	392.9	1.3×10^{-4}	1.93×10^{-6}	[illegible]	500

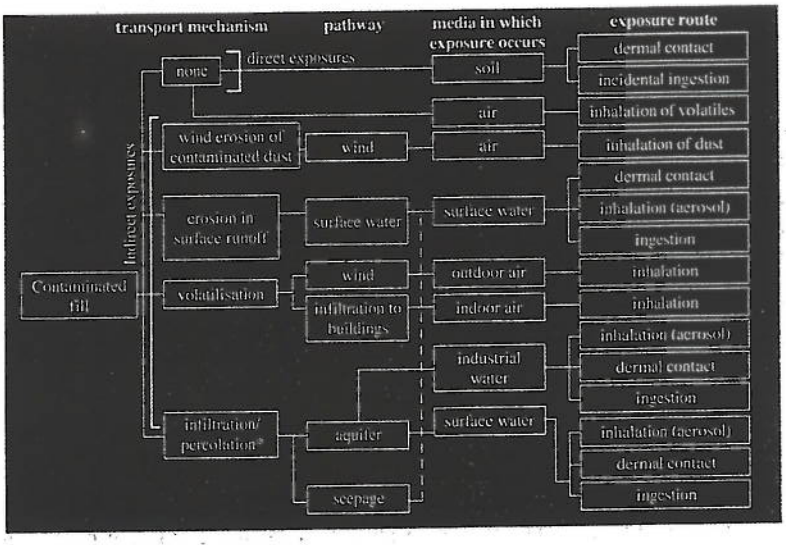
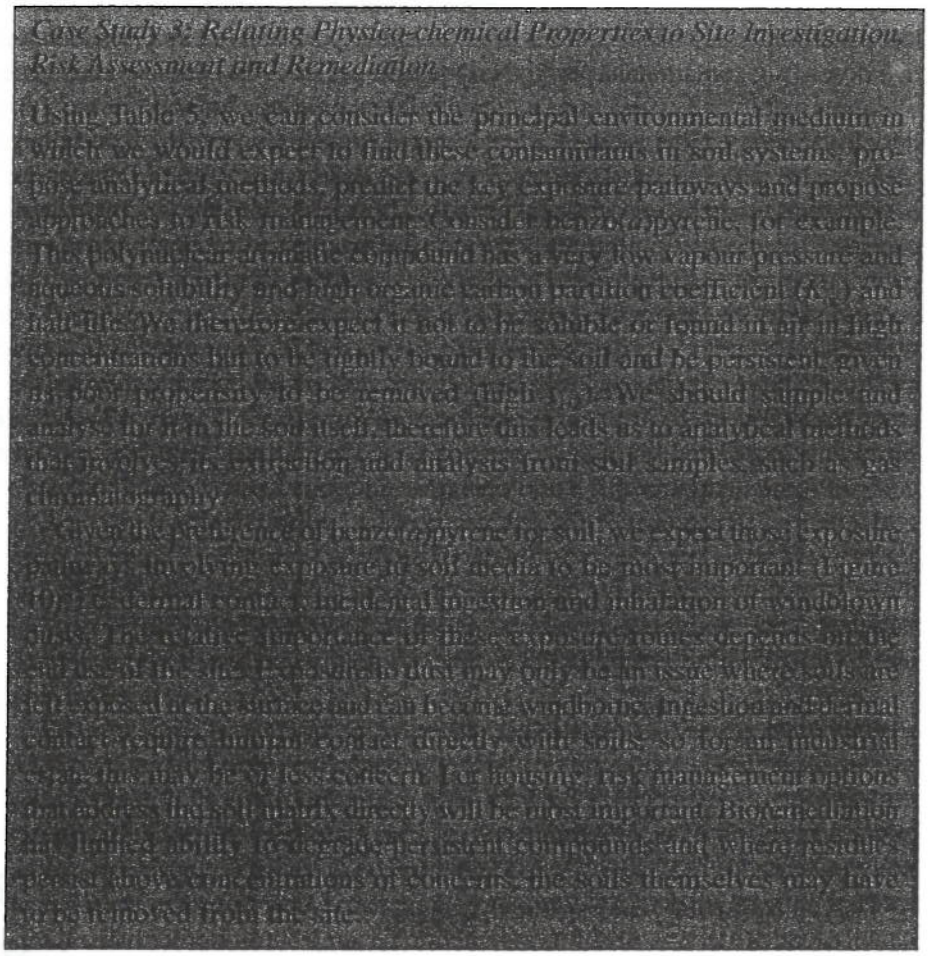


Figure 10 *Generalised exposure model for human exposures to contaminated fill*

phases for sampling and analysis; (ii) identify the key exposure pathways by which contaminants may be transported to receptors; and (iii) inform the selection of remediation technologies, whose principal focus should be the key environmental compartment (soil, water, gas, free organic phase) within which risk-critical compounds are present (Case Study 3).



4.6.1.2 Using Risk Assessment Tools. Assessing the risks to human health, ecosystems and other receptors has become central to making sound decisions at contaminated sites. International approaches adopted in the US, the Netherlands, Australia and the UK have been devised, in general, by considering a notion of an 'acceptable risk' below which further remediation has marginal benefit, and developing toxicologically-based site assessment criteria as triggers for detailed site assessment. These site assessment criteria are

often presented as 'soil screening levels'. When individual contaminants exceed these levels, site owners are guided to consider detailed investigations that will help them better understand the nature and magnitude of the risk.

To assist decision-makers, many of the standard exposure pathways encountered at contaminated sites (Figure 10) have been coded into desktop risk assessment software packages. For potential risks to human health, these allow the concentrations of soil contaminants identified on site to be translated into environmental concentrations at an off-site exposure point and into indicative doses (mg contaminant per kg body weight per day) that can be compared with acceptable daily intakes or national reference doses. To facilitate a quick initial screening, most models adopt generic exposure scenarios (conditions of exposure and specific land uses) that standardise many of the numerous assumptions made in assessing the site risk. Using such models, land managers can identify the key pollutants, exposure pathways and receptor types that contribute most to the site risk. Risk assessments can then be used to inform and help prioritise the management of risk.

Probabilistic models, that account for the myriad of uncertainties in a stochastic fashion, are now widely used. They are powerful in identifying the principal sources of variance in estimates of exposure[21] (Figure 11) and in providing more credible assessments of risk. This is important because the costs of remediation are high and contamination must be managed to ensure cost-effective protection of the environment and public health.

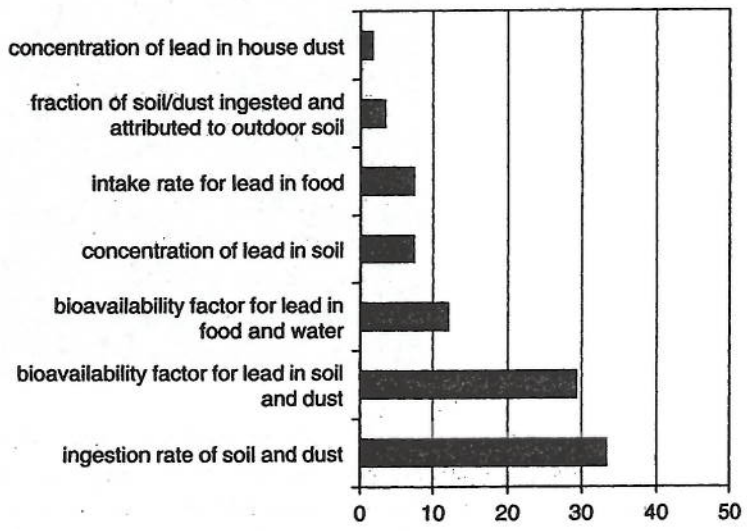


Figure 11 *Contribution to % variance in total lead uptake from key parameters in a probabilistic blood lead exposure model*
(Redrawn from Lee *et al.* (1995))

4.6.1.3 Scientific Rigour in Site Investigation and Environmental Analysis. The confidence with which decisions can be taken on the remediation of contaminated sites relies heavily on the quality of the site investigation data. Risk assessments conducted in the absence of quality data provide a false sense of security in their estimate of the magnitude of the risk. Using risk as the basis for prioritising remediation across a 'portfolio' of sites requires managers to compare the nature, extent, magnitude and depth of contamination. Databases and decision-support systems that can store and process vast amounts of site data are improving practice in this area.

Central to many pollution issues is the characterisation of the source of pollution – often called the 'source term'. Understanding the source, its chemical, physical and microbiological characteristics allows the nature of the hazard to be identified – benzene, for example is a known human carcinogen by inhalation. It has a considerable vapour pressure and a slight aqueous solubility; hence it volatilises from soils and also dissolves in groundwater.

Because many risk estimates rely on modelled exposures rather than measured data at the point of exposure, high-quality data on the source term is critical. The interpretation of site investigation data, especially for large sites, often employs statistical analysis. Many risk assessment tools require contaminant distributions, or at least the use of 'worst-case' and mean concentrations within deterministic exposure assessment models. A central concern is how to best present 'hot spots' (highly contaminated areas for immediate treatment), total contaminated areas (of value for liability assessment) and randomised site data in statistical risk assessment packages. Where these different needs of the site data are combined in the same site investigation, the overlay of sampling points and separation of data sets to avoid the introduction of bias will be required.

Examinations of site risk frequently reveal the significant geochemical and analytical uncertainties associated with land contamination. Despite substantial improvements in environmental diagnostics and instrumental analysis over the past 25 years, risk estimates remain constrained by analytical uncertainties and an overriding variance in contaminant concentrations in soils.[22] Analytical techniques, even for well understood contaminants such as arsenic, harbour significant methodological uncertainties. Figure 12 illustrates the performance of a range of laboratories (individual bars) and analytical methods (grouped together as methods 131–135) about a grand median value of arsenic in a reference soil sample of 33 mg kg^{-1}. The scale of this variance must be considered by regulators in evaluating the significance of soil contamination; here for example, in the context of a soil guideline value for arsenic of 20 mg kg^{-1}. Case study 4 illustrates the number of assumptions involved in estimating exposures from a single exposure route, the incidental ingestion of soil by children.

Case Study 4: Quantifying Exposure

Exposure assessment is used to quantify chemical doses from contaminated soils to humans. Estimates of exposure rely, in principle, on straightforward equations, such as that for the incidental ingestion of soils. However, there is considerable debate about the amounts of soil ingested by infants, for example, as well as the inherent variability associated with the analysis of contaminants in soil (Figure 4.2). This just for two of the parameters involved. For carcinogens, the lifetime average daily dose (LADD) is:

$$LADD = \frac{C \times IR \times B \times ED}{bw \times AT}$$

where C is the mean exposure concentration (mg kg^{-1}), IR the soil ingestion rate (kg d^{-1}), B the bioavailability (unitless), ED the exposure duration (d), bw the body weight (kg), and AT the averaging time (lifetime) (25 550 days = 70 years).

Say we wish to estimate the LADD for an infant exposed every day to soil containing 10 mg kg^{-1} arsenic for 4 years of its early life. We assume that the infant ingests, on average, 100 mg d^{-1} (though this may vary between 20 and 1000 or even more).

$$LADD = 10\ mg\ kg^{-1} \times 1 \times 100 \times 10^{-6}\ kg\ d^{-1} \times 0.10$$
$$\times 4 \times 365\ d / (25\,550\ d \times 5\,\text{kg}) = 0.000007\ \text{milligrams of arsenic}$$

per kg of body weight per day, averaged over a lifetime.

Risk assessments that use single data points are referred to as 'deterministic'. These provide single numerical estimates of risk using a combination of assumptions populated by individual data points, some gathered by site investigation and analysis, some modelled and some assumed from the literature. A deterministic risk estimate is an increased likelihood of a specific adverse event occurring over a specified time period; for example, an above-background theoretical cancer risk attributable to specific exposures from carcinogens present at a contaminated site. For most sites, these incremental risks are usually very small indeed (10^{-5}, 10^{-6}, 10^{-8}). Because they are estimated using deterministic tools, deterministic risk estimates do not reflect the considerable uncertainties in the assumptions and data that they rely on. Managing these uncertainties has become one of the key difficulties in applying the risk-based approach to situations such as the buying and selling of land where uncertainties can undermine the confidence of the parties involved. For decision-makers, focusing on the relative magnitude of the risks to

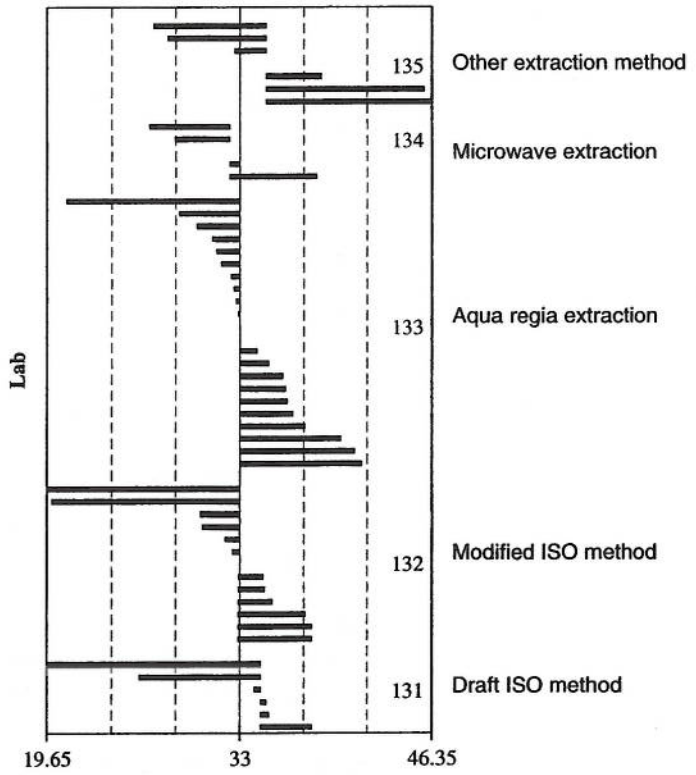


Figure 12 *Distribution of analytical data for arsenic in a sample of homogenised soil*

inform management of the land rather than the absolute value of risk estimates is one approach to overcoming these difficulties.

4.6.1.4 Bioavailability. Risk analysts are aware that risk estimates based on doses received at exposure points are only surrogates for the toxicological risk, because they do not account for processes that occur inside the body. Here, what counts is the availability of the species to the biological system that it interacts with. The bioavailability of compounds *in vivo* is an important concept therefore with respect to the toxicological response[23] (Figure 13).

4.6.1.5 Communicating Risk, Environmental Justice and Participation in Decision-Making. The regeneration of contaminated land has always required a multi- and trans-disciplinary approach. Increasingly, scientists, engineers, planners and lawyers are turning to the social sciences for advice. Researchers and practitioners are now gaining valuable insights into how we might involve others in decision-making and into issues of equity and the perceptions and reporting of risk. The interpretation and communication of an environmental risk assessment often plays a key role in the decisions that are

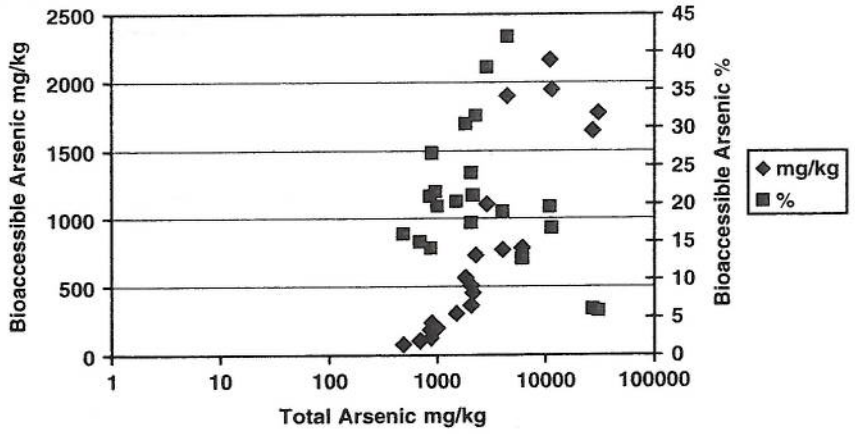


Figure 13 *Bioaccessible arsenic sourced from Great Devon Consoles. Different soils with similar concentrations of total arsenic may have exhibit different bioavailabilities* (After Bragg *et al.* (2001))

made on land contamination. Historically a technical preserve, the new agenda on risk-based land management is requiring us to consider how the risk assessment process might be made more accessible to non-expert audiences. Recognition of this social dimension to land regeneration and the need to engage wider constituencies in risk-based decision-making has stimulated research on participation in risk assessment.[24] The following aspects are important:

- providing information, consulting with others and involving stakeholders in decisions are critical so that decisions about land contamination remain credible;
- consultation that allows options to be developed and explored, rather than offering single solutions are preferred;
- decision processes that have clearly defined stages help;
- taking time to clearly identify and define the problem under consideration is important; and
- involving a wide range of people in decisions also needs to be sensitive to the timescales within which regulatory decisions must be made.

4.7 CONCLUSION – MANAGING SOIL FOR SUSTAINABLE COMMUNITIES

This chapter has summarised the pollution science that supports our understanding of soils in the natural and built environment. It is clear that soil can only be protected as a resource where there is respect for its functions. The risks

that contaminated soils pose need to be managed cost-effectively and in consultation with the communities whose health and well-being is at the heart of land regeneration strategies.

QUESTIONS

1. Describe the main functions of soil and how these are supported by the soil system. How does this system respond to pressures, including pollution from the atmosphere and wastes?
2. How do soil-forming factors, such as climate and parent material affect soil type and variability? What are the consequences of soil variability for soil protection?
3. Describe the main variables controlling the chemistry of Fe in soil systems.
4. How does SOM interact with geochemical cycles? Consider the cycling of metals and other elements as well as carbon.
5. What are the properties of soil that affect its ability to absorb pollutants and attenuate their release to groundwater?
6. What are the benefits of a risk-based approach to land management? What arguments would you advance that this was a cost-effective means of managing land contamination?
7. Describe the environmental fate of phenol. How would you devise an analytical strategy for phenol at a creosote-contaminated site where phenol was present? What might you expect the key exposure routes to be?
8. Distinguish between deterministic and probabilistic risk assessment. What advantages does probabilistic risk assessment offer site remediation engineers?
9. Summarise an approach to investigate a former gas works site. What would you do first? What information would you require to make a judgement on the significance of the risks posed?

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Evaluating fugacity models for trace components in landfill gas

Sophie Shafi [a], Andrew Sweetman [b], Rupert L. Hough [a], Richard Smith [a], Alan Rosevear [c], Simon J.T. Pollard [a,*]

[a] *Integrated Waste Management Centre, Sustainable Systems Department, Building 61, School of Industrial and Manufacturing Science, Cranfield University, Cranfield, Bedfordshire MK43 0AL, UK*
[b] *Department of Environmental Science, Lancaster University, Lancaster LA1 4YQ, UK*
[c] *Science Group – Waste and Remediation, Environment Agency, Reading RG1 8DQ, UK*

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Fugacity for trace component in landfill gas.

Abstract

A fugacity approach was evaluated to reconcile loadings of vinyl chloride (chloroethene), benzene, 1,3-butadiene and trichloroethylene in waste with concentrations observed in landfill gas monitoring studies. An evaluative environment derived from fictitious but realistic properties such as volume, composition, and temperature, constructed with data from the Brogborough landfill (UK) test cells was used to test a fugacity approach to generating the source term for use in landfill gas risk assessment models (e.g. GasSim). SOILVE, a dynamic Level II model adapted here for landfills, showed greatest utility for benzene and 1,3-butadiene, modelled under anaerobic conditions over a 10 year simulation. Modelled concentrations of these components (95 300 $\mu g\ m^{-3}$; 43 $\mu g\ m^{-3}$) fell within measured ranges observed in gas from landfills (24 300–180 000 $\mu g\ m^{-3}$; 20–70 $\mu g\ m^{-3}$). This study highlights the need (i) for representative and time-referenced biotransformation data; (ii) to evaluate the partitioning characteristics of organic matter within waste systems and (iii) for a better understanding of the role that gas extraction rate (flux) plays in producing trace component concentrations in landfill gas.
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Keywords: Landfill gas; Risk assessment; Fugacity; Emissions modelling

1. Introduction

1.1. Background

Waste management technologies are increasingly subject to environmental risk assessments that inform operational practice, environmental permitting and regulatory intervention. The quality of any environmental risk assessment is influenced by the input data for the distribution and dispersion of potentially harmful substances, and by the exposure models that support an analysis of the probability and consequences of exposure. Landfills pose a hazard to workers and to local communities because of the landfill gas (LFG) they generate. Considerable literature exists on the hazards of bulk LFG (mainly CH_4 and CO_2) and, more recently, on the gas phase concentrations of trace hazardous components in untreated LFG (Allen et al., 1997; Scheutz and Kjeldsen, 2003; Environment Agency, 2003a, 2004). Risk assessment models used to evaluate the nature and significance of exposure risks are now instrumental in improving landfill siting, operation, and some aspects of design (Pelt et al., 1998; Environment Agency, 2002a). The GasSim model (Environment Agency, 2002a), for example, generates a source term for bulk gases using a first order rate equation for the biodegradation of the organic component of the waste, and uses default values for trace components based on concentrations in the bulk gas reported in the literature. In GasSim, the source term gas is partitioned between two fates: (i) combustion in an engine or

* Corresponding author. Tel.: +44 1234 754 101; fax: +44 1234 751 671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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flare; and (ii) passive loss of untreated gas through the landfill cap or sidewall. The latter is the most important when considering potential exposures of human or ecological receptors to harmful components.

Whilst progress has been made in modelling the distribution of potentially harmful components around a site (and hence an approximation of exposure) using standard air dispersion models, risk estimates are constrained by the absence of a credible source term relative to waste input. In practice, concentrations of trace components are generated by the loading of chemicals in the initial waste mass (the source term) and the fate processes, including biotransformation, which deliver measurable concentrations in the gas phase. Risk analysts are keenly aware of the need for improved source term models that, it is hoped, will engender greater confidence in risk assessments and risk management measures (El-Fadel et al., 1997a,b; Pollard et al., 2006). In this paper, an attempt is made to reconcile measured concentrations of four priority trace components in LFG, with potential source term loadings estimated retrospectively using fugacity modelling. The potential for the fugacity approach to improve current risk assessment models for landfill, e.g. GasSim (Environment Agency, 2002a), is introduced, reviewed and critically appraised.

1.2. Rationale

Fugacity modelling (Mackay, 1979, 2001) has received a comprehensive treatment in a recent special issue of a peer-reviewed journal (Gobas and Muir, 2004). Among its uses from global-scale to *in vivo* modelling, its application to waste problems is increasing, albeit with an attending need to address the gross heterogeneity and multiphase character of wastes. Applications include its use for directing site remediation decisions (Pollard et al., 1993; She et al., 1995), in quantifying vapour emissions at contaminated sites (Mills et al., 2004) and in assessing the environmental fate of hydrophobic compounds in landfills (Kjeldsen and Christensen, 2001).

Three models are worthy of review and establish the context of our work. The SOIL model (Mackay, 2001) comprises four environmental compartments: air, water, soil mineral matter and soil organic mater. Densities, volumes, areas and depths of soil are user-specified, enabling total volumes and masses to be calculated, from which individual fugacities and environmental concentrations are derived. Other input parameters include densities and volume fractions, of air, water, organic and mineral matter, the mass of total soil, dry soil and organic carbon, a water-leaching rate and mean diffusion distance. With regards to chemical input data, an original mass in the soil needs to specified, along with physicochemical data on molecular weight, aqueous solubility vapour pressure (K_{ow}), and first-order reaction half-life ($t_{½}$). The model accounts for losses from degrading reactions, leaching (D_W) and volatilisation (D_A) by the designation of '*D* values' (Mackay, 2001). An adaptation of SOIL, SOILFUG (DiGuardio et al., 1994) has been designed for pesticide application to soil with subsequent surface water runoff. Adaptations include incorporating the effects of sequential rainfall events with input parameters that include inflow and outflow rates. Leaching is replaced by run off (D_{roff}) taken from the amount of water flowing out of the system, here a river basin. The authors attempted verification by comparing the predicted concentrations of pesticide in the outflow with environmental monitoring data (DiGuardio et al., 1994). SOILFUG may have relevance for a landfill environment, given the flushing of landfill cells and where leachate recirculation events might be considered analogous to successive 'rainfall' events. Finally, She et al. (1995) describe a fugacity approach (SOILVE) to predicting the efficiency of soil vapour extraction (VE) in removing volatile organic compounds (VOCs) from the unsaturated zone of a contaminated soil; a situation physically analogous to modern landfill sites where gas is actively extracted. SOILVE accounts for degradation, volatilisation and leaching and includes a term for gas phase extraction. The extraction is designated a *D* value, D_X, determined by a gas flow rate (G_X m^3 h^{-1}), combined with the fugacity capacity (Z_G, mol m^{-3}Pa):

$$D_X = G_X Z_G \tag{1}$$

The model accounts for the non-uniform distribution of VOCs in soil and introduces the concept of a 'sweep efficiency' *E*; a ratio of the effective air extraction rate (G_E) to the applied airflow.

$$E = G_E/G_X \tag{2}$$

The effective *D* value (D_E) is then:

$$E D_X = E G_X Z_G \tag{3}$$

Here, *D* values for D_E, D_A and D_W are calculated as with the SOIL model, but with the substitution of gas phase diffusion in the soil (D_G), for the air in soil (D_A);

$$D_G = B_{EG} A Z_G / Y \tag{4}$$

Where B_{EG} is gas phase diffusion (mol Pa^{-1} h), *A* the area m^2 and *Y* the path length (m).

The model recognises that the effectiveness of gas extraction declines exponentially as a result of removal of the gas from more permeable areas, followed by extraction from areas where the permeability is lower. This is given by:

$$E = E_f = E_i \, e^{-k_3 t} \tag{5}$$

Where E_f is at infinite time, E_i is at time 0 and k_3 is a decay constant. The presence of the decay term makes application of SOILVE particularly applicable to the landfill environment.

1.3. Trace components in landfill gas

The composition of LFG is dominated by the bulk gases methane, CH_4 (40–70%$^v/_v$) and carbon dioxide, CO_2 (30–60%$^v/_v$) with smaller concentrations of hydrogen, hydrogen sulphide and other trace components (Table 1). Despite their low concentrations, hazardous trace components may pose a potential risk to human health where exposure is either acute, repeatedly episodic or prolonged (Brosseau and Heitz, 1994;

Table 1
Generic classes of trace components in landfill gas with concentration ranges (El-Fadel et al., 1997a)

Chemical class	Typical concentration (mg m^{-3})
Alcohols	2–2500
Ketones	0–50
Aldehydes	0–200
Organosulphur compounds	3–240
Hydrocarbons	
Alkanes	20–4500
Alkenes	6–1100
Cycloalkanes	1–1000
Cycloalanes	8–600
Aromatics	30–1900
Halogenated hydrocarbons	1–2900
Esters	0–1300
Ethers	0–250

Allen et al., 1997; El-Fadel et al., 1997a; Zou et al., 2003). Due to its heavy reliance on landfill, many of the more significant studies have been undertaken in the UK. Early work on the trace composition of LFG (Young and Parker, 1983; Allen et al., 1997; Eklund et al., 1998) identified 100–140 trace components of concern, typically constituting <1% $^{v}/_{v}$ of the gas (Young and Parker, 1983). Some authors believe these constituents to be ubiquitous, regardless of whether the site operated a co-disposal (hazardous and municipal) or municipal waste-only disposal strategy (USEPA, 1997).

A study looking at the composition of trace gases from six different landfill sites revealed approximately 80 trace components (Meynell, 1983). Further trace components were characterised in the late 1980s following monitoring at three UK-based landfill sites over a period of three years (Dent et al., 1986; Department of Environment, 1988). In this case, 136 organic compounds or isomeric groups were identified. A 1997 study of seven landfill sites in the UK observed 140 trace components, 90 of which were common to all seven sites (Allen et al., 1997). Concentrations of volatile organic carbon (VOCs) were closely related to methane production rates and displayed variation (although not significant) with ambient temperature and atmospheric pressure. The VOCs identified included vinyl chloride (chloroethene) (Young and Parker, 1983; Allen et al., 1997), tetrachloroethene, 1,1-dichloroethane, 1,2-dichloroethane, benzene, chlorobenzene, trichloroethylene (TCE), ethylbenzene, xylene and toluene, amongst others. A similar UK-based study identified 550 trace components (Environment Agency, 2003a).

The Environment Agency of England and Wales (EA) have published a list of priority components requiring monitoring in LFG defined by their typical concentrations and published toxicological and odour properties (Environment Agency, 2004 (Tables 10.1, 10.2 and 10.3)). The list includes chloroethane, 1,1-dichloroethane, vinyl chloride, trichloroethylene, 1,1-dichloroethene, 1,2-dicholoroethene and tetrachloromethane. The list was compiled acknowledging the toxicity, known or potential carcinogenicity and physical characteristics of these substances (Environment Agency, 2002b, 2003a,b; Table 2). The Environment Agency (Environment Agency, 2003b) monitored the concentrations of trace components in LFG at six

Table 2
Environment Agency priority trace components (Environment Agency, 2003b)

Priority trace component	Analytical method	Detection limit (mg m^{-3})	Component concentration [x] (mg m^{-3})			$[x]_{mean}$ P1-438 c.f. $[x]_{mean}$ P1-491 (mg m^{-3})
			$[x]_{min}$	$[x]_{max}$	$[x]_{mean}$	
1,1-dichloroethane	ATD	0.02	<0.02	3.90	0.57	−477
1,1-dichloroethene	ATD	0.03	<0.03	19.0	2.24	+2.10
1,2-dichloroethene	ATD	0.07	0.13	46.0	5.71	−10.5
1,3-butadiene	ATD	0.02	<0.02	<0.02	<0.02	−0.11
1-butanethiol	ATD	0.08	<0.08	<0.08	<0.08	−>0.09
1-pentene	ATD	0.16	0.24	21.0	5.49	+3.80
1-propanethiol	ATD	0.04	<0.04	0.09	<0.05	−0.43
2-butoxyethanol	ATD	0.04	<0.04	<0.05	<0.05	No change
Arsenic	Arsenic tube	<0.01	<0.01	0.43	0.05	+0.05
Benzene	ATD	0.03	3.10	73.0	18.4	+13.5
Butyric acid	ATD	0.08	<0.08	17.5	1.85	−7.00
Carbon disulphide	ATD	0.10	0.90	170	34.0	+34.0
Chloroethane	ATD	0.02	<0.02	5.30	0.49	−76.4
Chloroethene	ATD	0.30	1.10	730	102	+35.7
Dimethyl disulphide	ATD	0.03	<0.03	12.0	1.02	+1.00
Cimethyl sulphide	ATD	0.03	<0.03	24.3	3.69	≥0.37
Ethanal	DNPH	0.01	0.08	2.55	0.43	−2.60
Ethanethiol	ATD	0.08	<0.08	<0.08	<0.08	No change
Ethyl butyrate	ATD	0.09	0.41	42.0	7.22	−25.7
Furan	ATD	0.07	0.02	6.20	1.23	+0.50
Hydrogen sulphide	Lab GC	0.15	2.40	580	111	No change
Methanal	DNPH	0.01	0.03	0.19	0.07	−2.90
Methanethiol	ATD	0.30	<0.30	<0.30	<0.30	≥6.00
Tetrachloromethane	ATD	0.02	<0.02	<0.02	<0.02	≥5.20
Trichloroethene	ATD	0.04	0.25	88.0	8.59	−6.40

Key: ATD: automated thermal desorption; Lab GC: laboratory gas chromatograph; and DNPH: 2,4-dinitrophenyl-hydrazine derivatised aldehydes.

sites during 2002–2003 for the 26 highest priority substances (Table 2). Analysis of the data by reference to landfill type, age of gas and environment allows a summary, for selected chlorinated components, of the concentration ranges generated by different landfill environments (Table 3). Still unknown, however, are the initial waste loadings that could generate these concentrations. This, and the rate at which bulk gases are generated, affects the measured concentrations of trace components generated in the landfill. Addressing this knowledge gap was the starting point for this work.

1.4. Study aims

This study sought to build an evaluative environment (derived from fictitious but realistic properties such as volume, composition, and temperature) within which to back-calculate the potential source terms (loads) that could generate typical concentrations of trace components reported in LFG studies. Our study focussed on benzene, vinyl chloride, trichloroethylene (TCE) and 1,3-butadiene as representative of the main types of priority trace component, with a view to providing a source term for risk assessment models such as GasSim (Attenborough et al., 2002; Environment Agency, 2002a). The objectives were to (i) apply fugacity concepts to the partitioning of trace components within the landfill environment; (ii) test and select the most applicable approaches to an evaluative landfill environment; and (iii) compare observed concentrations of trace components with those modelled in the study.

2. Materials and methods

2.1. Evaluative landfill environment

The evaluative environment selected was a single cell of waste, rather than an entire landfill (Fig. 1), this was choice influenced by the availability of data from the Brogborough (UK) landfill test cells (Fletcher, 1989; Croft et al., 2001; Blackmore et al., 2003). Our evaluative environment allows for three phases: gas, water, and waste, and for the processes of water and gas flux through the system being represented. The Brogborough test cells were constructed during 1986–88 and were set up to evaluate the effects of pre- and post-emplacement management techniques on methane production rates (Croft et al., 2001). Six cells were constructed each with a different management technique such as leachate re-circulation, air injection and sewage sludge addition. A single cell contained a mix of domestic waste and non-hazardous commercial waste. Our study has adopted the design data from cell 1, the control cell, containing domestic waste placed in thin layers (Blackmore et al., 2003). The dimensions and characteristics of cell 1 are reported in Table 4. Leachate, gas and solid waste were monitored at Brogborough between 1986 and 2000, making it the longest field scale landfill study in the world (Blackmore et al., 2003). The cells have produced limited data on the concentrations of trace components in the gas, but the gas production data and physical characteristics of the cells (Table 5) provide a valuable base for this study. Test cell 1 was taken as being typical of most UK landfill sites accepting domestic waste. The evaluative environment remained constant for the fugacity studies that follow.

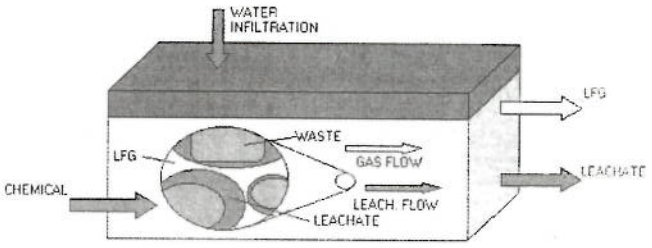


Fig. 1. An evaluative landfill environment.

Table 3
Selected trace component concentrations (mg m^{-3}) in landfill gas in different MSW landfill environments (Environment Agency, 2003b)

Category of waste gas age and environment	Large component of commercial & industrial	Domestic site with leachate	High Ash Content
Recent gas			
Chloroethene	17.6[a]	7.70	2.30
Chloroethane	<0.03	<0.02	<0.03
Tetrachloromethane	<0.02	<0.02	<0.02
1,1-dichloroethene	0.28	2.80[a]	0.08
Trichloroethene	0.90	7.30[a]	0.04
Recent gas with leachate			
Chloroethene	9.00	55.0	17.0[a]
Chloroethane	<0.03	<0.03	<0.03
Tetrachloromethane	<0.02	<0.02	<0.02
1,1-dichloroethene	1.98	2.80	0.14[a]
Trichloroethene	2.45	8.00	0.55
Mature gas			
Chloroethene	1.10[a]	100	31.0[a]
Chloroethane	<0.03	<0.03	<0.03
Tetrachloromethane	<0.02	<0.02	<0.02
1,1-dichloroethene	<0.03	1.88	<0.03
Trichloroethene	0.25[a]	3.50	0.33

[a] Sample volume of 100 ml, else 400 ml standard.

2.2. Chemical input

A recurrent issue for modelling landfills is the uncertainty associated with the composition of incoming waste. Understanding the load and characteristics of the waste is important if generalised findings are to be extrapolated between sites with comparable operational histories. However, selecting values for chemical input parameters for a model is challenging without detailed information on the chemical composition of the wastes under study, which are universally absent. Due to these difficulties, a scalable initial value of 10 mg kg^{-1} for all of the chemicals was initially selected (Pollard et al., 1993). This represented a load to the cell of 160 kg. Having generated an initial set of gas concentrations, this enabled review and then back-extrapolation to determine possible initial inputs of the chemical to the landfill. Molecular mass (g mol^{-1}), temperature (°C), water solubility (g m^{-3}), vapour pressure (Pa), log K_{ow} melting point (°C) and the Henry's Law constant (Pa m^3 mol^{-1}) were required for each substance in order to parameterise Eqs. (1) –(5). All parameter values were derived from those reported in Mackay (2001).

Table 4
Dimensions of the landfill evaluative environment

Parameter	Value
Cell length	40 m
Cell width	20 m[a]
Cell depth	25 m
Cell volume	20×10^3 m^3
Cell mass	16×10^6 kg[b]
Waste density	830 kg/m^3[a,c]

[a] Brogborough test cell 1 (Blackmore et al., 2003).
[b] Calculation m = ρv.
[c] Croft et al. (2001).

Table 5
Volumetric composition of the landfill evaluative environment

Parameter	Volume fraction	Justification/reference	Mass (kg)	Volume (m^3)
LFG/air	0.10	10% effective porosity of waste[a]	2.20×10^3	2000
Water	0.25	Estimated water content[a,b]	5.00×10^6	5000
Waste				
Organic	0.25	Estimated from type of waste input. Similar mean reported by Schwarze[c]		
Inorganic	0.40	Remaining volume		
Waste total	0.65	Accumulative	1.15×10^7	13 000

[a] Blackmore et al. (2003).
[b] Croft et al. (2001).
[c] Schwarze (2001).

2.3. Gas and water regimes

Gas flow through landfills is highly variable and dependant on a number of factors such as atmospheric pressure, design and operational parameters (Young, 1992; Croft et al., 2001; Christopherson and Kjeldsen, 2001; Kjeldsen and Christensen, 2001). Historic data from Brogborough test cell 1 shows gas production rates varying between 5–15 $m^3\ t^{-1}$ waste yr^{-1} (Croft et al., 2001). A mean of 10 $m^3\ t^{-1}\ yr^{-1}$ represents a gas extraction rate of *ca.* 20 $m^3\ h^{-1}$ from each cell. A log mean diffusion path of 4.55 m was adopted from a diffusion path of 12.5 m, judged as the maximum distance between gas extraction points at Brogborough and typical of a large, modern, engineered landfill in the UK. Finally, rather than set a leachate head for this study, a water flow rate though the cell was applied using an infiltration rate of 0.14 mm d^{-1} adopted from GasSim (Environment Agency, 2002a). This flow rate assumes the input of water into the system is constant and derived from limited infiltration through a clay cap alone (Environment Agency, 2002a).

2.4. Fugacity modelling

Level I fugacity calculations illustrate general partitioning behaviour and preferential partitioning to the organic fraction in the waste environment. Level II calculations account for advection and reactions in the form of residence time and half-lives respectively (D values). The calculations assume an environment in equilibrium, but under steady state flow; i.e. the amount entering the environment is mass-balanced by the amount lost to flow, reactions or degradation. The Level II model (Fig. 2) allows the estimation of a residence time for a substance within the system. The characteristics of the system are presented in Table 6. Reaction half-lives for each chemical in air, water and waste were required and aerobic values were adopted from Mackay (2001). Anaerobic conditions were subsequently modelled using degradation rates obtained from aquifer studies (Aronson and Howard, 1997). Control runs set the degradation term to zero.

An adapted level II fugacity model, SOILVE is dynamic, in that time and extraction rates can be specified. The model (She et al., 1995) was re-coded using Model Maker 4™ (Modelkinetix.com, 2000). In concept, SOILVE has many similarities to the processes of LFG extraction. Parameterisation is complex and includes concentrations in various phases, as well as D values (transport parameters). To obtain these, a level II calculation was conducted prior to the SOILVE run. Table 7 displays the additional parameterisation required for SOILVE and Table 8 lists the series of model runs undertaken to evaluate the fate of trace components in LFG (Christopherson and Kjeldsen, 2001). The selection of runs reflects the acknowledged (Kjeldsen and Christensen, 2001) importance of (i) the free organic carbon phase (represented by f_{oc}) (ii) the gas extraction rate; and (iii) the redox status to estimating the concentration of trace components in LFG.

3. Results and discussion

3.1. Level I and II fugacity modelling

Here, discussion is reserved for the results offering greatest insight. (Shafi (2005) presents a comprehensive analysis). Level I modelling (Fig. 3) illustrates the role of organic matter (f_{oc}) in determining the partitioning of trace components in the landfill system. Organic carbon can be represented by conventional soil organic (humic) matter or by the presence of a free organic phase common to many hazardous waste systems (Pollard et al., 1993; Kjeldsen and Christensen, 2001). Level II modelling has improved utility, producing illustrative data on persistence, losses due to advection and reaction and other dynamic trends. Again, it highlights the influence of organic carbon in the waste matrix on the mass of chemical in the gaseous phase and the residence time of a chemical, given the flux (Fig. 2) in the landfill (Fig. 4). The concentrations of trace components in each phase using a 10 mg kg^{-1} input, compared with the observed ranges in monitoring studies, are presented in Table 9. Observed benzene concentrations

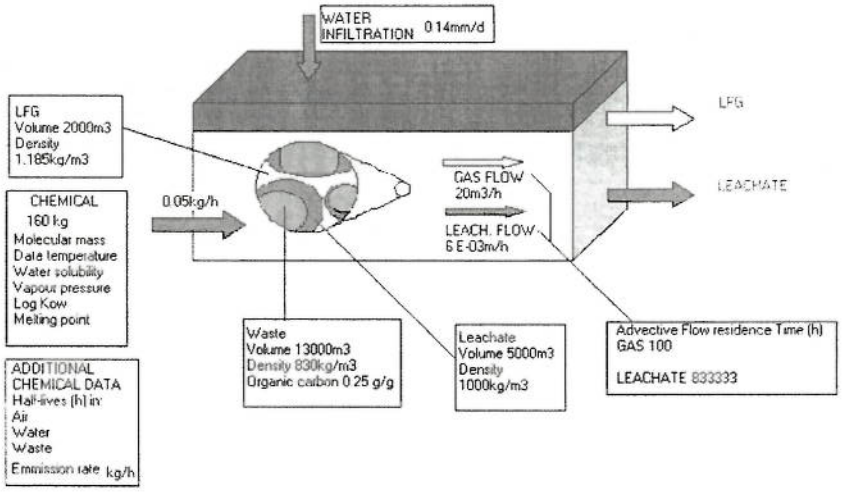


Fig. 2. Evaluative environment for Level II model.

Table 6
Parameters for Level II fugacity calculation

Parameter	Value	Justification/reference
Emission rate of chemical into environment	0.05 kg h^{-1}	Calculated using 10 ppm (160 kg) of chemical with filling time 4.5 months[a]
Gas flow rate	20 $m^3 h^{-1}$	Adapted to evaluative environment[b]
Leachate flow rate	6 × 103 m h^{-1}	Calculated from water infiltration rate of 0.14 mm d^{-1} through environment
Advective residence time for LFG	100 h	Calculated using gas flow rate and level one calculation; assumes chemical concentration in incoming gas of zero
Advective residence time for leachate	833 333 h	Calculated using leachate flow rate as above

[a] Fletcher (1989).
[b] Croft et al. (2001).

are between 3500–150 000 μg m^{-3}. Modelled concentrations range between 32 700–139 000 μg m^{-3} suggesting that, assumptions holding, a 10 mg kg^{-1} (160 kg) input of benzene may be a good first approximation of the source term. The modelled concentrations for vinyl chloride, trichloroethylene and 1,3-butadiene were elevated above the observed ranges, although vinyl chloride was of the same order of magnitude as the observed concentrations. One approach to estimating the initial load is to back-extrapolate, taking the model assumptions as valid and the observed concentrations for each component as input (Table 10). This provides a set of candidate loads that can be re-assessed with anaerobic degradation rates to generate a new set of phase distributions

Table 7
Parameterisation of SOILVE

Parameter/unit	Explanation	Justification/calculation/derivation
Chemical input	Amount of chemical in kg	160 kg
Z values	Fugacity capacity of each phase	Generated from level II calculation
G ($m^3 h^{-1}$)	Gas flow rate	20 $m^3 h^{-1}$
E (unitless)	Sweep efficiency	She et al., 1995
k_3	Rate constant for decay	She et al., 1995
t½ (h)	Half life of chemical in soil	Aerobic[a]; anaerobic[b]
k_r (h^{-1})	Rate constant for degrading reactions	$0.693/t_{1/2}$
Z_T (Pa)	Total fugacity	
V_T (m^3)	Total volume	
D_R (mol $Pa^{-1}h$)	D value for degrading reactions	$DR = KrZ_TV_T$
D_L (mol $Pa^{-1}h$)	D value for water leaching	Water flow rate/Zwater
D_X (mol $Pa^{-1}h$)	D value for gas phase advection	Gas flow rate/Zgas
K_v (m s^{-1})	Mass transfer coefficient	From diffusivity calculation[c]
D_E (m s^{-1})	Diffusion across a stagnant boundary layer	DE = kv Azgas
B_{EG} (mol $Pa^{-1}h$)	Gas phase diffusion	
D_G (mol $Pa^{-1}h$)	Gas phase diffusion in soil	
B_{EWI} (mol $Pa^{-1}h$)	Water phase diffusion	
D_W (mol $Pa^{-1}h$)	D value water phase diffusion	

[a] Mackay (2001).
[b] Aronson and Howard (1997).
[c] Lyman et al. (1982).

Table 8
Range of adapted SOILVE model runs

Trace component	Load (kg)	Duration (y)	Redox status	f_{oc}	Gas extraction rate ($m^3 h^{-1}$)
Vinyl chloride	160	1.00	Aerobic	0.05	20.0
				0.25	
				0.40	
	16.0			0.25	10.0
					20.0
					40.0
Benzene	160	1.00	Aerobic	0.05	20.0
				0.25	
				0.40	
Trichloroethylene	160	1.00	Aerobic	0.05	20.0
				0.25	
				0.40	
1, 3-butadiene	160	1.00	Aerobic	0.05	20.0
				0.25	
				0.40	
Vinyl chloride	160	1.00	Aerobic and no deg. comparison	0.25	20.0
Benzene					
Trichloroethylene					
1, 3-butadiene					
Vinyl chloride	16.0	10.0	Aerobic	0.25	10.0
					20.0
					40.0
Benzene	16.0	10.0	Aerobic	0.25	10.0
					20.0
					40.0
Trichloroethylene	16.0	10.0	Aerobic	0.25	10.0
					20.0
					40.0
1, 3-butadiene	16.0	10.0	Aerobic	0.25	10.0
					20.0
					40.0
Vinyl chloride	16.0	10.0	Anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0
Benzene	16.0	10.0	Anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0
Trichloroethylene	16.0	10.0	Anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0
1, 3-butadiene	16.0	10.0	Anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0

(Table 11), the air phase concentrations for which may be compared with the observed ranges of trace components in LFG. One must be cautious as to the utility of this approach. The absence of representative anaerobic degradation rates within landfills is a serious constraint. Further, it is clear from the analysis that the complexities of the landfill environment stretch the capabilities of Level II fugacity modelling.

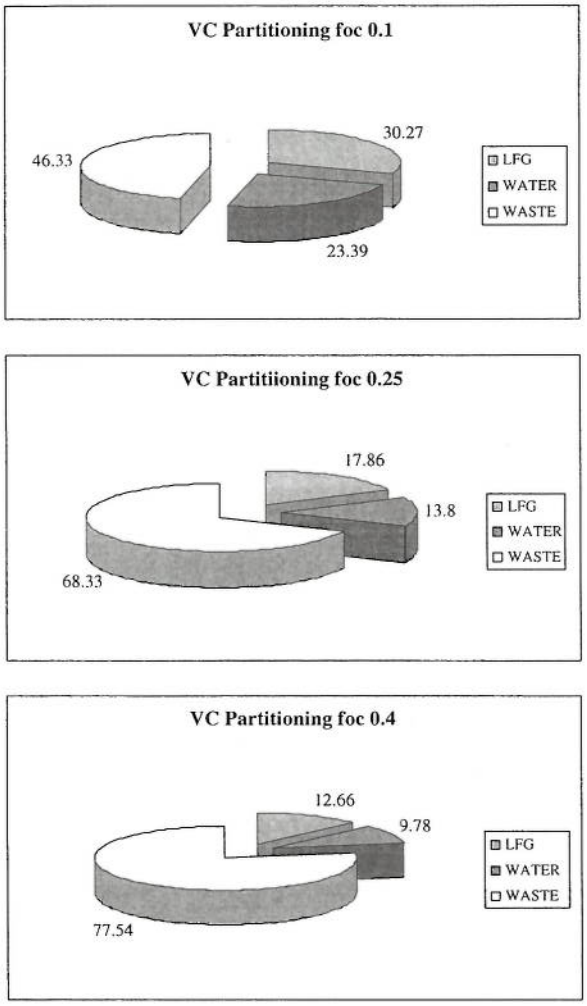


Fig. 3. Illustrative mass contributions ($\%^{w}/_{w}$) of vinyl chloride (VC) to landfill gas (LFG), water and waste phases contingent on the fraction of organic carbon (f_{oc}) in the system.

3.2. Dynamic fugacity modelling

Landfill processes (e.g. redox status, settlement, gas and leachate generation and chemical composition) develop over decades. Exploratory SOILVE model runs were performed (data not shown; see Shafi, 2005) (i) for *ca.* 1 year (8000 h) under aerobic and zero degradation conditions; (ii) for individual components at gas extraction rates of 10, 20 and 40 $m^3\ h^{-1}$; and (iii) for the first year, aerobically, at f_{oc} values of 0.05, 0.25 and 0.40. D values, along with other input parameters, were derived from a prior set of Level II calculations (note limitations above), using an illustrative 10 mg kg^{-1} input concentration (Table 8). Of specific interest is the effect of the gas extraction rate on the long-term concentrations of trace components presented in LFG. A set of SOILVE model runs was performed for a *ca.* 10 year period (90 000 h) using zero and anaerobic degradation rates at gas extraction rates of 10, 20 and 40 $m^3\ h^{-1}$. For the anaerobic simulations, trace component concentrations in the gas phase were inevitably higher than for aerobic degradation. Predicted concentrations of vinyl chloride appeared to be too low for all three extraction rates (Fig. 5). Once extrapolation to 160 kg input is considered, a 10 $m^3\ h^{-1}$ extraction rate produces an order of magnitude concentration for vinyl chloride akin to that observed in recent field investigations (Environment Agency, 2003b) between 0.3–4.1 years. There is no information on the age of the field data, however and no conclusive correlations can therefore be made. Fig. 5 illustrates the impact that degradation and extraction rates have on the concentration of trace components in LFG. These factors change throughout the lifetime of a landfill (bi-, tri-phasic behaviour) generating additional complexity.

Vinyl chloride behaviour is recognisably complex given its generation in landfill as a biotransformation product of chlorinated organics (Vogel and McCarty, 1985). A more appropriate assessment of the utility of the SOILVE approach may be achieved using less complex substrates. The trace components 1–3 butadiene and benzene might be expected to exhibit more straightforward characteristics, being resistant to biotransformation (Fig. 6). Fig. 6 exhibits near linearity for benzene and an exponential decrease for 1–3 butadiene, becoming more pronounced at rapid extraction rates. In both cases, the concentrations achieved are within the observed range (Table 11). For these less complex substrates, modelled without the complexities of biotransformation, data that are more representative can therefore be achieved. Overall, however, the results

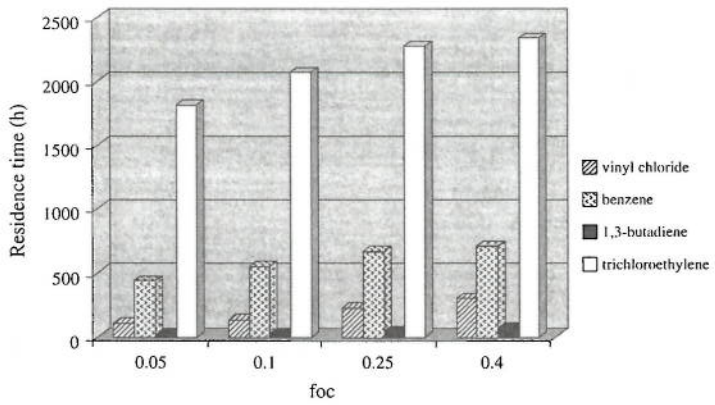


Fig. 4. Residence time of trace components in landfill as a function of the fraction of organic carbon (f_{oc}) using Level II fugacity modelling.

Table 9
Level II fugacity calculations

Foc	Benzene			Vinyl chloride			Trichloroethylene			1,3-butadiene		
	Air	Water	Soil/waste	Air	Water	Soil/waste	Air	Water	Soil/waste	Air	Water	Soil/waste
0.05	1.39×10^5	6.19×10^5	1.42×10^6	1.05×10^6	3.20×10^5	1.23×10^5	5.34×10^5	1.12×10^6	6.46×10^6	1.65×10^5	1.98×10^4	3.29×10^4
0.10	9.49×10^4	4.22×10^5	1.94×10^6	1.03×10^6	3.19×10^5	2.43×10^5	3.17×10^5	6.65×10^5	7.67×10^6	1.63×10^5	1.96×10^4	6.51×10^4
0.25	4.86×10^4	1.26×10^5	2.48×10^6	9.95×10^5	3.07×10^5	5.85×10^5	1.43×10^5	3.00×10^5	8.64×10^6	1.58×10^5	1.90×10^4	1.58×10^5
0.40	3.27×10^4	1.45×10^5	2.67×10^6	9.59×10^5	2.96×10^5	9.03×10^5	9.20×10^4	1.93×10^5	8.92×10^6	1.53×10^5	1.84×10^4	2.45×10^5
Observed: 3.50×10^2–1.50×10^5				2.43×10^4–1.80×10^5			1.95×10^3–7.01×10^3			<2.00×10^1–<7.00×10^1		

Modelled and observed concentrations of priority components in LFG assuming a 10 mg kg^{-1} waste input (all data in $\mu g\ m^{-3}$).

Table 10
Back-extracted estimates of trace component load to evaluative landfill cell

Trace component	Mean observed gas concentration ($\mu g\ m^{-3}$)	Estimated input to cell (kg)
Vinyl chloride	8.70×10^4	14.0
Benzene	4.86×10^4	160
Trichloroethylene	4.53×10^3	5.00
1,3-butadiene	4.50×10^1	0.05

produced with SOILVE illustrate the importance of using appropriate biotransformation rates.

3.3. Study limitations and utility as a source term generator for risk assessments of landfill gas

This study illustrates the complexities of LFG modelling under dynamic conditions even for a well characterised conceptual model. One of the major limitations for all three models is the requirement for site-specific data regarding input parameters. This is especially important in terms of input concentrations, but also for the volumes of waste and air that are required to characterise the evaluative environment. Representative mean values from the literature were used here, but site-specific information is necessary for precision in model output beyond the order of magnitude data presented here. A significant assumption is that the organic matter is the major partition medium for organic contaminants in waste, as it is in soil. It is widely accepted that in most waste-soil systems, free phase organic liquids, rather than soil humic matter, dominate the partitioning behaviour of hydrophobic contaminants (Boyd and Sun, 1990; Young, 1992; Zemanek et al., 1997). In addition, for simplicity, water has been substituted for leachate in the models and leachate will in practice express its own bulk density and possible co-solvency effects as it migrates through waste (Rao et al., 1990).

A further and influential limitation is the lack of representation of a leachate hydraulic head in the models used. This may further account for some of the discrepancies between the observed and predicted concentrations. The fact that a low-flow water regime has been applied in this study is a consequence of the clay capping that is assumed in the evaluate environment. In practice of course, gas and leachate flow rates fluctuate resulting in temporal variation in concentrations of trace components.

An underlying challenge with the application of fugacity to landfill modelling is the reliance on the physicochemical characteristics at standard values for 25 °C. Landfills undergo diurnal, seasonal and microbiologically induced temperature

Table 11
Estimating LFG concentrations with anaerobic degradation rates (Level II)

Trace component and input (kg)	Input (kg/h)	Gas concentration ($\mu g\ m^{-3}$)	Observed range in LFG ($\mu g\ m^{-3}$)
Vinyl chloride (14)	5.00×10^{-2}	4.92×10^5	3.50×10^3–1.50×10^5
Benzene (160)	4.30×10^{-2}	9.53×10^4	2.43×10^4–1.80×10^5
Trichloroethylene (5)	1.50×10^{-3}	1.30×10^4	1.95×10^3–7.10×10^3
1,3-butadiene (0.045)	1.30×10^{-4}	4.30×10^1	2.00×10^1–7.00×10^1

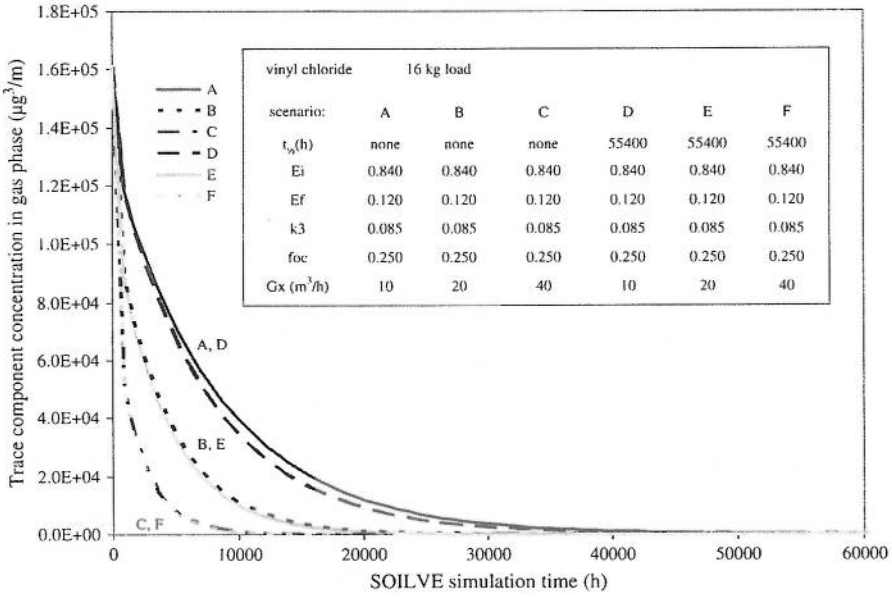


Fig. 5. Illustrative SOILVE simulations illustrating effect of gas extraction rate and varying degradation rates on vinyl chloride concentrations in LFG (16 kg input).

changes through the various stages of their lifetime, a feature that fugacity cannot address without running coupled simulations. This becomes particularly significant for factors such as vapour pressure and solubility, which are also effected by the changing pressure of the environment. Level II calculations have the limitation of requiring an emission source to be presented as an input rate (kg h^{-1}). In this study, this was estimated using Brogborough waste loading rates, whereas the observed monitoring data are sourced from landfills of very different ages and loading rates. Finally, a common source of uncertainty is the paucity of degradation rates for components of concern within the landfill environment and, as we have seen here, the referencing of waste monitoring data to input load, time of emplacement and landfill redox status.

4. Conclusions

Can fugacity models be used to generate source term concentrations of trace components in landfill gas? There are clearly substantial constraints as presented by the poor referencing of observed trace component data noted above. Back-extrapolation of waste inputs may assist, but there are substantial variables in the system. In GasSim (Environment Agency, 2002a), trace component concentrations are estimated (a) using distributed literature data using a uniform or triangular distribution, as appropriate; or (b) from site-specific data. The evaluative environment used in this study is similar to GasSim, the waste being considered a cuboid mass with vertical sides from which characteristics such as volume and area are deduced (Environment Agency, 2002a). If a site-specific fugacity model were constructed and applied, informed by an estimated inventory of solvent mass in the landfill, then a more representative source term might be produced and subsequent estimates of exposure and risk made more representative. SOILVE has the potential for producing meaningful concentrations for the GasSim source module, the system is more dynamic and there is an increased capacity for the propagation of error in the absence of better-characterised sites.

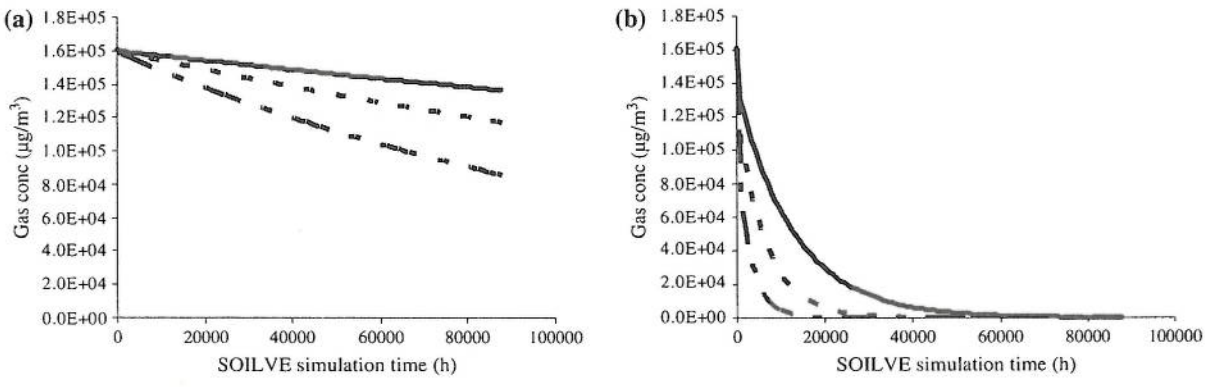


Fig. 6. Illustrative SOILVE simulations (10 y) showing the effect of 10 (solid), 20 (dotted) and 40 (dashed) m3 h^{-1} gas extraction rate on (a) benzene; and (b) 1,3-butadiene concentrations in LFG, assuming no biotransformation.

There is an explicit need for precise degradation data and firm evidence for the bounded ranges of key variables that influence the concentrations of trace components in landfill gas. Further work needs to be undertaken on the influence of successive redox regimes on trace component biotransformation. Notwithstanding these limitations, we believe to have illustrated the potential application of dynamic fugacity modelling and propose that this approach may have use for the generation of a better, time-dependent source term for regulatory LFG risk assessments tools such as GasSim.

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The challenge of contaminated sites: remediation approaches in North America

STEVE E. HRUDEY[1] AND SIMON J. POLLARD[2]
Environmental Health Program, Faculty of Medicine, University of Alberta, Edmonton, Alta., Canada T6G 2G3

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The pervasive occurrence of contaminated land has become a major issue facing society and involving enormous financial and social implications. Several problems arise at the interface between environmental science and public policy in dealing with future uses of such land. Contaminated sites need to have the nature and magnitude of the contamination identified. Such characterization must deal with the enormous complexity of many common wastes, the selection of appropriate analytical methods, and the heterogeneity of site conditions. Responses to these problems are limited by the capabilities of remediation technologies available. These may be categorized as containment/immobilization, mobilization, or destruction processes. In the last category, bioremediation has shown the most promise and general utility, but a number of specific requirements and constraints must be satisfied. For bioremediation to be feasible, the contaminants must be amenable to biological degradation, an appropriate and active microbial community must be provided, the contaminants must be accessible (bioavailable) to the microbial community, waste-specific constraints must be minimized, and appropriate environmental conditions must be provided for the microbial population. Cleanup criteria are fundamental to any decisions about contaminated sites. The U.S. Superfund approach has avoided developing generic contamination criteria, in contrast with the Canadian approach. Some common problems arise with either approach. There is a trend towards increasing reliance on risk assessment for site remediation decisions. Management challenges facing effective site remediation include the interdisciplinary nature of the issues, communication between laboratory and field personnel, and misrepresentation or inadequate attention to uncertainty. Constructive and positive advances to deal with these problems have been developed and include statistical sampling methods, tiered protocols, integrated toxicity testing procedures, multimedia partitioning models, and uncertainty analyses. Considering all the problems and challenges, there remains overwhelming evidence that prevention of contamination is vastly superior to remediation.

Key words: waste characterization, analytical methods, cleanup technologies, bioremediation, cleanup criteria, risk management.

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L'existence de plus en plus importante de sols contaminés est devenue un problème majeur à lequel doit faire face la société, avec des implications économiques et sociales énormes. Plusieurs problèmes se situent à l'interface entre les sciences de l'environnement et les politiques publiques concernant l'utilisation future de tels sites. Il est nécessaire de connaître la nature et l'étendue des contaminations. Une telle caractérisation doit tenir compte de la grande complexité mettant en jeu des déchets communs, la sélection de méthodes analytiques appropriées et l'hétérogénéité des conditions des sites. La solution de ces problèmes est limitée par le peu d'efficacité des technologies curatives disponibles. On peut les regrouper en processus de confinement/immobilisation, de mobilisation et de destruction. Dans la dernière catégorie, la bioremédiation s'est avérée d'intérêt général et prometteur, mais elle nécessite un nombre de prérequis et de contraintes. Pour que la bioremédiation soit faisable, les contaminants doivent être amenables à la dégradation biologique, on doit pouvoir y apporter une communauté microbienne active et appropriée, les contaminants doivent être accessibles (bio-disponibles) à la communauté microbienne, les contraintes spécifiques liées aux déchets doivent être minimisées, et on doit créer des conditions environnementales favorables pour la population microbienne. Les critères de nettoyage sont fondamentaux pour toute décision à propos de sites contaminés. L'approche U.S. Superfund a évité de développer des critères génériques de contamination, contrairement à la méthode canadienne. Chaque méthode comporte des difficultés. Il y a une tendance à donner plus d'importance à l'évaluation des risques dans le processus décisionnel de remédiation. Les défis d'aménagement qu'on rencontre dans la remédiation des sites incluent la nature interdisciplinaire du problème, la communication entre le personnel de laboratoire et de terrain, et la mauvaise représentation ou le manque d'attention accordés à l'incertitude. Des progrès constructifs et positifs dans la solution de ces problèmes ont été apportés et incluent des méthodes d'échantillonnage statistique, des protocoles par étapes, des méthodes intégrées pour mesurer la toxicité, des modèles de répartition multimedia, et des analyses d'incertitude. Considérant tous les problèmes et tous les défis, une seule évidence demeure, c'est que la prévention de la contamination est de loin supérieure à la remédiation.

Mots clés : caractérisation des déchets, méthodes analytiques, technologies de nettoyage, bioremédiation, critères de nettoyage, aménagement des risques.

[Traduit par la rédaction]

Introduction

Background

Human activities have always carried the potential of contaminating land. This potential has too often been realized. During the late 1970s, many situations were discovered where innocent parties had been exposed to hazardous substances that had been disposed without adequate regard to the potential for public health or environmental consequences. Infamous cases such as Love Canal became household names synonymous with hazardous waste mismanagement. Politicians duly responded to the public outrage in the United States with the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, now better known as "Superfund." The continuing discoveries of the past two decades have created a

[1]Author to whom correspondence may be addressed.
[2]Present address: Department of Chemistry, The University of Edinburgh, Edinburgh, Scotland EH9 3JJ.

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TABLE 1. Estimated number of contaminated sites in various countries (adapted from Smith 1991)

Country	Number of contaminated sites	Estimated "high risk" sites
Canada	10 000	1000
United States	33 000	1200
United Kingdom	est. 100 000	Not known
Netherlands	110 000	6000
Germany	100 000	Not known
Norway	2441	61
Finland	20 000	100–1000
Denmark	20 000	Not known
France		100 (priority sites)

phenomenal new emphasis on the identification, characterization, and cleanup (remediation) of contaminated sites.

Enormous expenditures have been directed at these issues. Superfund alone has expended some $15.2 billion since its creation (Miller 1992). Even these considerable figures reflect only activities related to abandoned or uncontrolled sites that were placed upon the U.S. National Priority List. Considerable contaminated-site remediation activity has also been undertaken by industries and government agencies at all levels to address problems ranging from industrial plant site decommissioning to the remediation of leaking underground storage tanks.

As each industrialized country has focused resources on these issues, each has found its own expanding inventory of contaminated sites. Table 1 summarizes some recent estimates of the number of contaminated sites in nine industrialized countries (Smith 1991). These situations have spawned the concept of "toxic real estate" that has become a basic liability factor to be considered by legal and financial professionals dealing with land transactions. Estimates that 100 000 sites in England and Wales may be registered as contaminated raise the prospects of severe social and economic consequences for current owners of the registered properties (Pearce 1992).

After more than a decade of intense activity directed towards these problems, many questions remain concerning an appropriate definition of contaminated land, the adequacy of the methods for identifying and characterizing the hazardous substances present, the utility of the various technologies that have been applied to site remediation, the value of soil contaminant standards that are set as cleanup criteria for contaminated sites, and the significance of health risks posed by contaminated sites. All of these issues fundamentally depend upon valid scientific input. Because there is considerable scope for questioning the efficacy of much of the site remediation activity that has occurred, there is also scope for questioning the utility of the scientific foundations for these activities.

This review considers some of the current challenges and outlines some of the critical needs for more effective scientific contributions. We offer some general insights aimed at a greater understanding of underlying issues. Details on the various specific issues raised can be found in several comprehensive reports, technical reviews, and manuals (Pollard and Hrudey 1992*a*, 1992*b*; CCME 1991*a*; Smith 1991; Sims 1990; Hoffmann and Hrudey 1990; WPCF 1990; U.S. EPA 1989*a*, 1989*b*; Mueller et al. 1989; API 1989; U.S. EPA 1988; Preslo et al. 1988; Lord 1987).

The underlying rationale for contaminated site remediation must be to achieve an overall reduction in both short-term and long-term environmental risk. Consequently, both immediate and long-term hazards to human health and to valued components of relevant ecosystems must be effectively managed in relation to other environmental hazards that exist in our society. Because of the complexity and detail that become involved in specific site remediation cases, there is continual danger of losing sight of this overall objective.

Fundamental challenges

An adequate definition for what should be judged as contaminated soil is a fundamental challenge underlying this entire issue. The ability to judge environmental contamination has been closely linked with the capabilities of chemical analyses. With the advent, during the 1960s, of routine and sensitive analytical techniques like gas chromatography for organic contaminants and atomic absorption spectrophotometry for metals, the emphasis expanded beyond a variety of approximate, integrated parameters (e.g., oil and grease, biochemical oxygen demand) to identification and quantitative measurement of more specific contaminants.

These early analytical advances often coincided with public health authorities viewing environmental contamination as an all or nothing issue. Based on this view, the public health tradition of erring on the side of caution could be honoured by specifying that specific contaminants should be nondetectable in environmental media. Meanwhile, analysts were dramatically lowering detection limits for most contaminants. The inevitable trend toward increasingly sensitive detection limits makes their current level arbitrary and untenable as a basis for specifying environmental contamination criteria. Despite these analytical advances, there is still a lack of consolidated data on worldwide background concentrations of many contaminants, particularly organic contaminants in soil.

As an illustration of the interpretive dilemma, consider 1 g of soil containing 1 ng of polychlorinated biphenyls (i.e., 1 part per billion of PCBs). This represents a level that would present sufficient challenge for current routine analysis that it would likely be reported as nondetected and would be commonly perceived as zero. Yet, this small mass of soil would still contain approximately 2 000 000 000 000 molecules of PCBs. This simple illustration leads to many other questions. Does this represent a large number or an insignificant number? Does the number represent soil contamination in need of remediation or does it represent an inevitable, but environmentally insignificant, consequence of previous human use of PCBs? If remediation was deemed necessary, by what criteria would it be judged to be successful?

These basic questions exemplify some of the difficult issues involved in managing contaminated land. Unfortunately, they lack easy answers. Yet, if the objective of remediating contaminated land is to achieve an effective overall reduction in environmental risk, there is a corresponding need to direct society's limited resources to the resolution of the most important problems and to disregard, with confidence, those situations that pose insignificant risks. Because there is no zero for environmental contaminants, remediation decisions must be made upon some understanding of the significance of contamination levels that do exist.

Beyond this general interpretive dilemma, there are numerous challenging problems facing contaminated site remediation, including characterization of contamination, capabilities of remediation technology, scientific rationale for cleanup criteria, and management of contaminated site remediation.

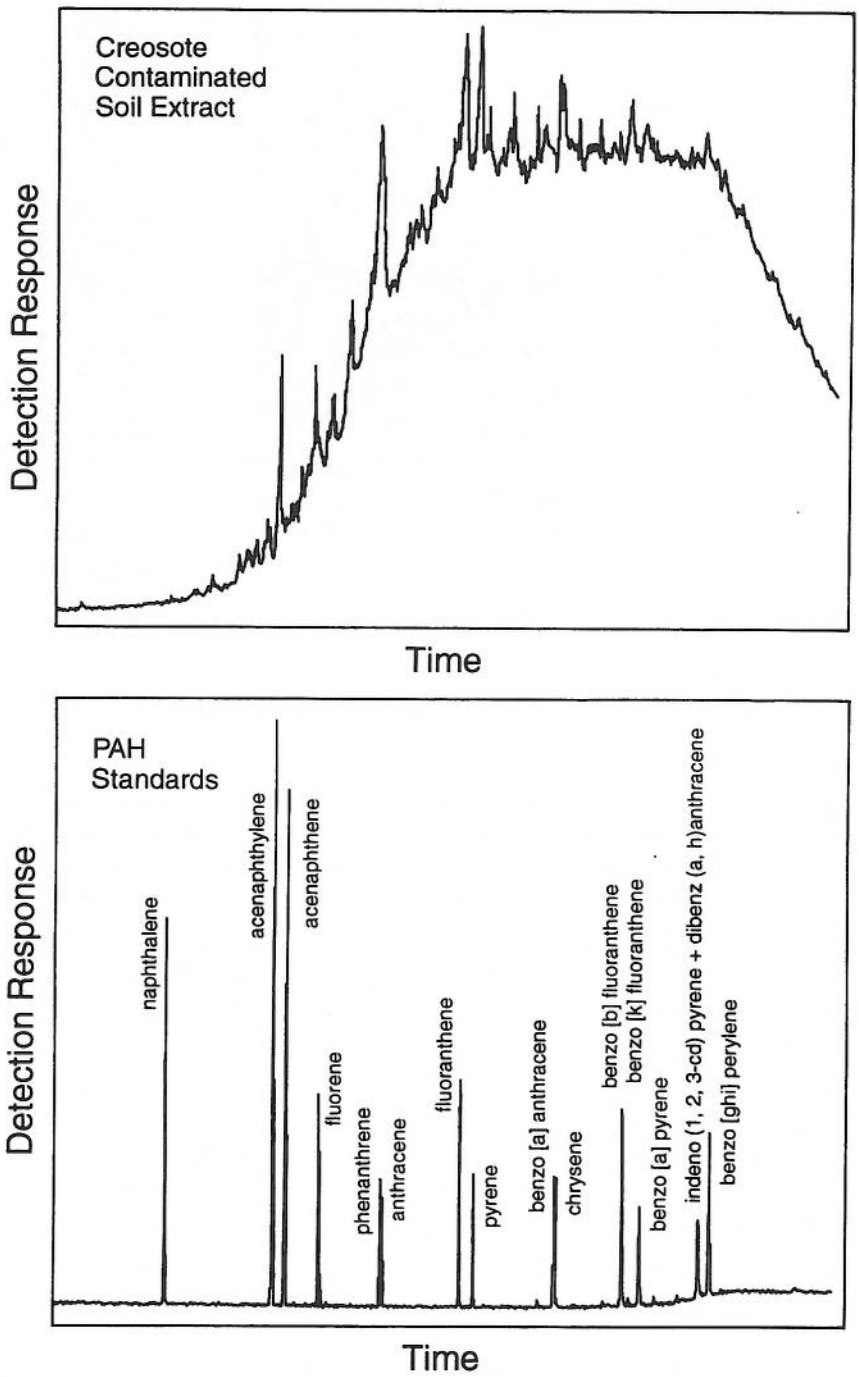


FIG. 1. Chromatogram of weathered creosote-contaminated soil compared with chromatogram of U.S. EPA priority PAHs.

Characterization of contamination

Waste complexity

As analytical techniques have advanced in recent years, we increasingly find that common industrial wastes are exceedingly complex chemical mixtures. In the case of organic wastes, mixtures will consist of many individual compounds. For illustration, coal tar creosote, a product that has been widely used as a wood preservative and is the source of contamination at many industrial sites, may contain several thousand individual compounds of which only a few hundred have been identified (ATSDR 1990).

Despite the considerable advances that have occurred in environmental analysis, the complex mixtures that may be present in many common organic waste streams represent a formidable challenge. Figure 1 shows a weathered creosote-contaminated soil extract compared with a chromatogram of the 16 polynuclear aromatic hydrocarbons selected by the U.S. Environmental Protection Agency (U.S. EPA) for their priority pollutants list. Although some of these priority compounds have been extensively studied and some are judged to be carcinogens in experimental animals, there is no assurance that targeting analyses only on the "priority" compounds will avoid ignoring many other compounds that may be more important contributors to the toxicity of the overall waste mixture. Lee et al. 1981 summarized various screening tests for carcinogenic activity for over 350 polynuclear aromatic compounds.

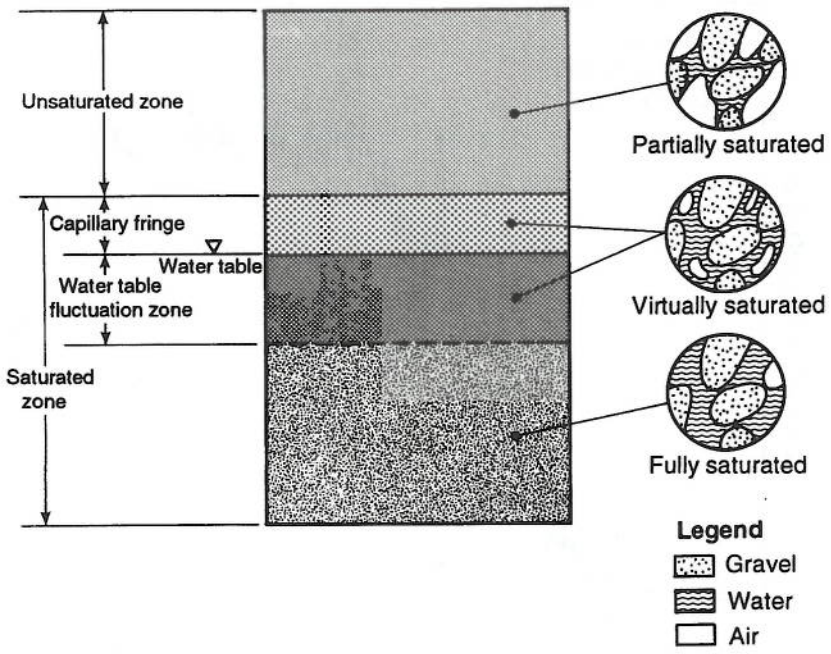


FIG. 2. Major phases present in the subsurface (adapted from API 1989).

However, most of the individual compounds occurring in complex, weathered, and partially decomposed wastes encountered at heavy oil or coal tar contaminated sites will not have been tested individually for any toxicological or environmental properties. Table 2 illustrates the enormous diversity of individual organic compounds that may be present in these complex mixtures.

In comparison with the infinite variety of chemical structures possible for organic compounds, inorganic contaminants have a much narrower range of possible variation. However, some inorganic contaminants may still present a very complex array of chemical forms because of their variety of oxidation states and their ability to combine in organic forms. The example of arsenic is illustrated in Table 3. The availability of individual elements to participate in biological processes is strongly influenced by their specific chemical form. Consequently, total elemental analyses that are routinely performed for metals may provide little insight into a contaminant's mobility in the environment or the health risks it poses.

In cases where organic and inorganic contaminants are mixed, they may interfere with the analyses for each other. For example, organic matrices may interfere with metals analyses and inorganic contaminants may interfere with the cleanup and concentration procedures necessary for organic analyses. Mixtures can also reduce the efficacy of certain treatment processes by interfering, at a molecular level, with the mechanisms responsible for contaminant control.

Inappropriate analytical methods

Faced with the complexities posed by waste mixtures and the open-ended costs associated with pursuing compound-specific analyses, site investigations that must often be performed on limited budgets may resort to using surrogate parameters. In the case of organic wastes, the "oil and grease" parameter has often been used. This procedure, which is the quantitative determination of total solvent extractable matter, may have utility where the composition of waste materials has been well characterized and the sources of waste are relatively consistent. Unfortunately, such circumstances rarely exist at contaminated sites where individual pockets of contamination are derived from different sources or have experienced different degrees of weathering exposure. In real cases, the compound-specific composition of the waste can vary substantially. As a result, measuring the total material soluble in a particular extraction solvent will provide negligible insight into the degree of hazard posed to human health or the environment. Likewise, these generic measures will usually offer no useful insight into the cleanup potential for processes like microbiological degradation (bioremediation).

Even if more focused analytical approaches are pursued, effective characterization can be frustrated by the general absence of verified analytical protocols for contaminated soils. Most of the reference methods in current use have been adapted from waste or wastewater protocols with minimal accounting for some of the vagaries caused by the soil matrix. For example, the emulsifying properties of soil organic matter or the adsorption or gelling properties of clays may play havoc with an extraction procedure. Rarely will an analytical laboratory faced with producing priority results for a contaminated site have the luxury of fully evaluating and developing their methods into a verified analytical protocol.

Complexity of site conditions

Contamination of soils and subsurface strata is complex, in part, because the subsurface itself represents a complex environment. The concepts can be illustrated by first considering a very simple special case, an uncontaminated, homogeneous layer of fine gravel or coarse sand with an observable water table. The major phases for this case could be considered as water, air, and the gravel particles. The relationships between the phases are shown in Fig. 2.

TABLE 2. Complexity of chemical classes of monocyclic and polycyclic aromatic compounds found in hydrocarbon wastes

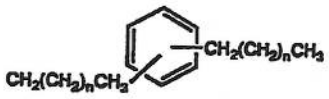
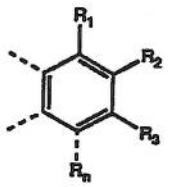
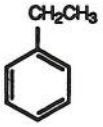
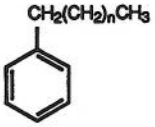
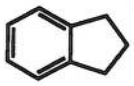
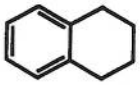
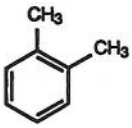
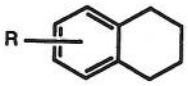
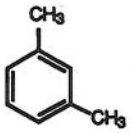
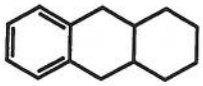
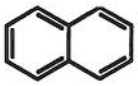
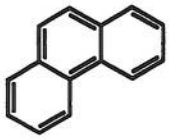
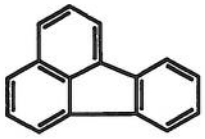
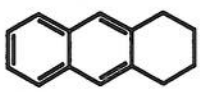
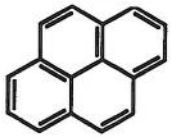
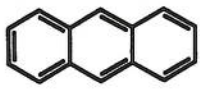
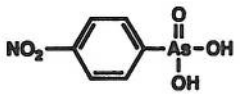
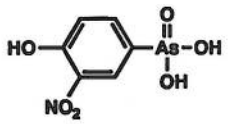
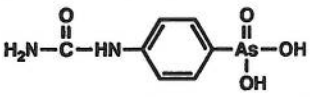
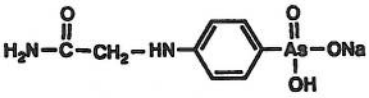
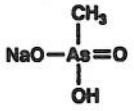
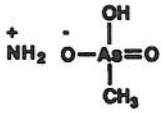
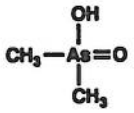
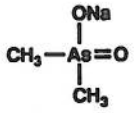
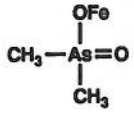
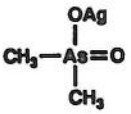
Compound	Chemical structure	Compound	Chemical structure
Monoaromatics			
Benzene		C_2-substituted	
Alkyl Benzenes		C_n-substituted	
Monosubstituted C_1-substituted (toluene)		*n*-Substituted	
C_2-substituted (ethylbenzene)			
C_n-substituted		Benzocycloalkanes Benzo(mono)cycloalkanes) Benzocyclopentanes (indans)	
		Benzocyclohexanes (tetralins)	
Disubstituted C_1-substituted (xylene) 1,2-Substituted (*o*-xylene)		Alkyl benzocycloalkanes	
1,3-Substituted (*m*-xylene)		Benzodicycloalkanes	
1,4-Substituted (*p*-xylene)			
Polynuclear aromatic hydrocarbons			
Naphthalenes		Phenanthrenes	
Alkyl naphthalenes			
Monosubstituted C_{1-n} substituted Disubstituted C_{1-n} substituted *n*-Substituted	Structures analogous to alkylated benzenes	Fluoranthenes	
Naphthocycloalkanes		Pyrenes, etc.	
Anthracenes			

TABLE 3 (*concluded*)

Compound	Chemical structure
4-Nitrophenylarsonic acid	
Roxarsone (4-hydroxy-3-nitrophenylarsonic acid)	
Carbasone (4-ureido-1-phenylarsonic acid)	
Melarsen	
Monosodium methane arsonate (MSMA)	
Amine methane arsonate (AMA)	
Calcium methane arsonate (CMA)	
Dimethylarsinic acid (cacodylic acid CA)	
Sodium cacodylate	
Ferrous cacodylate	
Silver cacodylate	

The heterogeneity of more realistic subsurface environments must be recognized. The surficial soils are unconsolidated materials with a wide variety of physical characteristics. The particle size distribution of the soil influences the ability of the material to transmit fluids (hydraulic conductivity) under a hydraulic gradient, or head. According to Darcy's law, which governs fluid movement through porous materials, for a unit gradient (1 m of water head exercised over a 1 m distance in the direction of flow) the hydraulic conductivity will represent the velocity of fluid movement in units of m/s.

Gravels and sands with large particle sizes will readily transmit fluids (high hydraulic conductivity, up to 1 m/s for water in gravels) while finer grained soils like silts and clays will impede fluid flow (low hydraulic conductivity, as low as 10^{-12} m/s for water in low-permeability clays). There is often considerable variability in material composition both across the site area and with depth, thereby yielding significant variations in the capability of subsurface materials to conduct fluid. Consequently, the migration of contamination (either as a contaminant fluid like oil, or as contaminants carried by water) in the subsurface environment will be strongly influenced by the three-dimensional distribution of materials and their respective hydraulic conductivity. Thus, rather than a uniform migration of contamination through a homogenous medium, realistic conditions will usually produce discontinuous fingers of contaminant migration along the paths of highest hydraulic conductivity (Fig. 3).

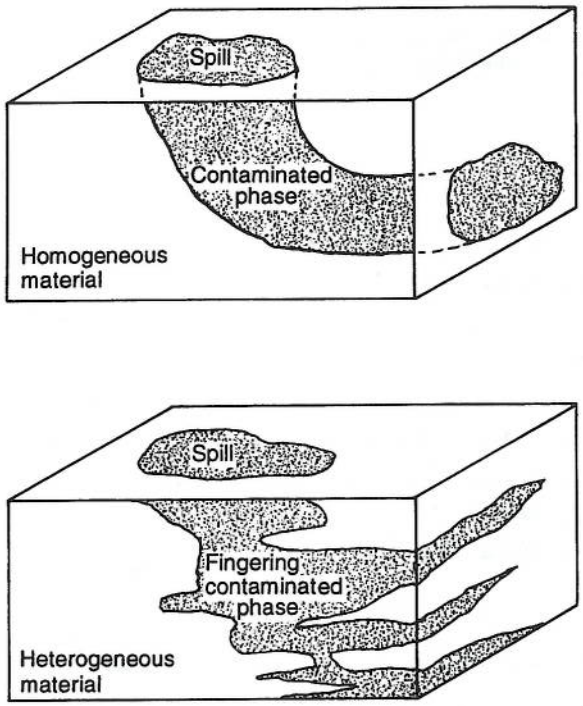


FIG. 3. Occurrence of discontinuities affecting contaminant migration.

Further complexity is introduced because soils consist of an inorganic core of variable sized particles associated with variable proportions of natural organic matter. Individual compounds in a waste mixture will have affinity for each of the available phases (water, air, inorganic soil particle, natural organic matter on soil, and the overall waste matrix) depending on a variety of intrinsic properties. Generally, the more nonpolar (i.e., charge is evenly distributed on the molecule) that a compound is, the lower will be its solubility in water, because water is a very polar solvent. For very nonpolar (hydrophobic) compounds, their low affinity for water will cause them to preferentially partition into air or the organic phases. The relative preference among these choices, given equivalent access, will depend upon the volatility of the compound, as reflected in its vapour pressure. Smaller molecules will be more volatile than larger molecules, for series of compounds of similar chemical structure.

The property of a specific chemical contaminant that determines its tendency to escape any particular environmental phase is represented by its fugacity (Mackay 1991). The relationship of the fugacity of a compound in one phase relative

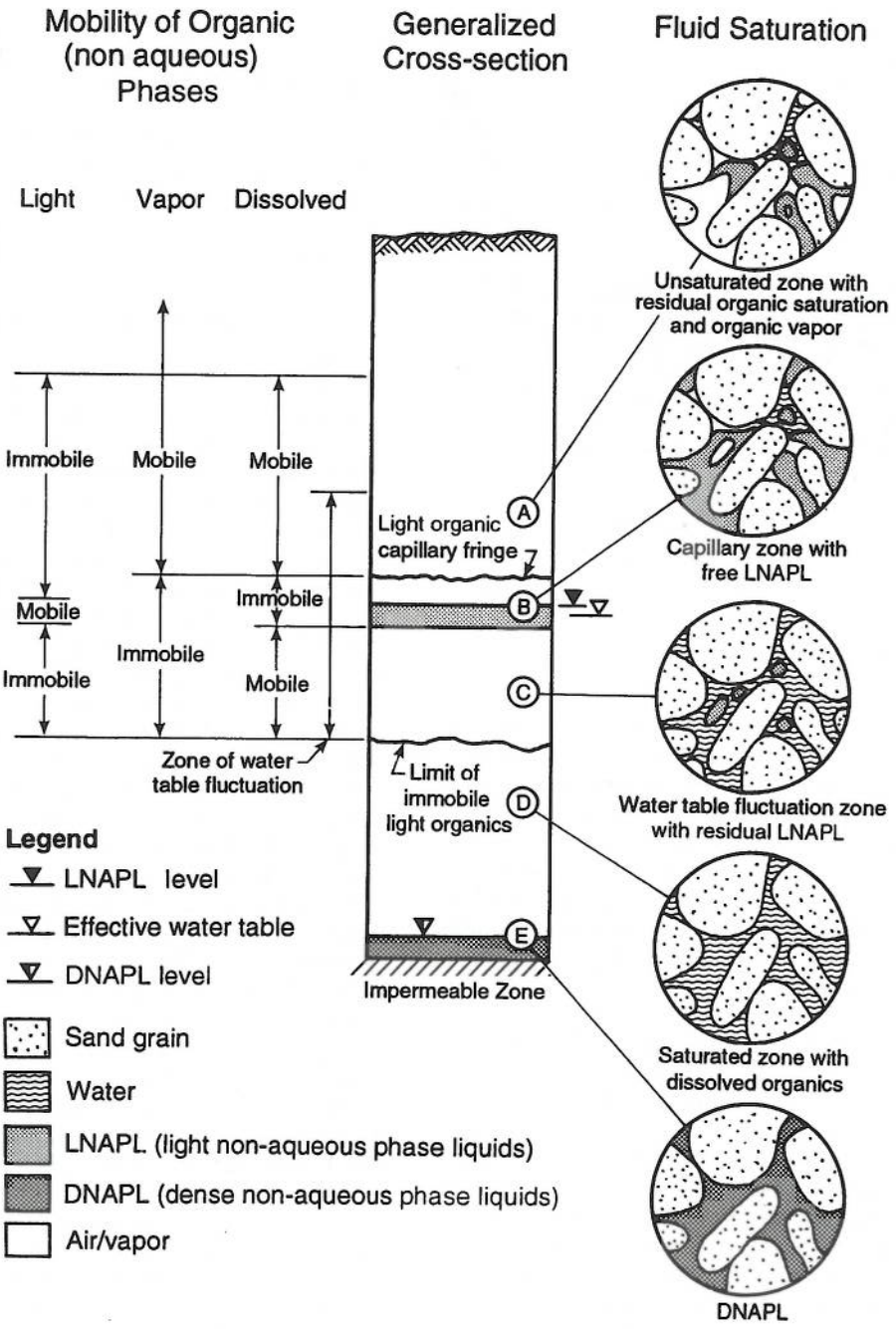


FIG. 4. Types of subsurface contamination (adapted from API 1989).

to its fugacity in another phase will determine whether it will show a net migration from one phase to another (moving from highest fugacity to lowest). These basic properties of contaminant compounds largely govern their partitioning among the various phases in the environment and provide the basis for very useful predictive modeling of contaminant distribution behaviour (Mackay 1991).

At any particular site, organic contaminants may be present in one or more of the following phases (Fig. 4):

1. An immobilized, but distinct organic waste phase usually attached to soil particles (residual saturation);
2. contaminant molecules adsorbed to soil organic or inorganic matter;
3. contaminant molecules present as vapours within soil pore space;
4. contaminant molecules dissolved in soil water in either the saturated (below the water table) or unsaturated (above the water table) zones;
5. a distinct, mobile organic (nonaqueous) phase liquid (NAPL) that may be lighter (LNAPL) or more dense (DNAPL) than the water phase;
6. droplets or emulsions of organic phase within the aqueous phase.

This range of possibilities poses challenges to an accurate and full characterization of the extent of contamination at a site and ultimately poses a challenge to effectively remediating

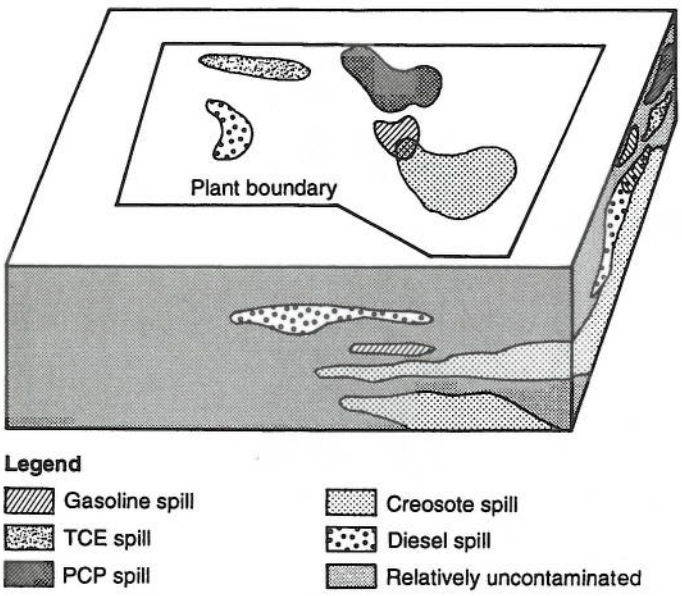


FIG. 5. Site heterogeneity.

the site contamination. For example, subsurface characterization programs based strictly on dissolved or emulsified contaminants found in groundwater will grossly underestimate the degree of contamination if they miss the presence of NAPLs or residual saturation. Groundwater concentrations of contaminants will be governed by their partitioning from NAPLs or residual saturation, the extent of which will be governed by their relative affinity for the organic and water phases. In cases of contaminants with low water solubility, large volumes of groundwater may be contaminated up to the water-soluble limits of the contaminant without substantially reducing the quantity of contaminant retained in the organic phase. In such cases, a strategy of pumping contaminated groundwater to collector wells and treating at the surface to remove the contaminant, followed by use or reinjection (the so-called "pump and treat" approach), will be extremely inefficient at removing the source contamination (Mackay and Cherry 1989).

These different phases for contamination and the partitioning of the contaminant among the phases also play a major role in determining the fate and behaviour of contaminants that govern possible human exposure scenarios. More volatile contaminants can be expected to partition to the soil gas phase while more polar contaminants can be expected to partition to the water phase. In the former case, vapour migration and ultimate inhalation exposure will be a concern. In the latter case, groundwater contamination and ingestion exposure will be a concern. These fundamental partitioning tendencies for individual contaminants must be recognized in designing sampling programs for the subsurface environment.

Finally, site characterization must recognize the fundamental heterogeneity of the original contamination processes. Generally, soil and groundwater contamination has occurred through discontinuous and localized spills of various wastes rather than a generalized distribution of a single homogeneous waste over a large area (Fig. 5). Because of the inevitable heterogeneity, sampling programs that are randomly based must involve very large numbers of samples if they are to provide reasonable assurance that contamination is adequately characterized. Because a strictly random sampling approach is likely to be inefficient and expensive, maximizing knowledge of site history through the use of plant records, aerial photographs, and personnel interviews is necessary to effectively focus a sampling program. The longer the delay between closure of the contamination source (e.g., industrial plant operation) and the site assessment, the greater will be the challenge in locating records about the problem activities. These more difficult circumstances are commonly encountered at orphaned sites (i.e., those for which responsibility cannot be assigned).

Capabilities of remediation technologies

When contaminated sites have been uncovered in an ad hoc fashion, their discovery often results in considerable public pressure for immediate action. The most common technological response during the early remedial actions under the U.S. Superfund was to excavate and remove contaminated soil and buried wastes to another location. When Superfund was reauthorized in 1986 (Superfund Amendments and Reauthorization Act, SARA), it was not surprising that the U.S. EPA was required (Sect. 121) to select remedial actions involving some form of treatment that "permanently and significantly reduces the volume, toxicity, or mobility of hazardous substances, pollutants, and contaminants. . ." While the logic of these instructions is obvious, the capability of remediation technologies to fully meet these performance expectations is often more limited than may be commonly realized.

Although an expanding array of potential remediation technologies is being developed and demonstrated, they can be broadly classified into three categories: (*i*) containment or immobilization, (*ii*) mobilization, or (*iii*) destruction.

In each case, these options may be performed in situ or following removal of contaminated media (soil or water) from the original site. Because the costs and risks associated with excavation are often unreasonable, in situ processes are generally preferable. However, in situ processes are also faced with the greatest challenges arising from practical site constraints. The U.S. EPA has undertaken the Superfund Innovative Technology Evaluation Program (SITE) to encourage the development of new remediation technologies that may be able to meet the obligations specified under SARA (U.S. EPA 1990*a*).

In considering remediation technologies, it is essential to recognize that a single technology will rarely accomplish all remediation goals for all contaminants at a remediation site. Generally, if there is any mix of contaminants and (or) complexity to the distribution of contaminants, a sequence of processes that will work together to accomplish the remediation goals will be needed. This combination of processes is often described as a treatment process train (Sims 1990). Finally, site-specific treatability studies must be regarded as essential to the development of viable remediation process alternatives (Dupont 1991; Sims et al. 1987).

Containment/immobilization

Containment or immobilization technologies performed in situ might include isolation by capping and (or) low-permeability cutoff walls, solidification/stabilization (cement-, pozzolanic-, or polymer-based), or vitrification. Containment or immobilization following excavation could involve landfill or some other form of long-term storage, with or without solidification/stabilization. Generally, solidification/stabilization options are the only choice for inorganic wastes unless they can be economically recovered and reused. But even inorganic

wastes of relatively simple composition (e.g., some electroplating wastes) will require treatability studies because they may contain organic components capable of retarding the cement setting process or the toxic metals may be inadequately immobilized by the high pH of cement hydration.

Mobilization

Mobilization options are primarily directed to in situ processes and they include pump and treat for groundwater, soil vapour extraction, soil heating, and soil washing. Pump and treat will only be effective for relatively soluble contaminants present in reasonably permeable formations. Furthermore, the mass of contaminant present as a NAPL or as residual saturation must be insignificant for pump and treat to be viable. In some cases, separate removal of the NAPL may facilitate the viability of pump and treat options. Soil vapour extraction can be very useful for relatively volatile contaminants, particularly if they also have relatively low water solubility. For example, vapour extraction is very effective for the removal of gasoline contamination. Soil heating may be useful as an adjunct to soil vapor extraction. Soil washing uses surfactants to mobilize contaminants that are poorly water soluble and this may be useful in combination with pump and treat approaches or as an adjunct to bioremediation.

Neither containment nor immobilization options, by themselves, accomplish any elimination of the hazardous contaminants. As such, their utility towards the goal of a net overall reduction in environmental risk requires close scrutiny. Simply isolating, concentrating, or relocating contaminants may provide short-term relief from a hazardous exposure scenario, but the long-term and overall environmental risk may be altered little for the level of investment involved.

Destruction: incinèration and bioremediation

Only destruction options provide for true elimination of the hazardous materials. They consist of thermal options, like incineration, and microbial treatment in the various forms of bioremediation. Unfortunately, destruction options can only be achieved with organic contaminants. Although inorganic contaminants can be altered in their chemical combination, if the hazard is associated with an element (e.g., toxic metals) the basic hazard cannot be destroyed.

Incineration is only viable option following soil excavation because the high temperatures, turbulence, and excess oxygen required for high destruction efficiencies can only be efficiently achieved by feeding contaminated soil into a combustion chamber. Even so, the economics of incineration are adversely affected by the mass transfer problems involved in handling and heating very large volumes of predominantly inorganic soil containing, at most, a few per cent of organic matter.

Given the foregoing limitations, it is not surprising that among all remediation technologies, bioremediation receives the most optimistic forecasts. Bioremediation uses the metabolic activities of microorganisms to destroy hazardous contaminants. This basic concept has been operative since long before any human contamination arose because microorganisms have always been decomposers within ecosystems. More recently, biological waste treatment of human sewage has been subjected to some engineering control since the invention of activated sludge in the late 1800s. A natural extension of these early engineered biological systems has been the land application of sewage sludge, followed by the use of land treatment systems for other organic sludges, such as petroleum refining wastes. Although land farming has earned a mixed reputation because of many poorly operated systems, land treatment of organic sludges in a controlled setting can be very effective in achieving a true destruction of organic wastes.

While the potential for bioremediation processes to achieve destruction of organic contaminants is substantial, the limitations to this process need to be recognized, particularly with the explosion of biotechnology vendors trying to capitalize upon the lucrative market for cost-effective site remediation technologies and the growing recognition of limitations for most other processes.

The minimum conditions for a bioremediation process to function effectively are (*i*) a substrate amenable to biological degradation; (*ii*) an appropriate and active microbial community; (*iii*) bioavailability of the contaminants to the microbial community; (*iv*) minimization of waste-specific constraints; (*v*) appropriate values for critical environmental conditions.

Substrate amenable to biological degradation

The intrinsic resistance of any contaminant to microbial attack is a critical factor in determining the feasibility of bioremediation options. Before any bioremediation process can function, there must be microorganisms that are capable of biologically degrading the organic contaminants concerned. At this stage, the distinction between biotransformation and mineralization should be understood. Biodegradation is often assumed to be synonymous with mineralization, which is the complete conversion of an organic substrate to mineral end products such as carbon dioxide, inorganic ions, and water. Only the most favourable systems will achieve complete mineralization of an organic substrate and then only for a portion of the organic matter. Some fraction of the substrate organic carbon must also be directed into the synthesis of new cells to support microbial population growth.

For many organic compounds, the parent compound is biotransformed into other organic compounds, some of which may be recalcitrant to further degradation. These may be left as metabolic by-products. In all cases, biotransformation through a variety of intermediate compounds will occur. If these intermediates require the participation of other microorganisms for further degradation, there may be a temporary or long-term buildup of intermediate compounds because of nonoptimal interactions within a microbial community.

The process of biotransformation is not always beneficial, even if the parent contaminant is destroyed, because the conversion products may represent a greater health hazard than the parent compound. For example, the common solvent, 1,1,1-trichloroethane, can be converted to vinyl chloride by a combination of abiotic and microbial conversion steps (Vogel et al. 1987). The parent compound has shown insufficient evidence to warrant classification as a carcinogen. However, the biotransformation product, vinyl chloride, is classified as a human carcinogen.

For the case of the polycyclic aromatic hydrocarbons (PAHs) commonly found in heavy oil and creosote wastes, the two-ring (naphthalenes) and three-ring (anthracene, phenanthrene, and acenaphthene) compounds are generally biotransformed, but the four- and five-ring PAHs, which include carcinogenic compounds like benz[*a*]anthracene, and benzo[*a*]pyrene, apparently have to depend upon cometabolism for biotransformation (Mueller et al. 1989). Cometabolism is a process whereby contaminants are fortuitously transformed by enzymes produced by the microorganisms for degrading other substrates. However, cometabolism fails to provide any metabolic

energy to the degrading microorganism and, therefore, cannot provide a source of subsistence.

Appropriate microbial activity

The possibility that a contaminant can be biotransformed by a microorganism under ideal, controlled, laboratory conditions does not guarantee that such microbial activity can or will occur in a bioremediation process at a contaminated site. Generally, soil will contain a diverse range of microorganisms with a wide range of biotransformation potential. Realization of the potential is usually the challenge. A microbial consortium that has been adapted to the target contaminant(s) will reduce lag times that may be necessary for the microbes to produce the degrading enzymes.

The concept of genetically engineering organisms to develop a microbial capability for degrading contaminants that appear to be inherently recalcitrant has been widely promoted. While the concept is intriguing, there are still some important practical realities that must be overcome in addition to the regulatory restrictions that will govern the introduction of genetically modified organisms into the soil environment. In particular, contaminants are usually trace components present amidst a dominant organic matrix. Microorganisms uniquely adapted to degrade a specific trace contaminant may not be able to survive the hostile conditions of the waste environment or the overwhelming competition from other organisms growing on the bulk organic matrix.

Bioavailability

Even if contaminants are intrinsically biodegradable, they are often present within the soil environment in a state that precludes their effective biotransformation. For example, contaminants that are present within pockets of bulk organic phase (NAPLs or pockets of residual saturation) may be inaccessible to microorganisms because they are fundamentally aquatic organisms. In such cases, only substances accessible at the water/organic interface will be available for biotransformation. Consequently, mass transfer limitations will severely restrict the overall level of biotransformation that is possible. Because many contaminants have low water solubility, they will favour partitioning to an organic phase and become generally inaccessible to the microorganisms.

Partitioning of organic contaminants into the soil's natural organic matter will also happen with many organic contaminants. This fate will not make the contaminants as inaccessible as when they partition into the nonmiscible organic waste phase because most soil organic matter (SOM) is water miscible and provides better access for the degrading microorganisms.

Waste-specific constraints

Wastes that have been chronically exposed to soil over decades present many difficulties for biological treatment. Weathering processes such as evaporation, photolytic loss, hydrolysis, and biotransformation selectively reduce the concentration of easily degradable substrates leaving behind refractory residues that resist further microbial attack (Bossert and Bartha 1984). Many of the residual compounds are nonvolatile or semi-volatile and they partition preferentially to the residual oil phase and to SOM. The bioavailability of these constituents is severely restricted.

A microbial population exposed to a particular waste may exhibit a treatability concentration range above which the waste inhibits metabolic activity and below which microbiota may switch to alternative substrates. In the latter case, further transformations of the contaminant may require cometabolism. Biotransformation products may themselves inhibit further microbial degradation of contaminants (Hosler et al. 1991).

Other waste characteristics such as high salinity levels can disrupt the tertiary protein structure, denature enzymes, and dehydrate cells (Atlas and Bartha 1987). At salt-damaged sites, remediation is often restricted by structural deterioration of the soil. Likewise, a number of metals may be found in various organic wastes and metal concentrations in local microenvironments may inhibit microbial metabolism.

Appropriate environmental conditions

A variety of other environmental conditions must be favourable for microorganisms to biotransform organic contaminants. These include soil temperature, redox potential and the availability of a suitable electron acceptor such as oxygen, pH, nutrients, and moisture.

Each microorganism possesses a temperature range over which it can remain active. Furthermore, widely fluctuating seasonal and diurnal temperatures are generally unfavourable to the maintenance of a stable, active, degrading microbial population. Temperature also affects the viscosity and aqueous solubility of organic substrates.

Redox potential and the availability of oxygen are critical to the natural selection of operative microbial populations. Generally, the most complete and rapid biotransformations are achieved by aerobic microorganisms. These require the availability of oxygen. For some compounds, anaerobic organisms offer attractive capabilities such as the removal of halogens, like chlorine from chlorophenols, under reducing conditions (Hrudey et al. 1987).

Normally, soil pH will be in a range that soil microorganisms can tolerate. However, strongly acidic or alkaline wastes may yield pH extremes that will prove inhibitory to degrading microorganisms. An adequate supply of nutrients is fundamental to the capacity of a microbial population to grow. Generally, a balanced soil environment will not be nutrient deficient, but a nutrient-deficient organic waste that dominates the soil phase may create localized conditions of nutrient limitation.

Soil moisture is critical to effective biological activity. Sufficient moisture must be present to allow transport of contaminants and degrading enzymes between the microbial population and the waste matrix. However, saturated moisture conditions will restrict the availability of oxygen because of the low solubility of oxygen in water. Consequently, saturated soil conditions will become anaerobic once aerobic biological activity consumes the available dissolved oxygen.

Soil texture is significant to bioremediation because of its overriding control of the water regime, aeration status, soil temperature, and workability. Although the soil surface provides a location for microbial attachment that can facilitate contaminant degradation, finer grained soils with very high surface areas also exhibit low hydraulic conductivity and may experience problems from the limited access and availability of oxygen and nutrients.

Cleanup criteria and objectives

Perhaps the area of greatest controversy for contaminated site remediation is deciding what constitutes contamination worthy of action. Even if a decision can be made that there is contamination warranting remedial action, a decision must also be made concerning what degree of cleanup will be judged as satisfactory.

U.S. Superfund approach

The U.S. Superfund, despite being the most expensive, ambitious, and first national remediation program for contaminated sites, has not supported the development of generic remediation criteria. Rather, Superfund has relied upon existing regulations and guidelines concerning environmental quality. These criteria must be evaluated by the designated site assessor to determine if they are both relevant and appropriate to the circumstances of the site in question. If a particular contamination criterion is judged to be relevant and appropriate, it may be formally adopted as an "Applicable Relevant and Appropriate Requirement" (ARAR), which then becomes a cleanup requirement for that contaminant at the specific site (WPCF 1990).

In place of a common set of contaminant criteria under Superfund, a detailed procedures manual for performing site-specific risk assessments at Superfund sites has been provided (U.S. EPA 1989*c*).This manual sets out a framework for the data acquisition and evaluation process. Combined with a growing inventory of published records of decision (RODs), where site-specific remediation plans have been formally adopted, this site-specific approach might have been expected to evolve into a pattern of consistent remediation decisions. However, a recent critique of cleanup standards evolving from Superfund decisions showed that remediation requirements for specified contaminants have been inconsistent with levels varying up to 100-fold among different remediation decisions (Booth and Jacobson 1992).

Canadian approach

The National Contaminated Sites Remediation Program in Canada has developed a different approach to the cleanup criteria dilemma (CCME 1991*b*). The CCME approach recognizes two types of criteria. Assessment criteria are intended to represent either approximate background levels or analytical detection limits for specific contaminants. If a particular site is under assessment, samples of environmental media that exhibit concentrations below assessment criteria levels are judged to be uncontaminated and no further action would be justified for that contaminant in that medium. Remediation criteria represent higher contaminant concentrations that may still be generally acceptable for specified land uses. These criteria are offered as the initial basis for developing site-specific remediation requirements. Alternatively, a site-specific risk assessment could be performed to develop the site-specific remediation requirements.

The Canadian approach provides the advantage of specifying a consistent starting point for the site assessment process. The guidelines (CCME 1991*b*) provide some direction concerning what constitutes contamination along with a set of remediation criteria that may be referred to in developing a site-specific remediation approach. These provisions provide greater consistency and less duplication of effort than the Superfund ARARs and obligatory site-specific risk assessment approach.

However, with any of these approaches, many problems and challenges remain. The logical problems with setting criteria based upon analytical detection limits have been outlined. The CCME approach only applies this questionable rationale to their assessment criteria (i.e., criteria to distinguish pristine conditions from potential contamination). Consequently, this approach should not lead to unjustifiable remediation actions, which might arise if it was used for remediation criteria.

TABLE 4. Examples of distinctions made for chemical form in contamination (CCME 1991*b*)

Parameter	Distinctions
Boron	Hot water soluble
	Total
Chromium	Hexavalent
	Total
Cyanide	Free
	Total
Fluoride	Free
	Total
Sulphur	Elemental
Phenolics	Nonchlorinated
	Chlorinated

Unfortunately, there is always a danger that some jurisdictions may arbitrarily adopt the assessment criteria as their remediation criteria because they fail to understand the absence of any risk context inherent in the detection limit approach.

For those cases where assessment criteria are based upon "background" levels, there is the difficulty posed by a lack of data for many organic contaminants and variability in natural contaminant levels, particularly metals. CCME has recognized this limitation and has initiated a program to develop a data base of background concentrations to provide a better basis for setting the assessment criteria (CCME 1991*b*).

Common problems with contamination criteria

All systems for developing criteria face the problems associated with the complexity of waste composition. While criteria can be set for individual contaminants, the occurrence of a large array of related contaminants must usually be acknowledged. In unique cases, where substantial research and evaluation has been done, it may be possible to combine a number of related contaminants into a single criterion using some equivalency approach. For example, many of the polychlorinated dibenzodioxins and dibenzofurans have been assessed for their toxicity relative to 2,3,7,8-tetrachlorodibenzodioxin and toxicity equivalency factors have been estimated (NATO 1988). These weighting factors are used to calculate a single, composite concentration value to represent a mixture of these individual compounds. Unfortunately, the basic knowledge on relative toxicity is not available for most other contaminants. For other groups of compounds (e.g., chlorinated phenols), single criteria have been specified that apply to all individual compounds belonging to the group, despite the expectation that each compound has differing environmental partitioning behaviour and differing health risks.

For many elements, the criteria may specify the total quantity of a contaminant, rather than a specific chemical form, despite the substantial differences in environmental fate, behaviour, and toxicity that may exist between the many possible forms of an element (e.g., Table 3). A few notable exceptions, where some attempt has been made to distinguish the form of the contaminant, are listed in Table 4.

A related concern is the concept of bioavailability. Our discussion on bioremediation noted that a contaminant may be present in a physical form that may prevent microorganisms from being able to access and degrade the contaminant. Likewise, a contaminant that is tightly bound or inaccessible within soil particles may not pose a substantive health risk because the contaminant cannot be extracted and taken up by individ-

uals exposed to the contaminated soil (Davis et al. 1992). Generic site contamination criteria cannot easily accommodate this type of very specific limitation on effective risk.

In some provincial criteria (e.g., MOE 1989; MENVIQ 1988), values for surrogate parameters like "oil and grease" have been specified. There is merit in this approach if the application is consistent with what is measured by the parameter. For example, a determination that 1% oil and grease constitutes a nuisance worthy of remedy, regardless of the specific composition of the observed oil and grease, may provide a valid nuisance criterion. However, if this criterion is incorrectly interpreted as dealing with any specific hydrocarbon for which a more specific criterion should apply, then the surrogate would be misleading. Likewise, the surrogate may be misused by assuming that there is a reliable relationship between the total concentration of oil and grease and the concentration of a specific contaminant dissolved in that oil and grease.

Risk assessment

Any program that seeks to make cleanup decisions on the basis of reducing overall environmental risk must be able to estimate what health risks may be posed by a site. Underlying any assessment of health risk from contaminated sites is the basic premise that there must be some route by which humans are exposed to the contaminants present. This same concept must be applied on a broader scale to assess the risks to other valued organisms in the environment when assessing the ecological risk component of environmental risk.

A risk assessment approach for evaluating a contaminated site will involve (*i*) source assessment, (*ii*) exposure assessment, (*iii*) toxicological assessment, and (*iv*) risk characterization.

The source assessment characterizes the nature and extent of contamination. The exposure assessment evaluates the contaminant migration pathways yielding routes of exposure, defines target individuals (receptors) that could receive contaminants via the defined exposure routes, and assesses the doses of each contaminant that each receptor could receive. The toxicological assessment considers the various toxic effects produced by each contaminant and estimates the likely health effects that would be produced for the dosage levels estimated. Finally, the risk characterization quantitatively evaluates the risk posed by the specified exposure scenarios. This process should also explicitly consider the uncertainty of each component of the calculation as well as the cumulative uncertainty associated with the overall risk estimate.

There is enormous scope for becoming overwhelmed with detail at any stage of the risk assessment process. Simplifying assumptions must be made at every stage of the process in order to continue. What seems less commonly recognized in risk assessment practice is the danger of becoming narrowly focused on the details of developing a numerical estimate of risk. A zealous preoccupation with generating numbers, often apparent in direct proportion to the number of significant figures used to express calculated risks, can miss the objective of risk assessment. Contaminant exposures must be subject to some verification and they must be placed in context with other exposures and environmental risks. Only when some realistic context for the risk is established can effective overall risk management decisions be made.

Management of site remediation programs

The best available scientific inputs will only contribute to the objective of reducing overall environmental risk if there are effective management approaches in place to make use of the available knowledge. The interface between detailed scientific knowledge and practical management decisions can be a major source of difficulty.

Interdisciplinary communication problems

Contaminated site remediation is a fundamentally interdisciplinary undertaking that typically involves chemists, microbiologists, soil scientists, hydrogeologists, toxicologists, and engineers. This mix creates both problems and opportunities. Serious problems often arise because of poor communication among disciplines, particularly between the field and the laboratory personnel. Field investigators often do not understand the limitations of the available analytical procedures and the data that they yield. In particular, because many analytical methods have not been explicitly evaluated for contaminated soil samples, their applicability to characterizing soil contamination may be inappropriate. Likewise, laboratory personnel, if not consulted in planning a field program, may not appreciate the overall objectives of the site characterization, the intended use of the analytical results, and the challenges facing field staff in trying to comprehensively and accurately characterize the extent of site contamination. These considerations are easily lost in the practical commercial realities of environmental consultants and analytical laboratories having to submit time-limited, cost-competitive proposals to win site assessment contracts.

In the absence of close consultation, the analytical methods selected may be arbitrary and ineffective. Likewise, difficulties encountered in performing analyses that may add uncertainty to the data will not be understood by those charged with making the ultimate interpretation. Only if there is effective and ongoing consultation between field and lab personnel can the most appropriate sampling and analytical strategies be developed and implemented.

Acknowledging uncertainty

Results from risk assessments often fail to acknowledge the enormous uncertainty associated with the risk estimates. If the data are also presented in a manner that implies confidence that is not warranted, there will be considerable scope for misinterpretation. Ultimately, any site characterization program must be communicated to a decision-maker who will be responsible for approving the site remediation expenditures. These individuals will be subjected to pressures from the affected public. If they are to make decisions serving the interests of that public and the rest of society, the decision-maker needs to appreciate the full dimensions of the risks, including the sources of uncertainty that are imbedded in the site characterization and the risk assessment process. Furthermore, decision-makers need to understand the practical limitations of the remediation options to be able to assess the incremental risk reduction benefits associated with each option.

Policy issues

Contaminated site issues have often involved cases of innocent parties being exposed to contamination placed by others who were strictly in pursuit of profit. In these cases, decisions have often been made to resolve uncertainties about potential health risk by taking all available measures to eliminate exposure, in an abundance of caution. In many cases, the only action available to achieve this cautious objective has been to excavate and remove the contamination to another location. Such actions may be counter to the objective of reducing over-

all environmental risk. If decisions are made to apply some remediation technology to treat the contamination, then some level of residual contamination will be inevitable because no remediation technology will be 100% efficient. Most technologies will be far less effective. Treatment decisions inevitably acknowledge, explicitly or implicitly, that some level of residual contamination is acceptable. Even with the conservative "excavate and remove" approach, some cutoff has to be accepted to define where the contamination is low enough to justify leaving the soil in place. Eventually, criteria defining acceptable concentrations for soil contaminants will be used either explicitly or implicitly.

On the other side, the scientific community must recognize that any contaminated site criteria must inevitably represent a pragmatic attempt to reconcile theory with reality. Cleanup criteria must reconcile the ideals and details proposed by a rigorous scientific approach with the hard realities imposed by the demand for practical management decisions about extremely complex situations.

Many of the problems posed by contaminated site remediation relate to the level of detail that can be pursued and the complexity that arises from all of the detail that can be characterized. The potential complexity can be disconcerting, yet there may be a loose analogy with some advancing frontiers of scientific knowledge. As physicists have developed the tools to look more closely at the nature of matter, they find that particles we previously believed to be indivisible are themselves made of smaller distinct particles. Pursuing this increasing level of detail may provide new insights into subatomic interactions and the fundamental relationship of matter and energy. Yet we also find that the rules of physical chemistry, which are based upon a simpler view of atomic structure, have not been fundamentally undermined by the newer discoveries. By analogy, the broad principles governing the fate and behaviour of contaminants, combined with an appreciation of the realistic levels of contaminant dosage necessary to produce significant harmful effects, should not be overlooked while pursuing an unproductive search for individual molecules of specfic contaminants (i.e., the search for zero contamination). The fundamental goal of achieving an overall reduction in environmental risk cannot be achieved unless individual remediation decisions make sense according to the basic principles governing contaminant behaviour and health risk.

Constructive advances

There are many challenges facing the implementation of a rational approach to contaminated site remediation. A comprehensive and unbiased appreciation of the scope and dimensions of these challenges can serve as a basis for developing better methods. In contrast, placing unwarranted faith in the accuracy or precision of site characterization data, risk estimates, or predictions of remediation technology performance will almost certainly lead to inappropriate site remediation decisions.

Fortunately, in addition to maintaining a healthy level of skepticism, there are a number of constructive avenues being developed that will provide better foundations for remediation decisions.

Statistical sampling methods and tiered protocols

Sampling a contaminated site should be treated no differently than any other generic sampling problem, regardless of the degree of complexity that may be involved. The nature of the sampling task must be clearly understood. Site contamination, as noted earlier (Fig. 5), is rarely homogeneous. Hence, a sampling strategy based strictly on random sampling would require an enormous number of samples to adequately characterize the localized contamination ("hot spots"). Because evaluations of hot spots and general site contamination are both required to make the ultimate risk management decisions for a site, the sampling strategy must address both objectives. Stratified random sampling combined with systematic sampling approaches has been recommended to deal with these needs (BSI 1988; Castanho 1987; Gilbert 1987; and Lord 1987). These sources propose various protocols for estimating the minimum number of samples that will be required to characterize the general level of site contamination.

Regardless of the sophistication used in planning a sampling program, the result must still satisfy the basic requirement of providing samples that accurately represent the nature of contamination at the site. The value of maximizing knowledge of previous site activities most likely to have been responsible for the site contamination cannot be overstated.

In addition to the need for a planned approach to sampling, there is also considerable value to a tiered approach to the analysis of samples. Because many samples from a heterogeneous site will show limited or negligible signs of contamination, subjecting all samples to a full analytical protocol will be wasteful. Rather, general screening methods may be appropriate at the first level of analysis, followed by more detailed analyses directed at those samples showing the highest levels of contamination. These tiered protocols require close consultation between field and laboratory personnel.

Integrated toxicity testing

The complexity that is commonly encountered at contaminated sites can present considerable difficulty for applications in risk assessment and planning of remedial actions. Because many contaminants that may be identified will have little or no toxicity information and what information can be found will not deal with the synergistic, antagonistic, or matrix effects, there is a need for toxicity assessment methods that can account for these problems. Toxicity reduction, identification, and evaluation programs (TRE/TIE) have been developed (Burkhard and Ankley 1989). These programs use the expanding complement of bioassay protocols for assessing some form of toxic response, in combination with analytical separations to determine those fractions of a complex waste that contribute the most toxicity. These approaches have been used to direct chemical analyses for determining toxic components in contaminated sediments (Samoiloff et al. 1983; West et al. 1988; Fernandez et al. 1992).

Multimedia contaminant partitioning models

There has been considerable effort devoted to the modeling of contaminant behaviour. These efforts have generally been useful in furthering our understanding the fate and behaviour of contaminants, but in many cases the sophistication of models has exceeded the capability to characterize the complexity of the site or the waste. The most useful advances from the viewpoint of understanding general contaminant behaviour are the fugacity modeling approaches that have sought to simplify predictions of intermedia transfers of contaminants (Mackay 1991). These models provide easily accessible and readily understandable predictions of the major partitioning behaviour of contaminants, based upon their fundamental physical and chemical properties.

A series of handbooks has recently been developed that provide predictions of the fate of a variety of common contaminants within a series of simplified environments (Mackay et al. 1992*a*,*b*). Likewise, the U.S. EPA Robert S. Kerr Environmental Research Lab has provided a summary of the relevant properties of several contaminants commonly encountered at Superfund sites (U.S. EPA 1990*b*). Tables are provided that rate the likely presence of the contaminant in the major subsurface phases and rate the applicability of common remediation technologies for these contaminants. These generic insights concerning the behaviour of contaminants can be extremely valuable for designing sampling and analytical programs and interpreting the results. They provide an important counterfoil to the overwhelming detail that may cause information overload and ultimately lead decision-makers to make ill-founded decisions.

Uncertainty analyses

The heterogeneous character of contaminated sites combined with the many other sources of complexity that we have outlined makes uncertainty an inevitable component of the risk management decisions. An essential prerequisite to dealing with the enormous uncertainties involved in these activities is to acknowledge that they exist. While this may seem obvious, contaminated-site remediation programs have chronically suffered from gross overconfidence in the accuracy and precision of environmental measurements and risk estimates.

The minimum recognition of uncertainty that must accompany data in site remediation decisions is some estimate of the variability of the data reported. This demands that sampling and analytical replication be fundamental to the site characterization program. For the case of risk assessment, there must be some acknowledgment of the variability of input parameters and a realistic expression of risk estimates. In particular, there could rarely be justification for reporting more than one significant figure on any final risk estimate and there should be confidence interval estimates accompanying all risk estimates.

Recently, a powerful tool for dealing with these uncertainty issues has become available in the form of personal computer versions of Monte Carlo simulation software. These programs can be integrated with spreadsheets that can be used for the risk assessment models. The simulation capability allows evaluation of distributions for individual parameters rather than the single value estimates commonly used. This approach was recently demonstrated for evaluating the uncertainties involved in the risk assessment of groundwater contamination with perchloroethylene, PCE (McKone and Bogen 1991). The analysis demonstrated the dramatic difference between using the 95% upper bound of the probability distribution for lifetime cancer risk derived from a Monte Carlo simulation and calculating the risk using single values, often the 95% upper bound estimate for each input parameter. The latter approach, which might previously have been used to err on the side of caution, produced a lifetime cancer risk estimate of 1×10^{-3} compared with a value of 4×10^{-6} using the Monte Carlo approach. Furthermore, approximately 65% of the variance in the overall risk calculation was attributable to variance in the estimates of cancer-causing potency for PCE, while only 20% was attributable to variance in PCE concentrations and only 10% to variance in components of the exposure model. Considering these findings, the dominant source of the risk estimate uncertainty, which was itself considerable, was attributable to toxicological data. These latter data lie beyond the scope that a site remediation team could resolve. Therefore, the level of uncertainty reduction that can be achieved by placing more resources into site characterization and assessment would be limited.

Conclusions

This overview of some major issues involved in contaminated site remediation leads to several conclusions concerning our ability to achieve an overall reduction of environmental risk through contaminated site remediation.

1. The complexity involved in several aspects of contaminated sites can be overwhelming. The major sources of complexity include the heterogeneity of site conditions both in terms of contamination sources and subsurface characteristics affecting contaminant migration, the complexity of the waste source composition, and the array of variables involved in assessing the risks posed by the site contamination.

2. The open-ended nature of problems that may be encountered in assessing a contaminated site demands that tiered approaches to sampling and analysis be used in an iterative manner. The knowledge gained at each stage must be carefully evaluated to direct subsequent steps in the process.

3. The range of problems encountered demands that meaningful interdisciplinary collaboration be implemented from the earliest stages of investigation and assessment. In particular, close collaboration between the field and laboratory personnel is essential to avoid many of the interpretive errors and oversights that commonly arise.

4. Remedial technologies that are currently available and applicable to most common contamination conditions are substantially limited in their capabilities. Both capabilities and limitations need to be independently, rigorously, and critically evaluated for a range of full-scale applications to provide a firm basis for selection of remediation technology.

5. The absence of rigorous scientific bases for many of the available environmental quality criteria is likely to remain a fundamental impediment to effective site remediation for some time. Ongoing efforts to collect more knowledge about background soil contaminant levels will help with assessment criteria. However, developing more meaningful remediation criteria will require the application of consistent and reasonable approaches for site-specific risk assessments, combined with ongoing review of the types of site-specific decisions that have been made.

6. All aspects of contaminated site remediation must clearly acknowledge and report the source and extent of uncertainty involved in all parameters used. In particular, there must be explicit consideration of factors contributing to the uncertainty in risk estimates. Ultimately, decisions need to reflect a reasoned understanding of the balance of probabilities involved.

7. Finally, looking to the future, even a cursory evaluation of the issues involved in contaminated site remediation makes a compelling case that prevention is vastly superior to remediation. If that message can be understood and reflected in the future behaviour of all parties capable of contaminating land, then society will have obtained some enduring value from the massive investments that have been made in dealing with our past mistakes.

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Screening of risk management options for abandoned wood-preserving plant sites in Alberta, Canada

SIMON J.T. POLLARD[1]
Environmental Health Program, Faculty of Medicine, University of Alberta, Edmonton, AB T6G 2G3, Canada
ROBERT E. HOFFMANN
Alberta Environment Help End Landfill Pollution Project, Room 1443, Standard Life Centre, 10405 Jasper Avenue, Edmonton, AB T5J 3N4, Canada
AND
STEVE E. HRUDEY[2]
Environmental Health Program, Faculty of Medicine, University of Alberta, Edmonton, AB T6G 2G3, Canada

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Several abandoned wood-preserving sites have been identified in Alberta, Canada, which pose a potential threat to human health and the environment. The physiochemical, environmental, and toxicological properties of wood preservatives are discussed together with the predominant human exposure pathways for these chemicals in the environment. A Level II soil fugacity model is used to illustrate the comparative environmental fate of individual organic wood treatment chemicals following release to the soil environment. An evaluation of risk management options at five priority sites is used to illustrate problems associated with the treatment and disposal of mixed organic and inorganic contaminated soils, soil property limitations, and the predominance of organic contaminants within the residual oil phase. The latter reality dominates options for exposure reduction and risk management.

Key words: contaminated soils, wood-preserving sites, remediation options, screening, fugacity model.

Plusieurs sites abandonnés d'imprégnation du bois présentant un risque pour la santé humaine et l'environnement ont été répertoriés en Alberta, au Canada. Les propriétés physiochimiques, environnementales et toxicologiques des produits de préservation du bois sont discutées dans cet article ainsi que les pistes prédominantes d'exposition des êtres humains à ces produits chimiques dans l'environnement. Un modèle de fugacité des sols de niveau II est utilisé pour illustrer le sort qui est réservé aux produits chimiques de traitement organique du bois lorsque ceux-ci s'infiltrent dans le sol. Une évaluation des options de gestion des risques à cinq sites de priorité est utilisée pour discuter des problèmes associés au traitement et à l'élimination des mélanges de sol organique-inorganique contaminé, des limites des propriétés du sol ainsi que de la prédominance des contaminants organiques à l'intérieur de la phase de résidus du raffinage. Cette prédominance se reflète dans les options proposées pour réduire l'exposition et contrôler le risque.

Mots clés : sols contaminés, sites d'imprégnation du bois, mesures correctives, criblage, modèle de fugacité.
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Introduction

Chemical wood preservation seeks to protect timber from insects, bacteria, and fungi that consume wood fibre as substrate and plays an important role in the conservation of worldwide timber resources. Wood preservatives poison the wood food source for these organisms and increase the useful lifetime of treated timber by five to ten times. The three principal wood-preserving mixtures employed have been based on coal-tar creosote, pentachlorophenol (PCP), and chromated copper arsenate (CCA) (Environment Canada 1988*a*, 1988*b*, 1988*c*). Lesser used alternative treatments include ammoniacal copper arsenate (ACA), acid copper chromate (ACC), zinc sulphate, and zinc stearate. The treatment mixtures consist of an active agent and a carrier, combined as a wood treating solution. The carrier (water, diesel, or fuel oil) provides appropriate dilution of the agent and facilitates wood cell penetration.

Misuse, accidental spillage, and improper disposal of wood treating solutions have resulted in extensive soil and groundwater contamination at many treatment facilities (U.S. Geological Survey 1984; Mueller et al. 1989; NETAC 1990; McGinnis et al. 1991). Facilities where all three major treatment solutions have been used are common, reflecting the changing technology of wood treatment. Presence of mixed contamination severely complicates the choice of site remediation options available for contaminated sites because the mixed organic and inorganic wastes encountered are not easily treated using technologies conventionally reserved for the separate treatment of organic and inorganic waste streams.

In Alberta, several abandoned wood-preserving facilities have been identified as potentially posing a risk to human health and the environment (Ceroici and Hingston 1992). Contaminated sites such as these have raised increasing concern across Canada (CCME 1991*a*, 1991*b*) because the contaminants commonly identified include the polynuclear aromatic hydrocarbons (PAHs), benzene, toluene, ethylbenzene and xylene (BTEX), PCP, lower chlorophenols and associated polychlorinated dioxins and furans (PCDDs, PCDFs), arsenic (all chemical forms), and hexavalent chromium (Fig. 1; Table 1). Effective risk management strategies

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[1]Present address: Department of Chemistry, University of Edinburgh, Edinburgh, Scotland EH9 3JJ.

[2]Corresponding author.

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TABLE 1. Composition of inorganic chromated copper arsenate wood-preserving solutions (Environment Canada 1988*c*)

Component	Composition in 50% CCA concentrate (% w/w)	Composition in 2% CCA treating solution (% w/w)
H_2O (carrier)	50.0	98.0
CrO_3	23.7	1.0
CuO	9.3	0.4
As_2O_5	17.0	0.7

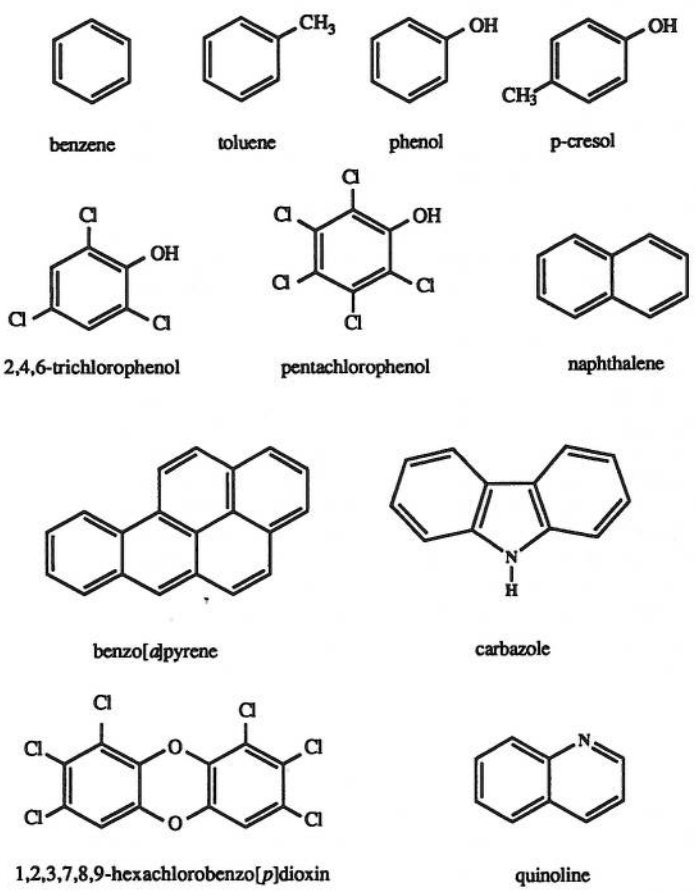


FIG. 1. Chemical structures of selected organic wood-preserving chemicals.

for these sites require the assessment and management of exposures on an individual site basis.

Properties of wood-preserving chemicals

Creosote-based wood-preserving mixtures contain coal-tar creosote dissolved in a petroleum carrier. Creosote, a secondary distillation product of gasified coal, is comprised of homocyclic (parent) PAHs, heterocyclic polyaromatics, and phenolic compounds (Mueller et al. 1989). Many of these are amenable to biotransformation in both aerobic and anaerobic environments (Arvin et al. 1989), although the high molecular weight (HMW) PAHs are generally recognized as refractory in nature and they will be transformed only under co-oxidative conditions (Perry 1979). In the environment, as opposed to under controlled laboratory conditions, complete mineralization is rarely achieved and so attention must always be directed to the fate and toxicity of biotransformation products arising from microbial processes occurring in the soil column (Atlas and Bartha 1987).

Certain HMW homocyclic PAHs and heterocyclic compounds present in coal-tar creosote are suspected human carcinogens. Benzo[*a*]pyrene, benz[*a*]anthracene, benzo[*b*]-fluoranthene, benzo[*j*]fluoranthene, benzo[*k*]fluoranthene, dibenz[*a,h*]anthracene, and indeno[1,2,3-*cd*]pyrene are classified as probable human carcinogens by the U.S. Environmental Protection Agency (U.S. EPA 1984). The composite toxicity of creosote mixtures has not been thoroughly assessed, although limited evidence from prolonged occupational exposure to coal-tar products suggests that creosote is likely to cause cancer in humans (Bos et al. 1984; ATSDR 1990*a*; Karlehagen et al. 1992). Creosote has also been associated with a number of adverse non-carcinogenic toxic effects such as embryo toxicity, feto toxicity, and dermatitis (ATSDR 1990*b*).

PCP-based wood preservatives are comprised of technical-grade PCP dissolved in a petroleum carrier, usually a fuel oil. Technical-grade PCP contains various production impurities, such as the lower chlorophenols and chlorinated phenoxyphenols, as well as traces of chlorinated dioxins and furans (Crosby 1981). Chlorophenols are weak acids, which ionize and become increasingly water-soluble at alkaline pH (Crosby 1981). Although often regarded as recalcitrant, chlorophenols are degraded by a number of microbial species at a variety of redox levels (Moos et al. 1983; Guthrie et al. 1984).

Technical-grade PCP has been associated with chloracne, embryo toxic, and feto toxic effects (WHO 1987; O'Malley et al. 1990). As a whole, the mixture is a suspected human carcinogen (Crosby 1981). This assessment, attributed to the presence of the probable carcinogens, 2,4,6-trichlorophenol, and hexachlorodibenzo[*p*]dioxin in the impure product, has recently been confirmed and extended (McConnell 1989) with the inference that PCP itself is a liver carcinogen. Whether the results of this latest single study constitute "sufficient evidence" for an IARC reclassification of PCP as a human carcinogen remains a matter of debate (Seiler 1991).

CCA-based wood-preserving mixtures are comprised of oxides of copper (CuO), chromium (CrO_3), and arsenic (As_2O_5) dissolved in water. The bulk fluid treating solution is freely miscible with surface and groundwater, although adsorption and partitioning of individual metal species to the soil fabric may occur upon release. Cation exchange, ligand exchange, co-precipitation with aluminum and iron oxy hydroxides, and adsorption by soil organic matter (SOM) are important mechanisms in the retention of metals by fine-grained soils (Evans 1989; Masscheleyn et al. 1991).

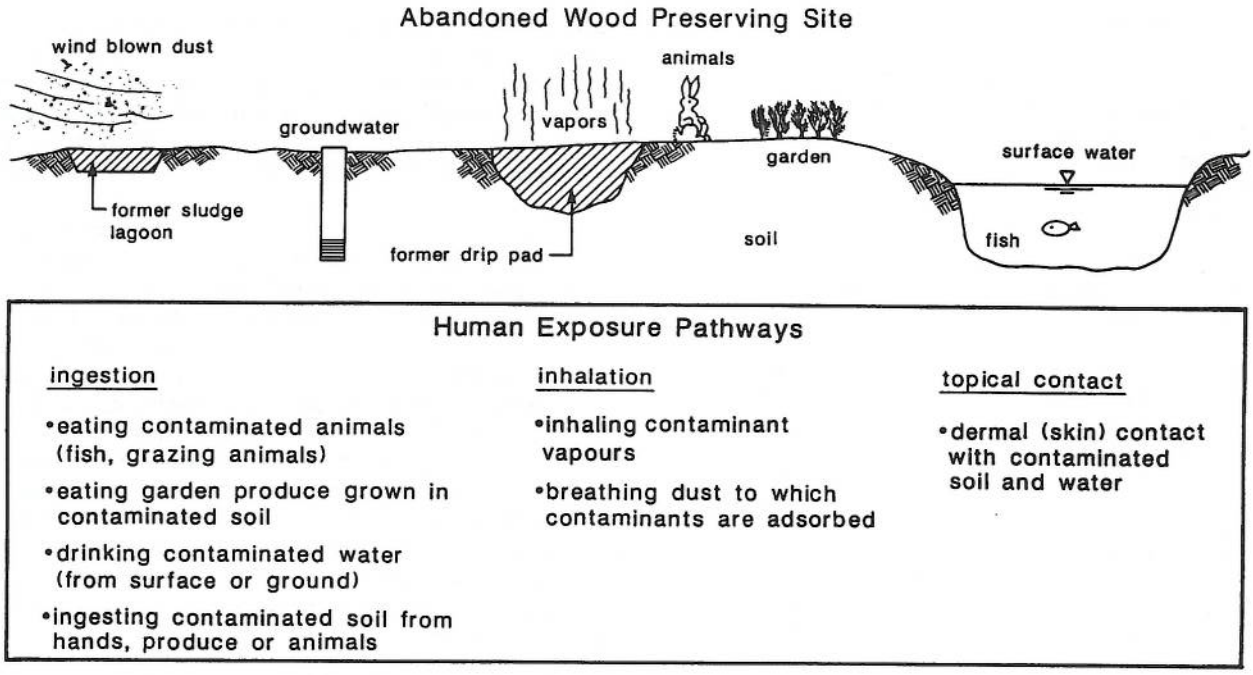


FIG. 2. Routes of exposure for wood-preserving chemicals.

Copper and Cr^{III}, in particular, are known to bond tightly to humic fractions of SOM (Evans 1989).

Site-specific behaviour will depend on localized pH and redox conditions, leaching properties of the soil, and groundwater flow characteristics. Arsenic exists in its pentavalent oxidation state as As_2O_5 in CCA concentrate. The effect of E_h and pH on the speciation and solubility of arsenic in a contaminated loamy upland soil has recently been discussed by Masscheleyn et al. (1991). Under aerobic and (or) acidic soil conditions, As^V species predominated with low solubility. These conditions favour the immobilization of As wastes. Reducing or alkaline conditions, however, enhanced mobilization of the more toxic As^{III}, although because of the slow kinetics of the reduction mechanism, a considerable amount of unstable As^V remained under reducing conditions. Mobilization of As has also been associated with the release of bound As from insoluble Fe^{III} oxides as they become reduced to soluble Fe^{II} oxides under anoxic groundwater conditions (Korte 1991). Therefore, attention must be directed at potential exposures to mobile As^{III} from anoxic groundwater sources. Chromium is present as hexavalent CrO_3 in neat CCA concentrate. Although reduction to Cr^{III} is expected under reducing soil or groundwater conditions, studies have demonstrated that under conditions prevalent in many soils, the more mobile and toxic Cr^{VI} species can predominate (Bartlett and James 1979; Environment Canada 1988*c*). Fendorf and Zasoski (1991) recently reported the oxidation of Cr^{III} to the hexavalent species in the presence of a naturally-occurring form of MnO_2 at pH values below 5. However, they reported that oxidation rates decreased as pH was increased to 5, so this oxidation mechanism should only be significant for acidic soils.

Individually, As and Cr^{VI} compounds are accepted human carcinogens, although the latter is based strictly on respiratory exposure. The metals also exhibit acute systemic toxicity. Over 90% of ingested As is absorbed, independent of oxidation state (Ishinishi et al. 1986). Chronic exposure may result in neuropathy, injury to the liver, and cancer of the skin, lungs, lymph glands, and bone marrow (Sullivan and Krieger 1992). Trivalent Cr compounds are generally poorly absorbed but acute ingestion of Cr^{VI} can lead to hemorrhagic gastroenteritis and renal failure. As a mixture, CCA is extremely toxic to fish, possibly exhibits synergistic toxicity (Warner and Solomon 1990), and has been associated with a wide variety of acute and chronic human health effects, including possible carcinogenesis (Takahashi et al. 1983; Environment Canada 1988*c*).

Problem definition

Wood-preserving sites in Alberta pose a number of problems for effective characterization and remediation because of (*i*) the occurrence of multimedia contamination (soil, soil vapour, groundwater, distinct hydrocarbon phase); (*ii*) the existence of a complex and problematic matrix of organic and inorganic contaminants with a diverse range of physiochemical, environmental, and toxicological properties; (*iii*) the presence of heterogeneous, anisotropic subsurface conditions which are difficult to characterize; (*iv*) suboptimal environmental conditions for on-site and in-situ treatment; and (*v*) expensive analytical procedures required for reliable characterization of the extent of contamination. Specifically, the selection of risk management options for these sites is complicated by the presence of mixed waste contamination, the predominance of hydrophobic organic contaminants residing in the residual oil phase, and the existence of low permeability soils.

Fugacity modeling of wood-preserving contaminants

Human exposure to wood-preserving wastes may result in the absorption of contaminants from environmental media via ingestion, inhalation, and (or) topical contact (Fig. 2). The relative importance of each exposure pathway is specific to the constituent considered because of the wide variation in partitioning behaviours between environmental compartments. Uncontrolled releases of oil-based wood-

TABLE 2. Selected properties of the evaluative soil environment

Model parameters	Assigned value
Temperature (°C)	25
Soil area (m^2)	1.0
Soil depth (m)	0.1
Soil volume (m^3)	0.1
Log mean diffusion distance (m)	0.039
Dosage (kg/ha) (mg/kg soil)	14.87 (10)
Densities (kg/m^3)	
Air	1.186
Water	1000
Organic matter	1000
Mineral matter	2500
Volume fractions in soil fabric	
Air	0.2
Water	0.3
Organic matter	0.04237
Mineral matter	0.45763
Mass (kg)	
Total soil	148.67
Total dry soil	118.64
Organic carbon	2.37
Organic carbon (g/g dry soil)	0.02
Organic matter (g/g dry soil)	0.0357
Water leaching rate (mm/d)	1.3

preserving mixtures (PCP, creosote) can take several physiochemical forms (Hoffmann and Hrudey 1990*a*): (*i*) a mobile continuous hydrocarbon phase (a non-aqueous phase liquid (NAPL) being less dense (LNAPL) or more dense (DNAPL) than water); (*ii*) a mobile discontinuous hydrocarbon phase (droplets, emulsion); (*iii*) an immobile discontinuous hydrocarbon phase (residual saturation); (*iv*) species dissolved in water; (*v*) molecules adsorbed to solid-phase organic or mineral matter; and (*vi*) soil gas vapours. The extent and direction of chemical partitioning between these individual phases can also be used to prioritize remedial activities at contaminated sites because these processes dictate the principal phase(s) in which contaminants reside.

From a remediation and exposure assessment perspective, a need exists to assess the distribution of wood-preserving contaminants between environmental media upon release to the soil environment. The fugacity approach (Mackay 1991) provides an efficient means of assessing the partitioning of individual chemicals released to a multimedia environment. The concept has been used for describing the distribution of organic chemicals between the atmosphere and water, for predicting the uptake of organic environmental contaminants by fish and for modeling the pharmacokinetic behaviour of indoor air pollutants in vivo (Mackay 1991).

Fugacity is essentially a measure of the escaping tendency of a particular substance (contaminant) from a particular environmental compartment or phase (air, water, organic matter). For any compartment, the fugacity of a contaminant will be determined by its fundamental (chemical, physical) properties. Fugacity modeling is primarily useful, for our current purposes, as a means to provide insight into the role that an individual contaminant's properties will play in determining the distribution of that contaminant in a multimedia environment such as soil, in comparison with other contaminants in the wood preservative waste mixture.

The absolute contaminant distribution values provided by the fugacity models will be influenced by the characteristics specified for the environmental compartments, which, in our generic application, are somewhat arbitrary. However, the comparative distribution among the environmental compartments for the full range of contaminants in wood-preserving wastes serves our purpose of illustrating the complexity and challenges facing remediation of these types of contaminated sites.

The simplest application of fugacity modeling, Level I, provides an equilibrium distribution of a contaminant among specified environmental compartments in the absence of any input or removal mechanisms (Mackay 1991). Level II models retain the requirement of equilibrium but add removal terms in the form of advection and reaction.

A four-compartment Level II fugacity model has been developed by Mackay (1991) for assessing the partitioning behaviour of organic chemicals among the air, water, soil organic matter (SOM), and mineral phases of the soil fabric. The model is less useful for describing the fate of toxic metals because they possess a complex environmental chemistry with solubility, mobility, adsorption, and partitioning behaviours all highly dependent on localized pH and redox conditions.

Adaptation of the model for surficial soil contamination at Alberta HELP sites requires definition of a representative soil environment. For illustrative purposes, a 0.1 m^3 volume of surficial (0–0.1 m) soil is assumed with a log mean diffusion distance of 0.039 m (Table 2). This specified depth allows volatilization losses to contribute to the overall reaction half-life without unduly dominating. Chemical dosage at 14.87 kg/ha is equivalent to 10 mg/kg deposition of an individual chemical species, homogeneously distributed throughout the soil volume, assuming a soil density of 1487 kg/m^3. In the absence of measured mineral–water partition coefficients for these compounds, a default value of 1.00 L/kg was adopted for illustrative purposes (Mackay 1991). Consequently, the predictions of contaminant distribution on the soil mineral phase may be substantially overestimated in this application.

Physiochemical properties of selected organic wood-preserving chemicals are identified from the literature (Table 3). Having performed a Level I distribution of contaminant concentrations among the four soil media, the model simulates the first-order decay of individual chemicals in soil by three simultaneous processes: volatilization, leaching, and reaction. In this simplified scheme, the process having the shortest half-life dominates and the overall half-life can therefore be used to rank chemical species according to their persistence in the soil environment. Model outputs include weight percent distributions among phases and estimated overall reaction half-lives (Fig. 3; Table 4).

Figure 3 demonstrates the overriding dominance of organic carbon (2% w/w of the soil fabric) in the sorptive uptake of hydrophobic contaminants by receiving soils. Organic matter in soil is considered to be 56% w/w organic carbon in composition and acts as the primary phase to which organophilic contaminants partition (Karickhoff 1981). However, since organic wood-preserving contaminants are originally discharged to the soil environment as NAPLs, the model must be revised to account for partitioning from the free or residual oil phase (NAPL, residual saturation) in the waste–soil matrix. This can be done by modifying the mass fraction of organic carbon to a level consistent with the solvent extractable organic content of the contaminated site soil so as to represent the combined

TABLE 3. Physical-chemical properties of selected wood-preserving chemicals

Compound	Molecular weight (g/mol)	Aqueous solubility (g/m^3)	Vapour pressure (Pa)	K_{oc}	Reaction $t_{1/2}$ (d)
Benzene	78.1	1780	12.7×10^{3}	64.5	68
Toluene	92.1	515	3800	257.0	39
Phenol	94.1	82×10^{3}	70.6	14.1	1
p-cresol	108.1	16.8×10^{3}	14.67	19.1	1
2,4,6-trichlorophenol	197.5	900	1.12	1070	5.3
Pentachlorophenol	266.4	14	0.23	50.12×10^{3}	20
Naphthalene	128.2	31.7	10.4	1290	10
Benzo[*a*]pyrene	252.3	3.8×10^{-3}	0.73×10^{-6}	549.54×10^{4}	450
Carbazole	167.2	1.03	0.093	1300	0.58
Hexachlorodibenzo[*p*]dioxin	392.9	1.3×10^{-4}	1.93×10^{-6}	25.87×10^{6}	500

TABLE 4. Level II soil fugacity model output for selected wood-preserving chemicals

Compound	Predicted amounts in phases of soil (% w/w)				Predicted half lives, $t_{1/2}$ (d)			
	Soil air	Soil water	Organic	Mineral	Volatilization	Leaching	Reaction	Overall (rank)
Benzene*	1.49	9.93	50.71†	37.87	4.5‡	160	68	4.1 (7)
Toluene*	0.72	3.95	80.27†	15.06	9.3‡	410	39	7.3 (5)
Phenol	0.00	16.86	18.84	64.30†	1470	95	1.0‡	1.0 (8)
p-cresol	0.00	15.82	23.84	60.34†	1540	100	1.0‡	1.0 (8)
2,4,6-trichlorophenol	0.00	1.12	94.62†	4.26	18.8×10^{3}	1430	5.3‡	5.3 (6)
Pentachlorophenol	0.00	0.03	99.88†	0.10	18.56×10^{4}	63.5×10^{3}	50‡	50 (3)
Naphthalene	0.01	0.94	95.48†	3.57	620	1710	10‡	9.8 (4)
Benzo[*a*]pyrene	0.00	0.00	100.00†	0.00	1.13×10^{8}	695.14×10^{4}	450‡	450 (2)
Carbazole	0.00	0.93	95.51†	3.55	1670	1720	0.6‡	0.6 (10)
Hexachlorodibenzo[*p*]dioxin	0.00	0.00	100.00†	0.00	7.56×10^{7}	3.27×10^{7}	500‡	500 (1)

*Despite the relatively low proportion of these volatile compounds predicted to reside in soil air at equilibrium (Fig. 3), volatilization provides the dominant clearance process when advection is considered by the Level II model.
†Dominant phase on a comparative basis.
‡Dominant clearance process on a comparative basis.

residual oil saturation and SOM as a single organic phase. This situation is illustrated using the fugacity model in Fig. 4. Increasing the organic content of the soil results in the progressive dominance of the organic phase as a partition medium for benzene. In such a system, the affinity of the residual or free oil phase for hydrophobic organic contaminants may exceed partitioning to SOM by as much as an order of magnitude (Boyd and Sun 1990). A current limitation to these evaluations is the absence from the literature of mineral–water partition coefficients for individual compounds sorbed onto composite soil mineral matter independent of SOM.

Table 3 shows the overall reaction half-lives for the selected compounds upon release. With the exception of benzene and toluene, removal from the system by reaction (abiotic and biotic) mechanisms would be necessary because neither leaching nor volatilization provides substantial removal mechanisms. The model demonstrates the persistence of refractory organics (benzo[*a*]pyrene, hexachlorodibenzo[*p*]dioxin, PCP) within the soil environment. With these compounds preferentially partitioned to the residual organic phase, their bioavailability is likely severely restricted and the reaction half-lives predicted by the model (based upon biotransformation half-life data) could be substantially underestimated. Because the residual or free NAPL represents the major sink for these compounds in the contaminated soil environment, the following discussion of risk management options focuses on the containment, isolation, recovery, and treatment of free product and residual saturation for wood treatment facilities at which organic preservatives were employed.

Site descriptions and potential exposure routes

A preliminary evaluation of risk management options for five priority abandoned wood-preserving facilities in Alberta has been conducted (Hoffmann and Hrudey 1990*a*). Site descriptions are provided in the following section. Rather than providing a case-by-case analysis of remediation options, we focus in this paper on some common themes and concerns encountered during remedial technology assessment for these sites and discuss the overall implications for risk management. These concerns will be of interest to remediation scientists and engineers conducting risk management evaluations at similar contaminated sites.

Site A

Site A is situated in central southern Alberta and operated as a wood-preserving facility from 1961 to 1970. PCP was the primary preservative used at Site A, though creosote is also suspected as an additional treating agent. The site area (5 ha) is almost completely covered with healthy prairie grasses with the exception of three small, contaminated areas: the former sludge lagoon, a section of trench leading to it, and a section of the former timber storage area.

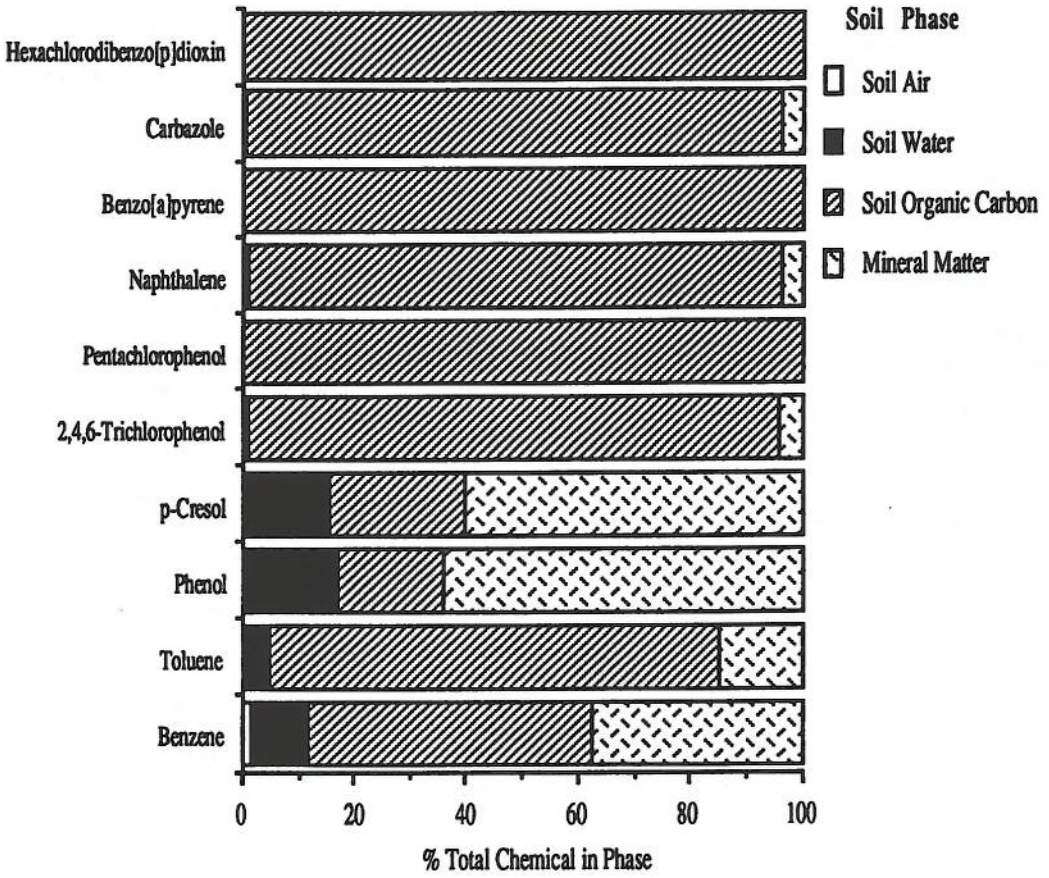


FIG. 3. Comparative distribution of selected wood-preserving chemicals among soil environmental compartments. Notes: (1) The absolute distribution values depicted are influenced by the properties specified for the evaluative soil environment (Table 2), but the distribution comparisons among contaminants are primarily determined by contaminant properties (Table 3). (2) The nonmeasured value used for mineral and water partition coefficient may have caused the model to overestimate the proportion of contaminant residing in the mineral phase.

Surficial deposits comprise a sequence of glaciolacustrine clays and silts to a depth of ~13 m overlaying a sandy clay till to 19 m. Depth of the water table varies from 4 to 11 m with an average horizontal conductivity, k, of 2×10^{-7} m/s. Average groundwater flow velocity both vertically and horizontally is estimated as 2 m/yr (Stanley Associates Engineering Ltd. 1989).

Two areas pose a concern. Soil sampled at 0.3 m depth near the former treater building exhibited an elevated concentration of 5826 mg/kg PCP. The value is uncharacteristic of general site contamination; the next highest PCP soil concentration of 134 mg/kg was found in the former sludge pond. This is either erroneous or suggests a small localized band of soil highly contaminated with PCP. The 1.0 and 2.0 m samples at this location contained 9.9 and 5.1 mg/kg PCP respectively. PCP was not detected at the 6.0 m level at this location and adjacent shallow and deep piezometers showed non-detectable PCP.

Secondly, groundwater with 120 mg/L PCP was identified below the former sludge pond. Because this value exceeds the water solubility of PCP, it indicates a separate organic phase in the aquifer. Two nearby piezometers contain PCP concentrations of 0.15 and 5.4 mg/L; the latter value confirms the existence of a distinct PCP-hydrocarbon phase. Only 4 of the 10 groundwater samples showed detectable PCP concentrations, three of which were obtained from piezometers in the sludge lagoon. The implication is that contamination at Site A is defined by a distinct PCP-hydrocarbon phase beneath the sludge pond and the groundwater directly in contact with it. The minimal contaminant movement implied agrees with estimates of 2 m/yr for groundwater movement. However, vertical fractures to a depth of 6 m were noted in the silt and clay deposits — fractures that, if extended to the water-bearing strata, could result in groundwater movement at rates in excess of those predicted by localized soil permeability tests. The existence of four domestic water wells within a 500 m radius of the site therefore necessitates the delineation of any contaminant groundwater plume.

Site B

Site B operated in southern Alberta from the early 1920s to 1962 for the creosote and PCP treatment of railroad ties and utility poles. Treatment cylinder residues, run-off water, solid wastes, and process sludges were disposed of in unlined sludge ponds on site which have subsequently released a DNAPL free product to the underlying coarse gravel aquifer. Goundwater traversing the site (300 m/yr) discharges through a riverbed to the adjacent river. Surficial soil at Site B is silt fill with debris, 1–4 m in depth, above sandy gravel (1–5 m in depth) alluvial deposits (hydraulic conductivity of 10^{-5} to 10^{-3} m/s) situated on an eroded bedrock of interbedded sandstones and shales. DNAPL released at the site has accumulated in localized depressions

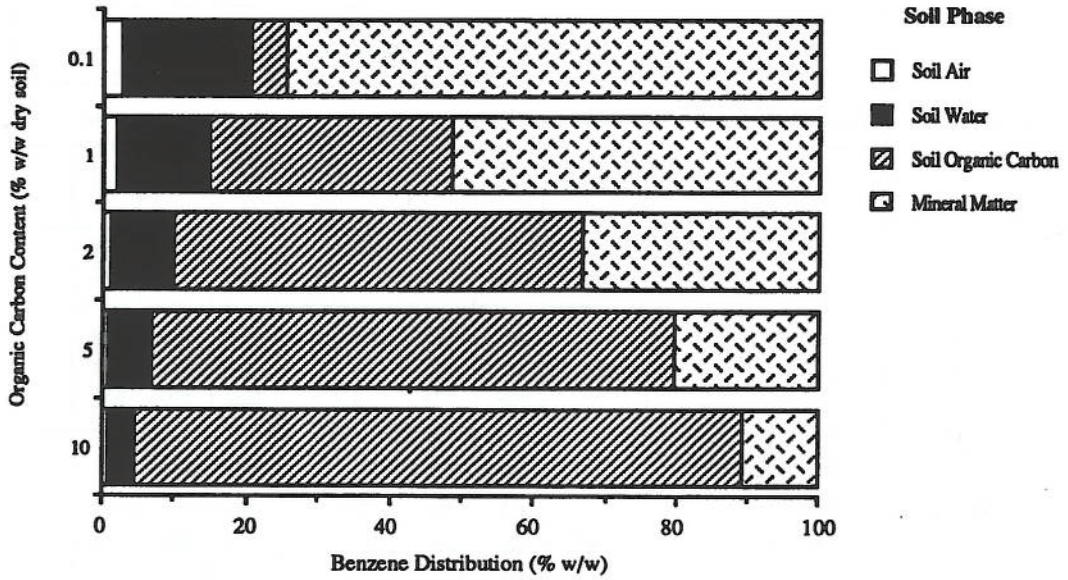


FIG. 4. Illustration of residual oil in soil as a dominant partition compartment for benzene as oil contamination of soil is increased. Note: The nonmeasured value used for mineral–water partition coefficient may have caused the model to overestimate the proportion of contaminant residing in the mineral phase.

in the bedrock surface. Recent excavations confirm the bedrock surface itself is weathered, thus further transmitting DNAPL to deeper strata.

Site investigations (O'Connor Associates Environmental Inc. 1989; Golder Associates Ltd. 1990) revealed soil and groundwater to be extensively contaminated with wood-preserving chemicals and associated carrier liquids. Principal exposure pathways are via the discharge of LNAPL, DNAPL, and contaminated groundwater to the adjacent river or via a vapour reservoir in the soil which may accumulate in substructures located on the site. At present, measured hydrocarbon vapours do not present a substantial risk of either explosion or toxicological exposure; however, continual monitoring is desirable as vapour concentrations are sensitive to changes in groundwater chemistry. There are no users of groundwater near the site, and surficial soils on the site consist of clean fill. Ingestion of contaminated groundwater or dermal contact with contaminated soils are not significant exposure pathways.

Of additional concern are bedrock depressions (which are likely sources of creosote contamination and which may be hydrologically separated from the rest of the aquifer) and contaminated river sediments. Creosote trapped in bedrock depressions will continue to partition PAHs to the aqueous phase, albeit slowly. Pumping wells drilled directly into the depression are required to recover residual-free product. DNAPL has also been observed in the bedrock fractures and bedrock wells may also require installation. LNAPL, DNAPL, and contaminated groundwater has contaminated large amounts of bottom sediment in the adjacent river with wood-preserving chemicals.

Site C

Site C, south of Calgary, operated from 1958 to 1982, pressure treating air-dried timber with PCP mixed in diesel fuel carrier oil (Monenco Consultants Ltd. 1989). Wastewater and process residues were disposed of on site in containment and evaporation ponds. General site geology consists of surficial silts and clays to a depth of 2 m, with underlying glacial till (geometric mean hydraulic conductivity of 5×10^{-9} m/s) to 8 m containing thin sand lenses situated on a shallow mudstone, siltstone, and sandstone bedrock (5.5×10^{-7} m/s). Initial site investigations revealed significant contamination of surface soils in the process and sludge pond areas. PCP-contaminated groundwater also exists at this site, but its amount and migration has been minimized by a tight underlying glacial clay till. Large areas are devoid of vegetation, implying extensive surface contamination.

Fairly consistent hydraulic conductivities exist for the clayey till; however, the permeability determined from one well is at least three orders of magnitude higher than that of other measurements. This value of 2.5×10^{-6} m/s was not included in the calculation of the geometric mean and was attributed to a fine silty sand lens within the till. Contaminated groundwater may therefore have migrated further than expected and may be responsible for the concentration of 33 mg/L PCP observed in one well, several times the aqueous solubility of PCP, and indicative of a distinct LNAPL phase on the water table. The three groundwater samples containing PCP above 1 mg/L also likely arose from LNAPL contact. Future investigations should therefore confirm the fracture status of the till and bedrock.

Of the 81 soil samples analyzed, 10 had a pH less than 8.0, and only 2 had a pH less than 7.5. At this pH, chlorophenols largely exist in their more mobile anionic forms. The low migration potential imposed on subsurface contamination at Site C by low permeability soils may therefore be offset by increased PCP mobility.

Site D

Site D in northeastern Alberta operated from 1977 to 1982 as a pressure facility for the treatment of fence posts using a CCA-based solution. Spent CCA was recirculated to a mixing tank and treatment sludges disposed of in an on site pit. Site geology consists of surficial, fine-grained silts to 0.25 m above glaciolacustrine clay and silty clay deposits to 1.0 m. Below this, a partially fractured till (10^{-8} to 10^{-9} m/s) exists to 14.5 m situated on a weathered sandy siltstone bedrock aquifer (Thurber Consultants Ltd. 1989).

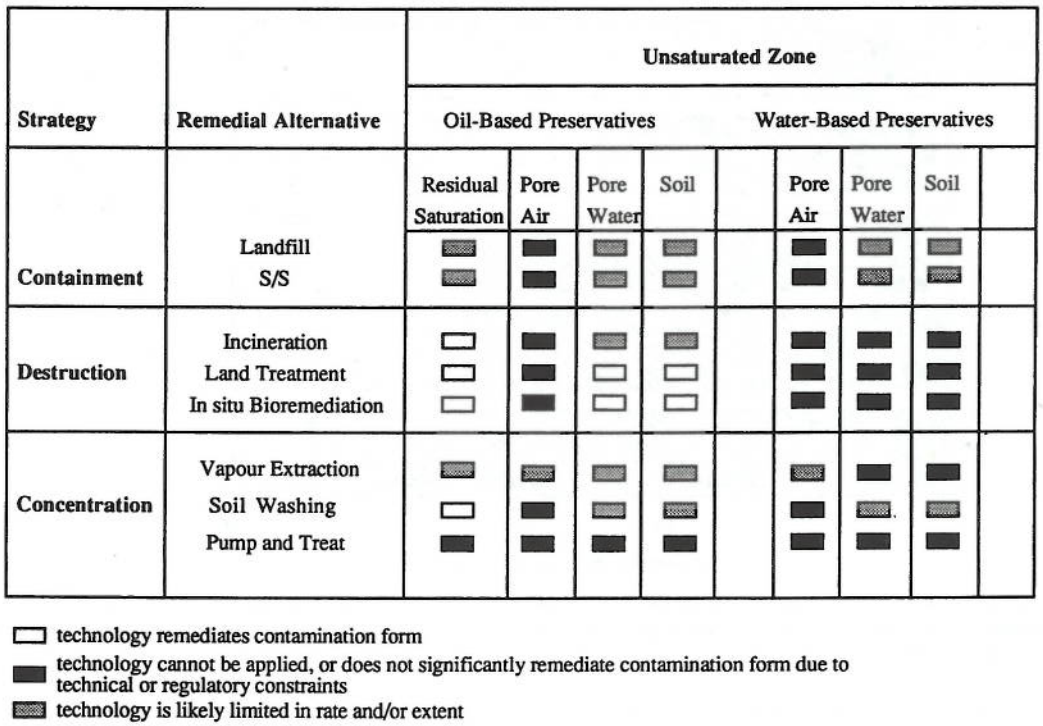


FIG. 5. Relative applicability of remediation options for wood-preservative contamination in the unsaturated zone.

Soil surrounding the sludge pit and in the swamp to the northwest of it is bare. The remainder of the site supports a thick, healthy crop of prairie grasses. CCA sludge was periodically removed from the sludge pit in drums and disposed of in a sawdust and chip fill area cut into the earth. Sludge in this pit presents a potential source of Cu, Cr, and As contamination to surrounding soils and the underlying aquifer. Indeed, a preliminary site report indicates high adsorption of Cu, Cr, and As to surface soils. These observations are consistent with predictions of high adsorption in the organic-rich clay present. Copper has migrated much less than either Cr or As which have traveled virtually the same distance. This is consistent with thermodynamic predictions, which suggest that anionic complexes of Cr and As migrate further than cationic Cu in clay soils. Where excessive metals contamination exceeds the adsorption capacity of the soil, CCA may travel unhindered through the vadose zone to the groundwater table.

The sludge pit is lined with a thin plastic sheet some 5 mm thick. Upon inspection, this liner appeared brittle in places, and missing or submerged in others. Residual material in the lagoon is likely percolating into the soil and possibly affecting groundwater. Sludge pond source material requires expedient removal. Furthermore, the pit is known to overfill during heavy rainfall events. This is confirmed by the high levels of adjacent surficial contamination, which suggest that overflow material must have run towards the slough, 45 m northwest of the sludge pit.

Dust and material in the former chemical preparation shed and drying platform contain extremely high concentrations of As, Cr, and Cu. Considering the contamination in these process buildings and in surficial soil near the sludge lagoon, inhalation of dust containing CCA must be regarded as a significant exposure pathway.

All groundwater samples analyzed satisfied the specified levels for As, Cu, and Cr in the Guidelines for Canadian Drinking Water Quality (Health and Welfare Canada 1989). Only three of the samples obtained, however, were from piezometers actually on the former plant site, the other two from background samples obtained from off-site monitoring wells. The installation of more piezometers at this site to provide additional groundwater quality data must be considered a priority. Any detection of high Cr or As levels in the siltstone units beneath the site would further justify the evaluation of neighbouring wells, as these siltstone units form the aquifer used for groundwater in this area.

Site E

Site E, situated in north central Alberta, operated from 1961 to 1974. From 1961 to 1967, raw timber was processed on site and pressure treated with CCA. In 1967, PCP replaced CCA as the main wood preservative. A fire originating in the treater building destroyed the plant around 1970; however, sawing of poles continued on site until 1974. Site geology consists of fill material (wood chips, soil, gravel) above variable silty deposits to 2 m (Hardy BBT Ltd. 1989). Below this, fine-grained silty sand overlying grey sand extends to 5 m, below which is a highly plastic unfractured clay at least 8 m in depth. The shallow sand aquifer represents the local groundwater supply and is found at an average depth of 1.7 m. Flow direction is north to an adjacent lake.

An area southeast of the current perimeter fence is covered with wood chips to a depth of 0.3 m. This area is completely bare of vegetation in many spots. Soil samples taken from this area exceed the CCME Interim Remediation Criteria (commercial and industrial lands) for Contaminated Sites (CCME 1991*b*) for both PCP (5 mg/kg) and As (50 mg/kg). Subsequent studies must address soil and groundwater contamination at this location. Additional bare areas exist in the swamp west of the site, which likely receives surface runoff, a pond area and a number of darkly stained soils

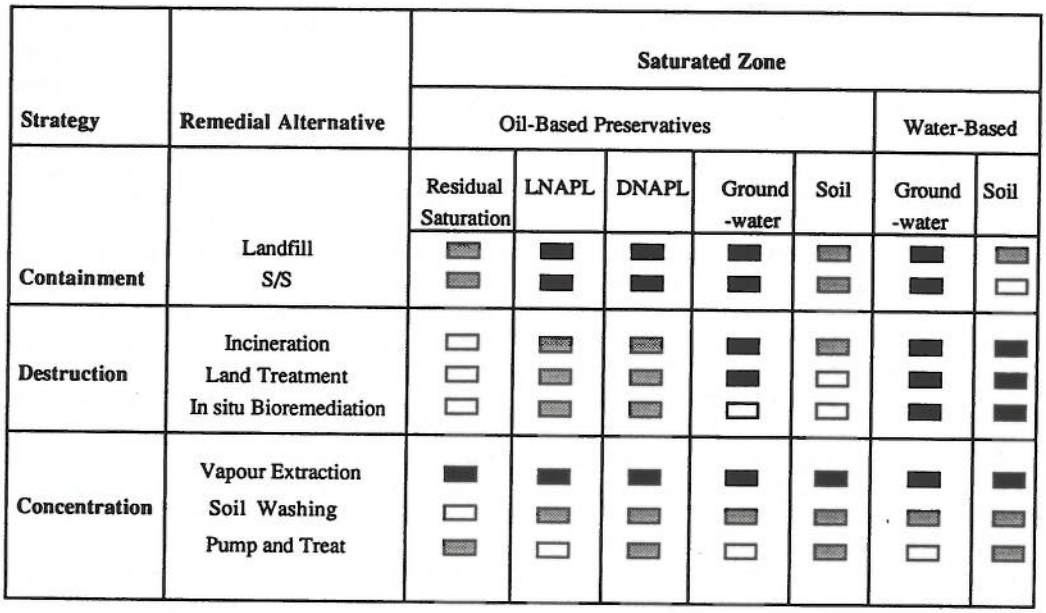


FIG. 6. Relative applicability of remediation options for wood-preservative contamination in the saturated zone. (See Fig. 5 for legends.)

inside the perimeter fence. A strong PCP odour detected over the site is of concern, considering operations ceased over 20 years ago. A crib-well filled in with soil which had subsequently slumped contains water with a distinct PCP odour and an oily sheen. This depression is likely transmitting contamination from the heavily contaminated process area directly to groundwater. The proximity of domestic groundwater wells and the adjacent lake demands that the removal of this structure and its replacement with a low permeability fill be made a priority.

The aquifer beneath this site is contaminated with PCP, may be discharging to the nearby creek or lake and may be affecting nearby domestic wells. Samples taken from perimeter piezometers, a nearby farm, and the creek during the preliminary site study imply that groundwater off the site is slightly contaminated with PCP, but not yet to a dangerous level. However, a sample from the one piezometer on site indicates grossly contaminated groundwater unsafe for human consumption. This result implies the presence of a distinct PCP-hydrocarbon phase in the groundwater as observed at the crib well. Considering the extensive sand zones beneath this site, sampling of nearby domestic water wells should continue. Only background levels of Cu, Cr, and As were found in all groundwater samples.

Surface soil at this site is highly contaminated with PCP and As. The site is also located in a groundwater discharge zone, and is about 3 m higher than the average water level in the adjacent lake. There is a corresponding potential for surface runoff to wash contaminated soil into nearby areas or the lake. Inhalation of contaminated soil as dust is expected to be insignificant because surface conditions appear to be moist and the site is fenced to reduce access.

Implications of site characteristics for risk management

The overall objective of risk management is the protection of human health and the environment. At contaminated sites, this can be achieved by managing contaminant exposure pathways and subsequently reducing health risks to nearby or on-site individuals. For sites requiring remediation, the development of site-specific clean-up criteria through the implementation of site-specific risk assessment is advocated (CCME 1991*b*; Hrudey 1992). The current approaches to site remediation emphasize on-site and in-situ technologies which can be linked in a process train of physio-chemical and (or) biological methods capable of tackling the range of multi-media contamination encountered (Sims 1990). This approach recognizes that no single technology alone can effectively remediate all forms of contamination present at wood-preserving sites.

In consideration of risk management options for wood-preserving sites in Alberta, three key themes arise for discussion: the limitations imposed on in-situ remediation technologies by fine-grained soils, constraints on treatment efficacy introduced by the presence of mixed organic and inorganic wastes, and the predominance of organic wood-preserving chemicals within the residual oil phase. The relative applicability of remedial technologies for oil- and water-based wood-preserving contaminants in the unsaturated and saturated zones is summarized in Figs. 5 and 6.

Applicability of in-situ treatment strategies

Pump and treat remediation uses withdrawal wells to recover contaminated groundwater and mobile bulk hydrocarbon phases (NAPLs) from the subsurface. However, sorbed contaminants, contaminants trapped in low permeability lenses, and residual hydrocarbon contamination are not effectively recovered or treated (Mackay and Cherry 1989). With the exception of Site B, the presence of low permeability lenses and heterogeneous subsurface conditions at sites in Alberta will constrain remedial technologies that rely on contaminant withdrawal in either the aqueous or gaseous phase.

Pump and treat technology is best viewed as a means of maintaining hydraulic control in the subsurface; for reversing existing flow gradients and reducing plume migration. Modified well systems have been used to recover LNAPLs and DNAPLs at wood-preserving sites and would appear appropriate for free product recovery at Site B. At the Union

Pacific Railroad tie treating plant in Wyoming, 950 m^3 of creosote were recovered from an alluvial sand and gravel aquifer, 2–5 m thick ($k = 10^{-5}$ m/s), using a drainage line system (Kuhn and Piontek 1988). A soil–bentonite cut-off wall prevented contamination of the adjacent river and physically isolated the treatment zone. Extracted groundwater was treated aboveground using gravity oil separation and activated carbon treatment. A similar approach is described by Dworkin et al. (1988) for the subsurface remediation of creosote-contaminated soil at the L.A. Clarke wood-treating site, Fredericksburg, Virginia.

The above approach is a potential risk management strategy for Site B. Principal exposure pathways are associated with the discharge of distinct-phase hydrocarbon and contaminated groundwater to the adjacent river. Management of exposure pathways at this site requires the prevention of further discharge with subsequent free product recovery. An impermeable slurry wall installed down-gradient of the site could be used to prevent continued contaminant migration into the river and aid the maintenance of hydraulic control. Pumping wells, installed on the up-gradient side of the barrier, could potentially recover NAPLS and contaminated groundwater and maintain the hydraulic integrity of the barrier. Barriers installed up-gradient of the site would prevent the influx of uncontaminated groundwater traversing the site, in which case the extraction wellfield near the down-gradient barrier could be decreased and flows then limited to barrier leakage and surface infiltration (Kuhn and Piontek 1988). The containment barrier(s) should be installed prior to addressing the DNAPL beneath the river, to prevent DNAPL recharge from the pool beneath the site.

Following containment, source areas of contamination must be remediated. The most desirable remediation alternatives would not disrupt surface activities. Strategies involving excavation of contaminated soil (incineration, landfill disposal, solidification and stabilization, land treatment) are less desirable. The alluvial sands and gravels beneath the site are extremely permeable ($k = 4 \times 10^{-4}$ m/s) and potentially amenable to in-situ biological treatment, provided hydraulic control can be maintained. Groundwater beneath the site flows north and northeast towards the river, and the formation is permeable enough for recovery wells located near the barrier to recover any elutriate or unused solution, completing the treatment cycle.

Limitations imposed by contaminant characteristics and fine-grained soils

In-situ vapour extraction is the vapour-phase equivalent of groundwater pump and treat. Contaminant vapours move along an enhanced gradient to recovery wells. The use of in-situ vapour extraction is limited to permeable, unconsolidated soils containing volatile contaminants (Henry's Law constant, $K_H > 10^{-3}$ atm·m^3/mol) in the unsaturated zone (Dupont et al. 1988; U.S. EPA 1990*a*). Wood-preserving sites in Alberta are not amenable to remediation by in-situ vapour extraction because of unfavorable soil and temperature conditions and the low volatilities of most wood-preserving contaminants (e.g., p-cresol $K_H = 3.5 \times 10^{-4}$ atm·m^3/mol; B[*a*]P $K_H = 1.8 \times 10^{-5}$ atm·m^3/mol; PCP $K_H = 2.8 \times 10^{-6}$ atm·m^3/mol; U.S. EPA 1990*b*).

In-situ bioremediation enhances existing subsurface microbial activity through the injection of required amendments and recovery of transformation products, and is restricted to relatively homogeneous and permeable formations of hydraulic conductivity greater than 10^{-6} m/s (Thomas et al. 1987). In-situ soil washing utilizes chemical surfactants to immobilize sorbed constituents or trapped hydrocarbons and is increasingly being considered as a pretreatment for bioremediation. The Biotrol™ system is an integrated process train consisting of soil washing, biological water treatment, and slurry phase bioreactor unit processes (Stinson et al. 1992), which has recently been demonstrated for the treatment of sandy soils contaminated with mixed wood-preserving wastes at the MacGillis and Gibbs Superfund site near Minneapolis. On the basis of chemical disappearance data, PCP and PAH removal efficiencies of 87% w/w or higher were achieved by soil washing, with 94% w/w PCP in the process water being removed subsequently using the biological water treatment process. PAH in the fines following soil washing were treated as a 7% aqueous slurry in the bioreactor over a 14-day period, with 70–90% w/w reductions in PAH being achieved despite some operational difficulties encountered.

In-situ technologies (bioreclamation, soil washing, vapour extraction, and pump and treat) for the recovery or treatment of the PCP LNAPL at Site A would be constrained by mass transfer limitations associated with the low permeability ($k = 10^{-7}$ m/s) clay which underlies the site. Similarly, subsurface contamination beneath Site C is trapped in a low permeability ($k = 5 \times 10^{-9}$ m/s) clay till.

Applicability of biological soil treatment

The objective of biological treatment is to transform readily degradable contaminants to less toxic forms. In enhanced land treatment, for example, soils are excavated and placed in land treatment units (LTUs) where nutrients, oxygen, and moisture can be supplied in abundance (Hoffmann and Hrudey 1990*b*). Bioremediation is generally assumed to be more economical than other remedial alternatives, involves on-site treatment, and theoretically results in products that potentially require no subsequent treatment or disposal. In practice, treatment times are generally longer and technologies are sensitive to substrate concentrations and accompanying toxicants. Furthermore, for sites in Alberta, treatment may be hindered by low field temperatures, weathered hydrocarbon waste compositions, and the microbial toxicity of associated metals at mixed waste sites (Hrudey and Pollard 1993).

Bioremediation technologies have, nevertheless, been successfully applied at a number of wood-preserving facilities across North America and Europe. For example, pilot-study in-situ bioremediation of the Champion International Superfund site, Montana (Utah State University 1991), involves efforts to remediate the upper (2.5–5 m) aquifer contaminated by previous wood-treating operations. The pilot design consists of two well clusters within the contaminant plume for peroxide and nutrient injection. Preliminary results indicate lower concentrations of PAH and PCP in groundwater recovered from the treated contaminated zone compared with the untreated region. A fixed-film bioreactor for the aboveground treatment of extracted groundwater is also under evaluation at this site.

The enhanced land treatment component of this study involves pretreatment of approximately 34 400 m^3 of uncompacted wood-preserving waste contaminated soil containing (mean concentrations) 189 mg/kg total carcinogenic PAH, 29 mg/kg PCP, and 0.0009 mg/kg 2,3,7,8-TCDD equivalents followed by subsequent biological treatment in

a prepared-bed unit (Utah State University 1991). The double-lined 8100 m^2 LTU is sloped (2%) to a central gravel drain and sump. Waste-pit soils contain 0–3% w/w clay, 10–41% w/w silt, 31–55% w/w sand, and 0.95–5.3% w/w organic carbon. Performance data for this site will be of specific interest to Alberta HELP sites because of its climatic proximity to Alberta. However, soil textural differences between this site and those typical to Alberta tills should be noted.

McGinnis et al. (1991) has reported soil treatability studies on eight creosote-contaminated soils in steel lysimeter units. Lined units were filled with a 30 cm layer of sand, 1 m of clean control soil and topped with heavily contaminated soils from the Roseburg wood-preserving Superfund site. Field evaluation over the 84-day test period examined the addition of chicken manure as a non-analogue substrate for co-oxidation, and the effect of waste concentration and of multiple waste application. Reported optimal reductions (100% w/w) in extractable PAH load were exhibited by the test plot containing 0.8% w/w PAH and manure addition. Drainage water appearing after a heavy rain event contained μg/L levels of LMW PAHs. Additional bioremediation studies at the pilot and field scale have been described in detail (Ryan and Smith 1988; Ellis et al. 1991).

Remedial options at Site C are not complicated by mixed waste problems. Excavation of surficial soil followed by incineration, enhanced land treatment, or landfill are potential risk management strategies at this site. Incineration alone would be extremely expensive for the soil volumes encountered. Landfill disposal may be problematic, given the high soil pH and associated potential chlorophenol mobility. A large, uncontaminated area is available for on-site construction of a LTU. Treatment costs will increase accordingly if temperature control is required. The efficacy of enhanced land treatment for contaminated Site C soils will depend largely on the bioavailability of contaminants in the waste–soil matrix.

All residual process equipment and rubble would be removed following examination for residual PCP prior to disposal. Remaining contaminated soil would be excavated, mixed with amendments and stored in a covered, lined stockpile on an uncontaminated corner of the site adjacent to the lined LTU. Sawdust, wood chips, and manure amendments exist on-site. Amendment requirements have been determined in laboratory-scale microcosms (Alberta Research Council 1992) and 5000 m^3 field pilot has been built. The site will require capping with a clean clay. Pumping wells, or existing monitors, will be used to recover contaminated groundwater which may require further separation to remove any LNAPL present. Collected LNAPL can be incinerated and the separated groundwater used to irrigate the LTU, provided it is not detrimental to microbial activity.

Incineration, landfill disposal, and enhanced land treatment may be applicable at Site A, although more precise information on costs and the volume of material to be treated is required. Land treatment is likely to be less expensive than incineration, and is more sound on the basis of long-term hazard mitigation than landfill disposal. Treatability studies will be required to provide site-specific information on the potential rate and lower treatability limit of land treatment for on-site wastes. Their use in the selection and optimization of engineering designs for the remediation of contaminated hazardous waste sites has been discussed at length by Sims (1990) and Dupont (1991).

Treatment and disposal of mixed waste-contaminated soils

The treatment and disposal of mixed waste-contaminated soils is problematic because of the interfering effects of complex waste components on the efficacy of treatment technologies capable of achieving effective management of separate organic and inorganic wastes. This is particularly relevant to the cement-based solidification and stabilization, bioremediation, and incineration of mixed wood-preserving wastes.

Cement-based solidification and stabilization (S/S) is a physiochemical process for the treatment of inorganic wastes that aims to either bind or complex components of a hazardous waste into a stable insoluble form (stabilization) or to entrap the waste within a cementitious matrix (solidification). This objective is achieved by the addition of ordinary portland cement (OPC) to the pretreated waste slurry, with structural integrity being provided by cementitious and pozzolanic reactions between OPC, added kiln dust and (or) fly ash and the available water (Wiles 1987). Conventional S/S processes are generally unsuitable for the treatment of mixed organic and inorganic wastes because of the interfering effects of contaminating organics on the various cement hydration reactions (Pollard et al. 1991). Consequently, forecasting the outcome of treating complex and variable wastes becomes extremely difficult. Solidification and stabilization of mixed wood-preserving wastes is expected to be especially problematic because of the increased mobility of chlorophenols at the high pH of the treated waste and because phenols, their chlorinated analogs, and the petroleum-based carriers are among documented inhibitors of cement hydration (U.S. EPA 1990*a*). High organic concentrations present in organic-rich clay soils, such as those encountered at Site D, may also affect matrix set.

Cement-based S/S processes are best suited to inorganic waste constituents that form stable precipitates at the high pH of cement hydration (pH ~ 11–13). For inorganic wood-preserving wastes, the minimum solubilities of constituent metals occur at different pH values; and $As^{III,V}$ and Cr^{VI} do not form stable precipitates above pH 11 and are thus poorly immobilized. Arsenic, in its oxidized, pentavalent form, is soluble over a broad range of pH values (pH ~ 2–14) and must be reduced to As^{III} prior to treatment. Careful monitoring and control of pH is required because the solubility of the more toxic As^{III} increases substantially at pH > 11 (Wiles and Barth 1992). Similarly, soluble Cr^{VI} must be reduced to the relatively insoluble Cr^{III} (pH ~ 5–13) prior to S/S treatment. In practice, precise pH control during cement hydration is difficult to achieve. These constraints underscore the need for detailed waste characterization and treatability studies prior to selection of S/S technologies (Wiles and Barth 1992; Kleppe et al. 1992).

Remediation efforts at Site D should focus on metal contamination of surficial soil. Groundwater exposure pathways do not appear to be significant following the preliminary investigation but will require further monitoring. Landfill disposal, soil washing, and solidification and stabilization can be screened as potential risk management strategies for the remediation of CCA-contaminated soil. Soil and sludge contaminated with CCA wood preservatives may be landfilled, contingent upon current provincial hazardous waste regulations. However, because the mobility (and toxicity) of many wood-preserving chemicals is dependent on localized redox conditions, contaminants could be mobilized by

acidic landfill leachate and escape containment. Landfill disposal rarely involves pretreatment other than neutralization, and the risk of contaminated leachate remains unless leachate collection systems are employed. There is considerable doubt that the excavation of contaminated soil with transportation and reburial at a new site represents an effective reduction in overall risk. As such, excavation and landfilling of wood-preserving wastes should be considered, if at all, as the least desirable disposal option.

On the basis of the above discussion, in-situ S/S remediation of CCA-contaminated soil at Site D is anticipated to be problematic because of the potential for As^{III} and Cr^{VI} mobilization. A combined approach in which sludge pit and adjacent soils are drummed and transferred to the Alberta Special Waste Treatment Centre at Swan Hills for dewatering, S/S, and secure landfill is suggested as a potential risk management option. This combined approach using S/S with secure landfill disposal will require strict process control and continued leachate monitoring for mobilized toxic metals as a minimum quality assurance requirement.

A paucity of information currently exists regarding Site E and consequently remediation alternatives are more difficult to evaluate. No estimation of hydraulic conductivity was made in the initial study. The combination of PCP, diesel carrier, and CCA contamination will likely eliminate S/S treatment as a potential remedial option for contaminated soils at this site and could potentially impede any efforts at soil bioreclamation. In-situ technologies such as soil washing or bioreclamation may be applicable, assuming formation permeability is sufficient and accompanying metals are not toxic to the native microbial population. Management of exposure pathways at Site E must focus on preventing further contaminant migration using a pump and treat system, provided hydrogeologic conditions are favourable. Inadequate hydraulic control or breaches in hydraulic containment could result in contamination of domestic water supplies.

Incineration involves the thermal oxidation of combustible materials to innocuous gases suitable for atmospheric release (Theodore and Reynolds 1987). Undesirable combustion products must be removed by flue gas cleaning and solid residues (kiln slag and fly ash) landfilled. Inorganic and mixed wood-preserving wastes are not amenable to incineration because they generally have a low calorific value, and metal species such as volatile organic As compounds present a flue gas emission problem. Waste-soil characterization is therefore integral to remedial technology selection and particularly important for soils contaminated with organic wood treatment chemicals that are also known to be or suspected of being contaminated with problematic metals, such as the soils at sites A and E.

Organic wood-preserving wastes (such as sludge pond liquid, highly contaminated with 4000–6900 mg/kg PCP at Site C) are generally amenable to incineration. Test burn data indicate effective destruction of waste constituents, provided adequate residence times and operating temperatures are maintained (U.S. EPA 1990*a*). Residues may require subsequent treatment and disposal (e.g., S/S) if they contain toxic combustion products, thus increasing overall treatment costs. Specific concern exists over emissions of polychlorinated dioxins (PCDDs) and furans (PCDFs) as well as acid gases (HCl) generated during combustion of chlorinated organic wastes. Creosote and PCP-contaminated soil and sludge at Alberta HELP sites could be incinerated on site, or at the Alberta Special Waste Treatment Centre in Swan Hills, Alberta. Operating costs are high, however; and incineration may be prohibitive for the volumes of soil requiring treatment. Mobile, on-site units, whilst conceptually more economical, may encounter sufficient regulatory and public resistance to negate any theoretical cost savings.

Oil phase partitioning

Partitioning of hydrophobic organic contaminants and their primary, abiotic reaction products in the environment is dominated by their residence in the oil phase (Figs. 3 and 4), which exists either as free oil (NAPL) or as residual saturation on soil resulting from the gravitational movement of NAPLs through the soil column.

Isotherm studies of the three-phase (oil, soil, water) partitioning of semi-volatile hydrophobic organics, PCP and 2-chlorobiphenyl, suggest that the oil phase could be as much as tenfold more effective than SOM as a partition medium (Boyd and Sun 1990). Similar results were observed by Jackson and Bisson (1990) for the three-phase partitioning of polychlorinated dibenzo[*p*]dioxins (PCDD), polychlorinated dibenzofurans (PCDF), and PCP in wood-preserving oil, with K_{os} values (oil–soil partition coefficients) of between 47 and 100 and between 10 and 57 for aged and fresh wood-preserving oils respectively. A preliminary evaluation of the partitioning behaviour of benzene in the contaminated soil environment (Fig. 4) further illustrates the progressive domination of the residual organic phase as a partition medium with increasing soil organic carbon content. These findings have important implications for the potential feasibility of bioremediation strategies at wood-preserving sites. Beyond the immediate effects of the organophilic oil-phase substantially reducing the concentration of degradable contaminants in the aqueous phase, retention of degradable substrate within the *weathered* hydrocarbon matrix will further reduce their bioavailability to the degrading microbial populations.

Summary and conclusions

A preliminary evaluation of remedial alternatives for five uncontrolled hazardous wood-preserving sites in Alberta has been performed. Clearly, the significance of the potential environmental hazards discussed demands further site investigation to better quantify site hydrogeology, the contaminant distribution, and to obtain the parameters necessary to perform a quantitative health risk assessment.

Several important issues have been raised by this evaluation. The complex nature of mixed organic and inorganic wastes at many of these facilities complicates remedial technology selection. A soil-based fugacity model identified the organic phase (soil organic matter, residual saturation, free oil) as the principal recipient of hydrophobic organic contaminants following release to the soil environment. From a human exposure and from a remediation perspective, highest priority must therefore be given to isolation, removal, and treatment of this contaminant source term.

Site characterization efforts performed during the initial stages of the remediation process must address the full range and extent of contamination on site and must be capable of providing information on general site contamination as well as localized areas of immediate concern. Attention must be paid to the mobility of anionic chemical species in aquifer

material and therefore the redox and pH status of the vadose and saturated zones must be determined. Such information is essential to allow realistic site-specific quantitative health risk assessment for these abandoned facilities. The wide range of factors affecting contaminant distribution and treatability underscores the waste, site, and soil specificity of contaminated site remediation.

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Appendix: Glossary

ACA	ammoniacal copper arsenate
ACC	acid copper chromate
BTEX	benzene, toluene, xylene, and ethylbenzene
CCA	chromated copper arsenate
CCME	Canadian Council of Ministers of the Environment
DNAPL	dense, nonaqueous phase liquid
HMW	high molecular weight
IARC	International Agency for Research on Cancer
LMW	low molecular weight
LNAPL	light, nonaqueous phase liquid
LTU	land treatment unit
PAH	polynuclear aromatic hydrocarbon
PCDD	polychlorinated dibenzo[*p*]dioxin
PCDF	polychlorinated dibenzofuran
PCP	pentachlorophenol
SOM	soil organic matter

REPORTS

ENVIRONMENTAL ASSESSMENT AND RISK ASSESSMENT OF AN INCINERATION PLANT — A CASE STUDY

D.O. Harrop and S.J.T. Pollard
Aspinwall & Company

Introduction

Environmental Impact Assessment (EIA) refers to the evaluation of the impacts likely to arise from a development which may affect the environment. EIA has been applied to a plethora of development projects of varying scales and in particular, incineration. This paper seeks to explain the procedural steps of EIA for a proposed sewage sludge incinerator in Belfast, Northern Ireland, UK (Department of the Environment for Northern Ireland, 1994).

Screening

The initial step in an EIA process is to determine whether the environmental impacts of a proposed project indeed warrants a comprehensive EIA. This initial step is commonly known as screening. Under Schedule 1 of the UK *Town and Country Planning (Assessment of Environmental Effects)* Regulations 1988, a waste disposal installation for the incineration of chemical treatment of special waste requires an EIA. In the situation of the case study the developer elected to carry out an EIA even though it was not a mandatory requirement. The *Planning (Assessment of Environmental Effects) Regulations (N.I.) 1989* were applied to the case study. The UK EIA procedural system is detailed elsewhere (Department of the Environment UK, 1989).

Impact Identification

The first stage of the EIA involves the identification of most likely and most significant environmental impacts. This stage is commonly called the scoping study. The objectives of the exercise are to:

- canvass as wide a body of opinion as practicable, to ensure a comprehensive coverage of local issues and/or concerns;
- identify the *key* issues normally associated with the proposed development;
- focus the study on *key* issues relevant to the locality; and
- collect information or 'baseline' data held by certain bodies which is relevant and helpful in undertaking the EIA.

The scoping exercise provides a description of the most important environmental, social and economic issues together with the concerns of the community and interested

organisations alike in order to describe the potential impacts within the context of the environmental setting of an incinerator development. There are a range of EIA methods (e.g: checklists, matrices, networks, overlays, etc) to aid the individual in the identification of potential impacts. Two methods widely used in EIA to access incineration development impacts are checklists and matrices. An application of the use of a simple matrix for an incinerator development in Belfast is shown on Figure 1.

Development actions are broadly divided up into construction, commissioning and operation, and decommissioning. To aid the interpretation of the matrix which does not provide any weighting of the predicted impacts, a summary key has been used. Development/environment interactions are divided into four categories: the potential interaction can have no impact (no effect); can result in a potentially detrimental effect on the environment if not mitigated (potential adverse effect); can result in a beneficial environmental effect (potential positive effect); or subject to the detail of the design, could be beneficial or alternatively, could yield adverse effects (potential positive and negative effects).

Impact Prediction and Measurement

The principal environmental impacts emanating from an incineration development include emissions to air and indirectly to soils with associated health implications, visual intrusion, nuisance (odour, noise, etc), vehicular movements, effects on flora and fauna, and socio-economic effects. Depending upon the environmental sensitivity of the development site, water impacts may also necessitate consideration. Ultimately, the environmental concerns depend upon the proposed environmental setting. In this instance, the proposed development site is within an industrialised area of the Belfast Harbour.

For the most part, chimney flue gas (stack) emissions in incinerator EIAs and their effects on human health, fauna and flora have received and occupied the greatest attention in the submitted EISs. Therefore, the principal study is an Air Quality Impact Assessment (AQIA). This involves not only identification, prediction and variables such as source emissions and meteorological conditions, but changes of air quality as a result of emissions from the proposed incinerator. The AQIA may broadly be divided into three stages (Harrop and Carpenter, 1992).

- Stage 1 — The Existing Baseline Situation;
- Stage 2 — Characterisation of Emission Sources; and
- Stage 3 — Assessment of Impact

Atmospheric dispersion models have been developed for a variety of pollutants, time scales and operational scenarios. Short-terms models are used to calculate concentrations of pollutants over a few minutes, hours or days, and can be employed to predict worst-case conditions (i.e. high pollution episodes). Long-term models are designed to predict seasonal or annual average concentrations, which are useful in studying potential chronic health effects, impacts on vegetation, materials and structures. Figure 2 shows the predicted long-term dispersion of ground level concentrations from the Belfast study.

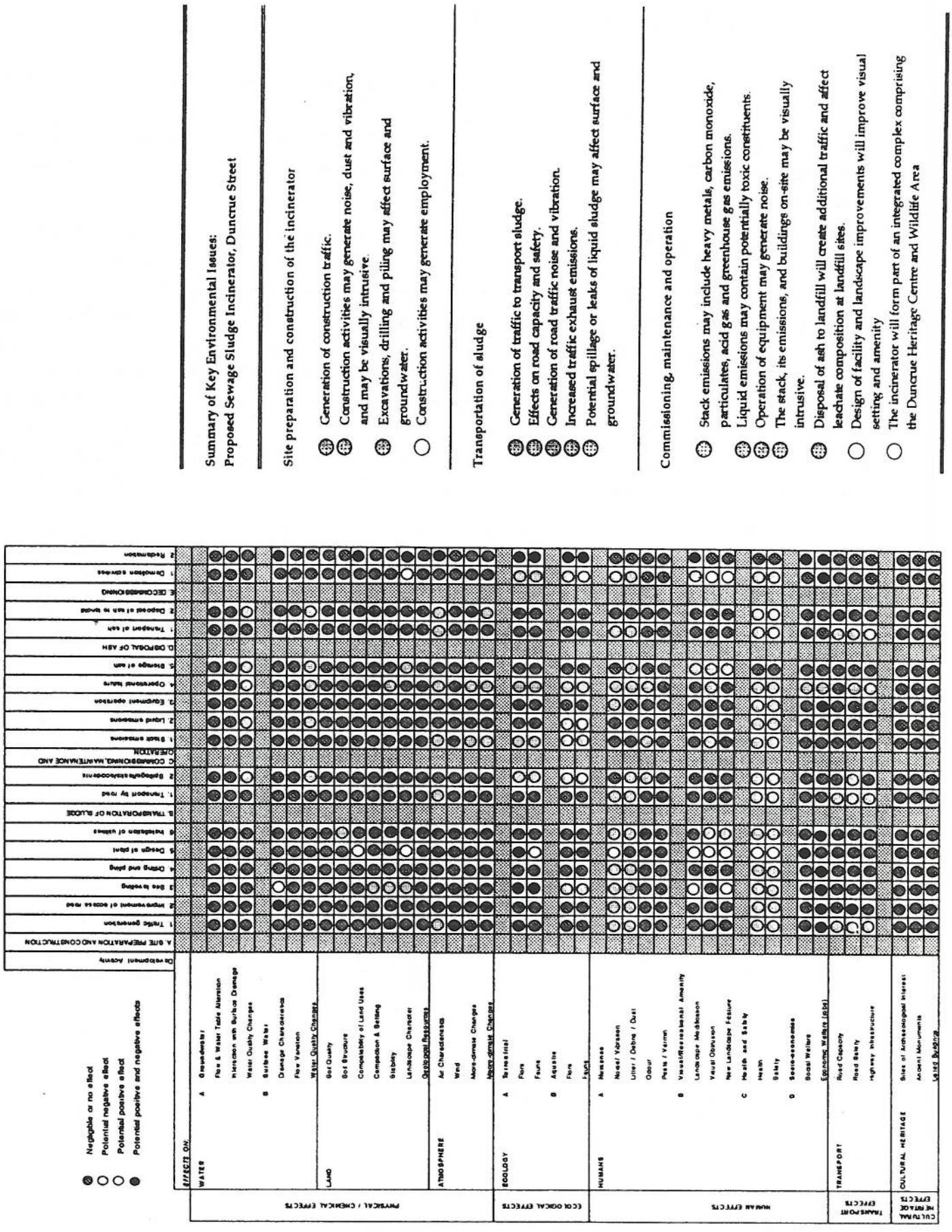


Figure 1 A Simple Matrix for an Incinerator Development in Belfast, UK. (Water Executive of the Department of the Environment for Northern Ireland, 1994).

Impact Description and Evaluation

Maximum 1-hour and annual concentrations were used in the assessment from a baseline monitoring study and available air quality data for Belfast. The impact of emissions (assuming the plant was emitting to the maximum emission level allowed in the Her Majesty's Inspector of Pollution (HMIP), Guidance Note IPR 5/11) from the chimney were, by convention compared with short-term and long-term air quality criteria.

For potential carcinogens, potential risks were estimated as probabilities. It is customary in risk assessment to assume worst case exposure scenarios so as to be protective of public health. It was assumed, conservatively, that emissions of the carcinogenic contaminants were at the maximum limit permitted by the incinerator plant design criteria, and were continuous over 365 days per annum for 70 years, the average lifetime of a hypothetical exposed individual. Further, the individual was assumed to have spent an entire lifetime at the point of maximum impact inhaling the emissions from the incinerator and absorbing 100% of the material inhaled. This worst case scenario was used to predict the increased individual lifetime risk of developing cancer, to the hypothetical maximum exposed individual, as a result of inhalation of the

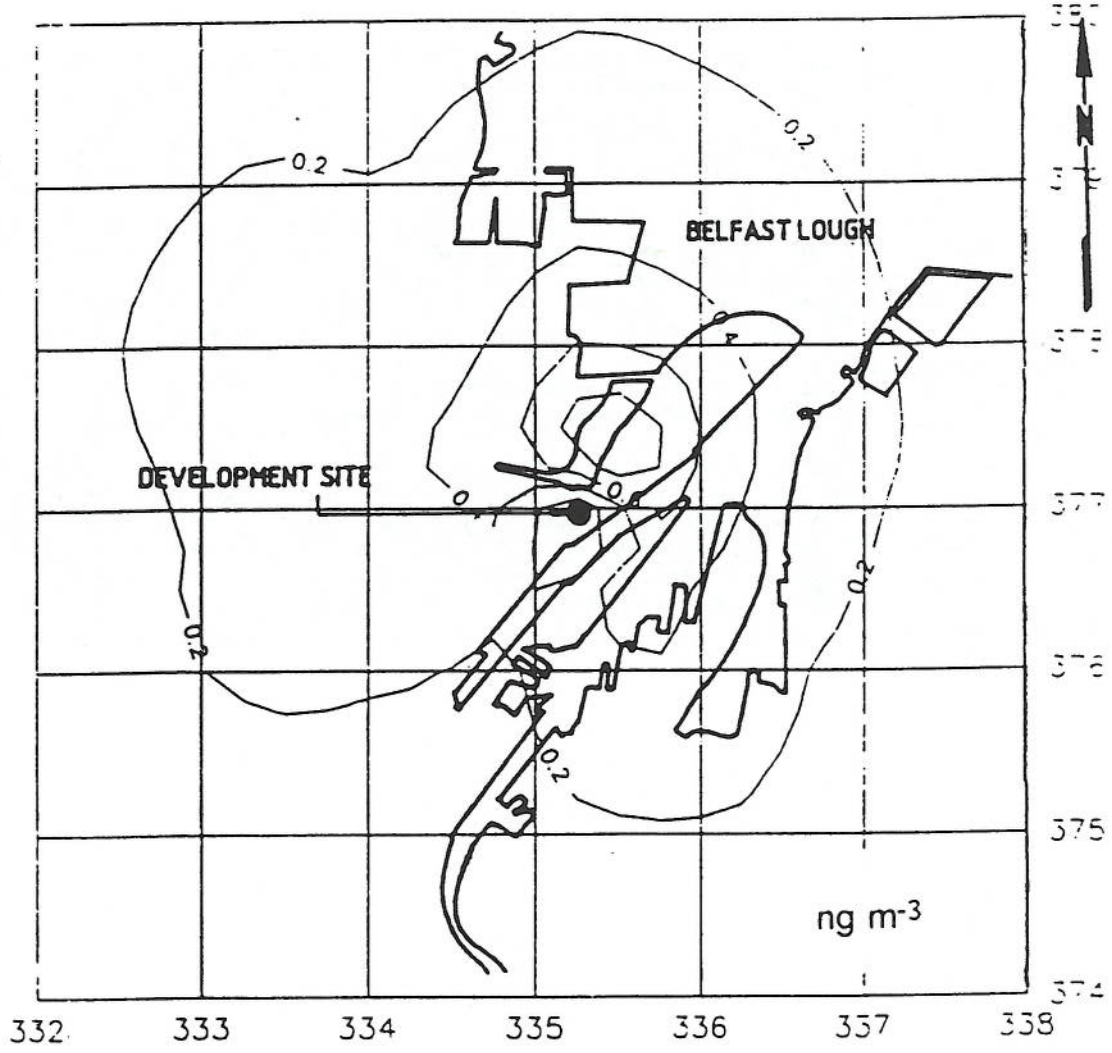


Figure 2 Predicted Ground Level Concentrations from the Incinerator (Department of the Environment for Northern Ireland 1994).

emissions. Hence the risk estimates produced are representative of extreme levels of exposure. Risk estimates were finally adjusted to cater for realistic exposure and absorption levels. Over a typical lifetime of 70 years the risks corresponded to a range of incremental values from 0.4×10^{-6} to 0.2×10^{-6} per year. These compare with a risk of 1 in 1000000 that by consensus represents a reasonable upper bound level, beyond which measures to achieve a further reduction in the risk would not be justified in terms of the benefit gained. The calculated risk range of 0.4×10^{-6} to 0.2×10^{-6} per year corresponds to risks of between 0.4 and 0.2 per million per year.

The EIA concluded that predicted increases in maximum short-term and long-term ground level concentrations were low compared to existing air quality levels. Existing and predicted ground level concentrations were below recommended air quality criteria with the exception of short-term levels for SO_2 which very occasionally exceeded the World Health Organisation air quality guideline. SO_2 levels in Belfast have shown a marked decrease in concentrations in recent years.

Presentation and Communication of Information

In conclusion, perhaps the most important activity in the Belfast EIA process was the ultimate presentation of the EIS. The EIS aids the decision-makers in their final decision relative to the particular project, and being a public document it would be scrutinised by interested agencies and groups. Canter (1991) summarises from other authors five basic principles to be remembered:

- always have in mind the audience of the report; in the case of an EIS assume the reader is intelligent but uninformed;
- decide on the purpose of report, to convey the environmental consequences of the proposed development;
- use simple and familiar language, the EIS requires the submission of a non-technical summary;
- ensure that the presentation of the report is well-structured; and
- make the report visually attractive.

Those criteria proved themselves to be essential during presentation of the Belfast EIS.

Acknowledgements

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Risk Assessment for Environmental Management: Approaches and Applications

By S.J. POLLARD, PhD, MRSC, CChem *(Member)*, D.O. HARROP, PhD, FRGS, P. CROWCROFT, MSc, CEng, MICE, S.H. MALLETT, MSc CGeol, FGS, S.R. JEFFRIES, MSc, FGS and P.J. YOUNG, BSc, MRSC, CChem, MIWM *(Member)**

ABSTRACT

Effective risk-management measures concerning the health, legislative and financial implications of environmental risk rely fundamentally on a robust risk assessment. Risk-assessment strategies exist at various levels of sophistication, and their application should be staged and matched to (a) the magnitude and significance of risks under study, (b) the sensitivities of receptors, (c) the quality of data available, and (d) the means by which risks are to be communicated. Three risk-assessment approaches are examined and their role is reviewed with respect to the completion of multi-media environmental management projects.

Key words: Applications; quantitative risk assessment; risk-assessment strategies; risk communication; risk screening.

INTRODUCTION

Environmental risk analysis involves the assessment of potential risks to a receptor (e.g. individual, community, ecological habitat) following exposure to a hazardous agent[1]. Central to the toxicological basis of chemical risk assessment and risk management is the concept of dose, and the connectivity between source, pathway and receptor if hazards are to be realized (Fig. 1). Planning a reduction of risk or a safe response to a hazardous release to the environment relies on applying these basic toxicological principles. Effective risk management, therefore, focuses on isolating or removing receptors, intercepting exposure pathways or isolating (or removing) sources of hazard. This paper is concerned with methodologies for environmental risk assessment arising from an identified or predicted hazard of concern. It does not deal with incident or emergency predictions for chemical-engineering plant failure or with fault tree analysis used to demonstrate *a priori* whether environmental risk assessment is warranted.

Risk management is most effective when it (i) benefits from an appropriate level of risk assessment[2] which identifies specific hazards, (ii) assesses potential routes and levels of exposure, (iii) relates dose to potential effects (where required), and (iv) characterizes risks according to their relative importance. Risk assessment can be an ill-defined technical exercise[3], and those assessing risk must acknowledge and address potentially controversial debates regarding the public perception of risk[4], risk communication and acceptability[5] and, indeed, the underlying sociological aspects of environmental risk[6].

This paper was presented at a CIWEM symposium entitled *Emergency Planning and Incident Management in the Water Environment* held in London on 21-22 March 1995 and in Glasgow on 2-3 May 1995.

* Senior Chemist, Director, Director, Senior Engineer, Senior Hydrogeology and Operations Director, respectively, Aspinwall & Company, Baschurch, Shrewsbury, UK.

SELECTING STRATEGIES FOR RISK ASSESSMENT

Environmental risks will always be contingent on the variable conditions of exposure and, under a range of exposure scenarios, risk can be envisaged as a distribution of risks ranging from low to high-risk conditions. High-risk situations are those where direct, short-exposure pathways exist from a high hazard source to a particularly sensitive receptor; whereas low-risk situations are those where indirect or diffuse pathways exist from a source of low hazard to a receptor of low sensitivity, or where substantial dilution occurs along the exposure pathway.

The risk-assessment strategy can be selected by answering the question, 'What level of uncertainty can be tolerated in the final expression of risk? The answer determines the extent of data collection required for input, the technical sophistication of the risk-assessment method applied and the cost of completing the entire risk-assessment process (Fig. 2). Therefore it is prudent to stage risk assessments in order to avoid (a) inappropriate expenditure on low-risk situations or those risks easily resolved, (b) matching of over-ambitious methodologies with insufficient or poor-quality data, and (c) claiming levels of confidence in the final output which cannot be justified by the methodology used.

Strategies for environmental risk assessment can be classed as qualitative, semi-quantitative or quantitative[8] in nature and are used respectively for the screening, ranking and estimation of risks. Historically, the UK has adopted a pragmatic approach to the qualitative assessment of environmental risk, but recent pressures for the application of quantitative risk assessment (QRA)[9-12] have raised a vigorous debate over the merits and limitations of each approach. Important to the debate is a discussion of the paucity of human toxicological data at low levels of environ-

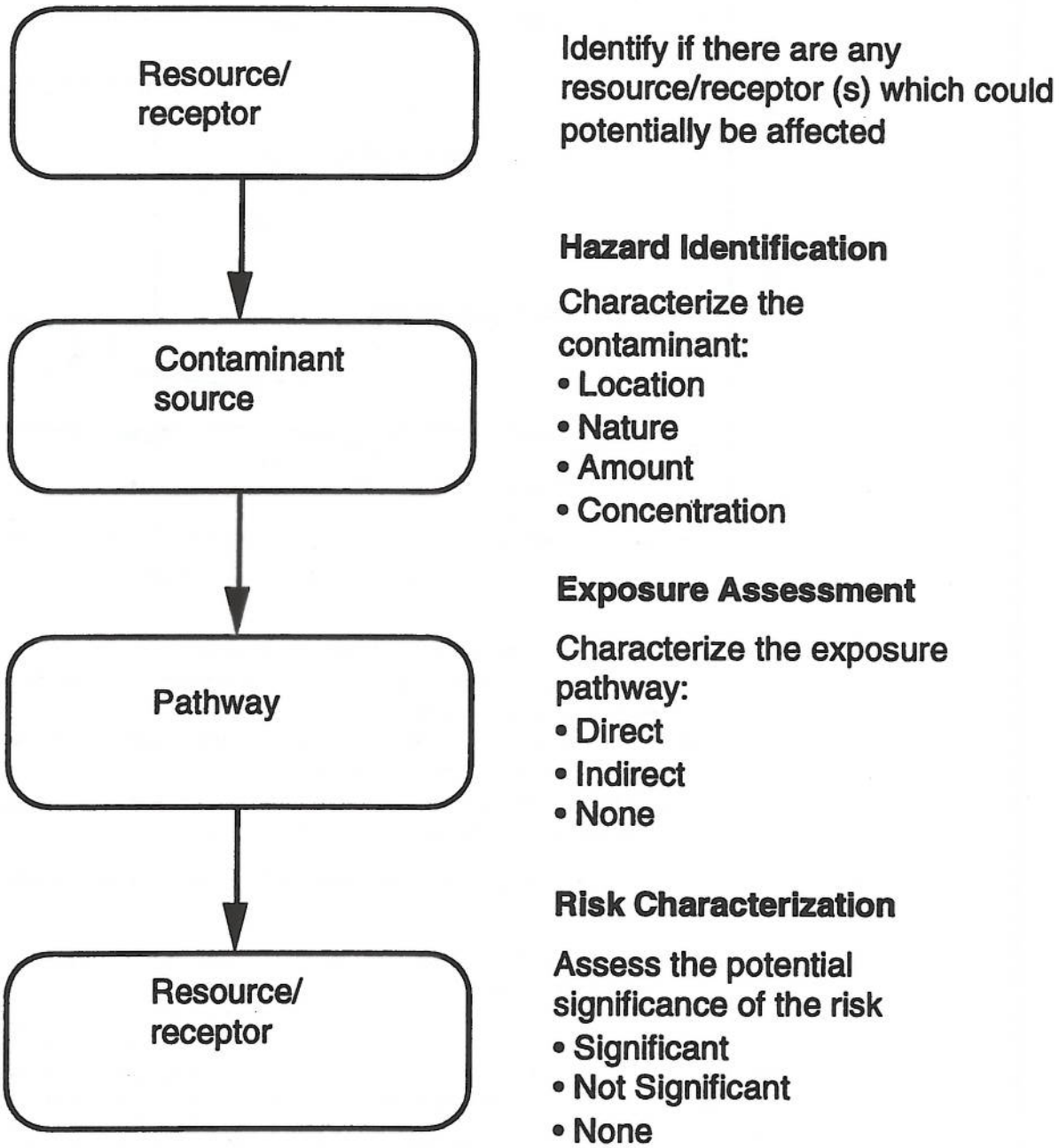


Fig. 1. Toxicological basis of risk assessment: source-pathway-target model

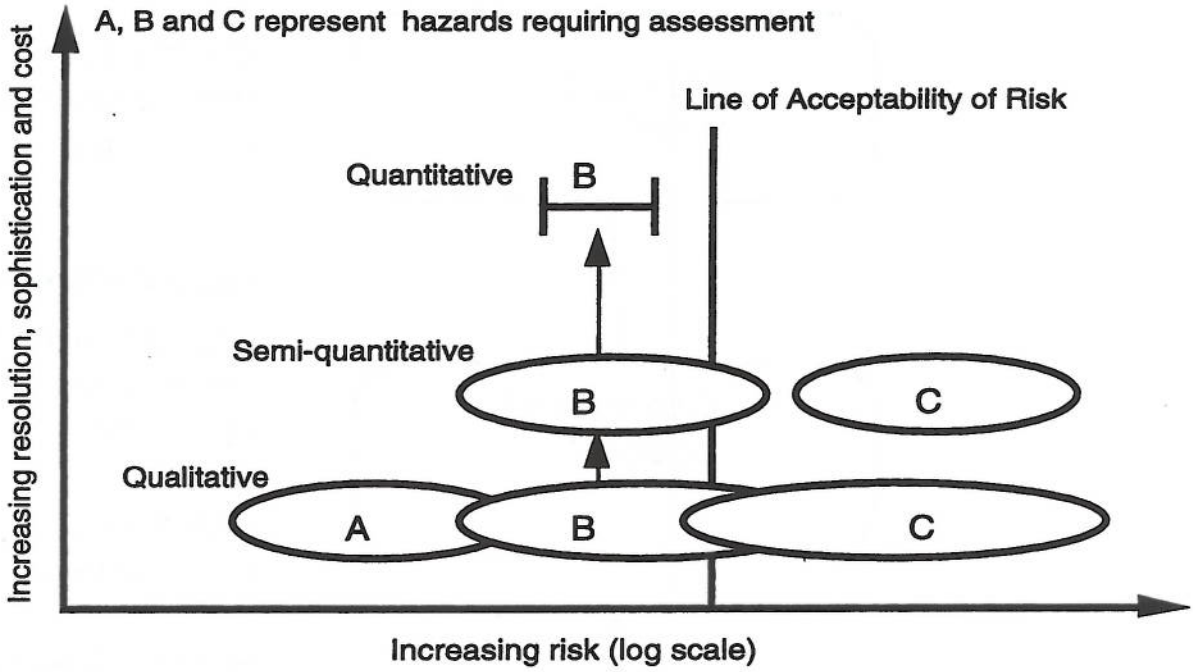
mental exposure and the levels of uncertainty associated with the models used by regulatory authorities, mainly in the USA, to translate animal data obtained at high doses to human dose equivalents[13].

Practical issues requiring clarification during selection of a risk-assessment strategy include:

(i) *Objectives.* Are the risks requiring assessment legal liabilities, risks to human health, ecological risks or financial liabilities?;

(ii) *Data quality.* Risk assessments are frequently performed on data collected under an unrelated set of data-gathering objectives and may be inappropriate for quantitative approaches; and

(iii) *Risk communication.* Risk assessors must account for the expectations of the study stakeholders; how risks will be communicated, and how the outputs will be utilized (e.g. in deriving environmental quality criteria, directing remedial efforts or calculating liabilities or levels of financial investment).



Key for risk assessment of hazards A, B and C:
Qualitative: A, risk identified as acceptable by qualitative risk assessment; B and C unresolved; B < C;
Semi-quantitative: C, risk identified as unacceptable by semi-quantitative risk assessment; B acceptability unclear;
Quantitative: B, shown acceptable by quantitative risk assessment though still exhibiting uncertainty in estimation.

Fig. 2. Appropriate selection of risk assessment methodologies[7]

SCREENING RISKS: QUALITATIVE RISK ASSESSMENT

Approach

The central feature of the qualitative methodology is a source-pathway-receptor analysis performed with the objective of establishing connectivity and assessing receptor sensitivity. Without the key components present, risks can be deemed to be negligible and screened out at an early stage (A; Fig. 2). The qualitative approach offers a screen for assessing environmental risks, has specific utility in identifying impacts from major hazards at an early stage (B and C; Fig. 2), and can be used effectively to assess situations which require further interrogation by quantitative methods (B; Fig. 2)[7]. The subsequent decision to move to an increased level of sophistication must be judged against the necessity and likelihood of resolving the inherent uncertainties, the magnitude of the perceived risk, and the potential cost of the entire risk assessment/risk management process.

Application: Potentially Contaminated Land Sites

A qualitative risk-assessment methodology was used for screening potential risks from multi-media exposures at contaminated land sites along the route of the Channel Tunnel Rail Link[14]. This project involved the assessment of 228 potentially contaminated sites, and the screening of risks was effectively streamlined through use of a qualitative assessment matrix for each receptor type (e.g. for groundwater acting as a receptor; Table I). For risk characterization, sensitivity criteria were established prior to individual site screening through professional experience and judgement.

Hazard identification was performed by relating historical operations and site management practices obtained via a desk study and site walk-over to potential contaminative land use, and hence to contaminant characterization. Effects were classified in relation to the nature and quantity of possible source contaminants present on the basis of site use, professional

TABLE I. QUALITATIVE ASSESSMENT MATRIX FOR GROUNDWATER RECEPTORS

Source			Pathway	Effect on receptor	
Nature	Concentration	Quantity		Sensitive	Less sensitive
Likely to be a potential risk	High	Major	Direct	S	NS
			Indirect	S	NS
			None	N	N
		Minor	Direct	S	NS
			Indirect	S	NS
			None	N	N
	Intermediate	Major	Direct	S	NS
			Indirect	S	NS
			None	N	N
		Minor	Direct	S	NS
			Indirect	S	NS
			None	N	N
	Low	Major	Direct	S	NS
			Indirect	S	NS
			None	N	N
		Minor	Direct	S	NS
			Indirect	S	NS
			None	N	N

S - Potentially significant effect
NS - Not significant effect
N - No effect

judgement, and established guidance[15]. Exposure assessment was performed by classifying pathways as direct (e.g. contact), indirect (e.g. via another medium such as inhalation of windblown dust) or none. Finally, risk characterization was achieved in this qualitative study by assessing the significance of impacts in relation to the connectivity of source-pathway and receptor and the sensitivity of the receptor under study. For example, sensitive ecological receptors were defined as international, national or county designated sites, whereas less sensitive ecological receptors were defined as locally designated and undesignated sites. Sensitive surface waters were defined as those with a low potential for dilution, also taking into account water quality. All human receptors were regarded as sensitive, irrespective of number. Potentially significant effects were therefore identified for all receptors on a consistent basis for the purposes of the environmental assessment (e.g. Table II for a fictitious site). At present, the assumptions regarding contaminant characterization are being examined in detail as part of an ongoing programme of site investigations.

RANKING RISKS: SEMI-QUANTITATIVE RISK ASSESSMENT

APPROACH

A higher level of resolution in the assessment of risk can be achieved by ranking risks according to a predefined assessment matrix which takes into account the relative degree of hazard (potency or concentration), the relative nature of the exposure pathway (extent of connectivity with receptor; direct, indirect or none) and the differential sensitivity of the receptor[16]. Default values assigned to each source-pathway-receptor condition can be incrementally related in terms of a simple linear scale, or logarithmic scale which attempts to take into account differences between risk situations based on professional judgement. Hazards can then be allocated scores which reflect their differential 'potencies' within the risk-assessment matrix.

TABLE II. RISK CHARACTERIZATION PROFILE FOR INDIVIDUAL SITE: EFFECTS OF RAIL LINK CONSTRUCTION: ATLAS FOUNDRY

Receptor	Contaminant source	Pathway	Effect
Humans (Camberwick)	Heavy metals, asbestos, high concentration, organics, leachate intermediate concentration, major disturbance	Indirect via windblown dust	Potentially significant, short term (mitigable)
Fauna (Great Wood SBI)	Heavy metals, asbestos, high concentration, organics, leachate intermediate concentration, major disturbance	Indirect via windblown dust	Not significant
Flora (Great Wood SBI)	Phytotoxic metals, high concentration, organics, intermediate concentration, major disturbance	Indirect via windblown dust	Not significant
Surface water (Long River)	Heavy metals high concentration, organics, leachate, intermediate concentration, major disturbance	Indirect via contaminated runoff	Potentially significant, long and short term (mitigable)
Groundwater (minor and major aquifers)	Heavy metals high concentration, organics, leachate, intermediate concentration, major disturbance	Indirect via migration through permeable strata	Potentially significant, long and short term (mitigable)
Materials/structures (Camberwick and prehistoric structures)	Organics, corrosive/aggressive, intermediate concentration, major disturbance	Indirect via migration of contaminated effluent	Not significant

Both qualitative and semi-quantitative approaches can make significant contributions to the risk-management process without the need for more sophisticated methodologies[7]. Examples of projects where semi-quantitative approaches are preferable include multiple land transactions (pre-acquisition or pre-divestiture) and the identification of environmental liabilities across several sites (e.g. manufacturing plants, active landfills, contaminated land sites).

Application: Screening Risk-Management Measures at a Bulk Inorganic Chemicals Plant

A semi-quantitative risk-assessment methodology was used to score risks to sensitive environmental receptors prior to and following proposed remedial measures at a former bulk inorganic chemicals manufacturing plant. The reclamation strategy under consideration focused on intercepting contaminant migration rather than source-term removal. The study focused on measures for protecting surface and groundwater resources in line with the National Rivers Authority (NRA) policy on contaminated land where, for areas with historic widespread contamination, efforts should be directed towards avoidance of further contamination rather than aquifer clean-up[17].

A simple risk ranking system was devised which considered the nature of the hazard (hazard identification) and potential for contaminant migration (exposure assessment) before and after the proposed reclamation strategy. Hazard identification in this study involved consideration of the nature of the processes undertaken at the site, the age of these processes, the nature of likely contaminants and the presence or absence of gas. Site investigation data were available from a number of reports previously undertaken at the site. Inorganic chemical processing and on-site waste disposal had led to contamination of the site, and the presence of coal-measure strata below the site gave rise to the possibility of mine gas. For the purposes of facilitating the exposure assessment and risk characterization, migration pathways were, in this instance, considered in isolation.

Characterization of the risks posed by contaminant migration in surface waters, groundwaters, and gaseous form was performed using a scoring system to provide an overall risk rating. The scoring was conducted on an arbitrary scale for illustrative purposes alone. Scores for the post-reclamation and pre-reclamation scenarios were then aggregated, and the net reduction in relative risk gained from the proposed risk-management measures was presented (Table III).

ESTIMATING RISKS: QUANTITATIVE RISK ASSESSMENT (QRA)

Approach

Application of QRA in the UK has provoked considerable debate because of the aforementioned limi-

TABLE III. Risk Scores Assigned to Various Contaminant Migraton Pathways

Pathway	Presence	Score	Pre-contamination	Post-contamination
Direct pipe discharge to surface water arising for example from an on-site process	Yes/No	2/0	0	0
Indirect discharge to surface water:				
Rainfall runoff over land surface	Yes/No	1/0	1)	
Surface water drainage via drains	Yes/No	2/0	2)=4	0
Flooding	Yes/No	1/0	1)	
Canal water and laternal continuity with groundwater	Yes/No	2/0	2	2
Direct discharge to groundwater via mineshaft/ borehole	Yes/No	2/0	2	0
Indirect discharge to shallow groundwater via vertical infiltration	Yes/No	2/0	2	0
Indirect discharge to deep groundwater via vertical infiltration / leakage	Yes/No	2/0	0	0
Shallow groundwater movement in upper aquifer off-site/on-site	Yes/No	2/0	2	2
Deep groundwater movement in upper aquifer off-site / on-site	Yes/No	1/0	1	1
Gas migration / protection control on-site	None	3		
	Partial	2		
	Complete	1	3	2
Gas migration / protection off-site	None	3		
	Partial	2		
	Complete	1	3	2
		Total	19	9

tations of the baseline toxicology[9]. In the USA, the development of QRA for environmental management has been an extension of regulatory toxicology aimed at regulating carcinogens in the workplace. Formulae have been developed which attempt to translate the high exposures administered to experimental animals in laboratory studies to the extremely low levels experienced by humans during environmental exposures[18, 19]. Arguably, these methods have concentrated too heavily on mathematical calculations of dose rather than the biological mechanisms of response[20]. Nevertheless, the application of QRA is becoming increasingly prevalent within Europe. Recent initiatives include the EC Regulation on the evaluation and control of the risks of existing substances[10], the EC Directive for the assessment of risks to man and the environment of substances[11], and the Inter-governmental Forum on Chemical Safety's programme on assessing and managing chemical risk[12].

The key components for assessing risks from environmental chemical exposures are:

(a) *Hazard identification* (or data collection and evaluation);

[illegible] (or hazard analysis);

[illegible] (effect) *assessment*

[illegible]valuation).

[illegible]ss risks mathematically to source(s) present, [illegible]tes and key sources, [illegible] individual receptors [illegible]ove four stages refer [illegible]gents posing adverse health effects, the [illegible] the amount of exposure (intake) received by the receptor(s), the assessment of the relationship between exposure and the toxic response and finally, the characterization of exposure estimates through their translation into risk estimates. Like any mathematical model, QRA has its limitations, and these act to qualify the estimates of risk and place constraints on the means and manner in which risk is communicated and ultimately managed[20].

QRA necessitates a detailed data-collection process. This is often in conflict with the practical need to determine and characterize the source of hazard at its highest concentration, often performed deterministically on the basis of prior knowledge. Few projects can afford such detail, therefore QRA is correctly viewed as a specialist tool for situations involving a high degree of public interest (e.g. environmental impact assessments for siting waste management facilities) or one reserved for situations of perceived high risk requiring a greater degree of resolution.

Application 1: Environmental Assessment of Waste-to-Energy Incineration Plant

The recent attention given to waste-to-energy plants in various waste-management studies has heightened public anxiety towards incineration. Thus, for completeness of the risk and environmental assessment process, and in order to address the public perception of the risks, QRA is a useful management tool, provided that risk estimates are communicated effectively.

QRA has recently been applied to a proposed 70 000 t/annum energy plant in the south-east of England. The predicted long-term ground-level concentrations of arsenic, cadmium, chromium, nickel, and dioxins and furans were $7x10^{-8}$, $4x10^{-7}$, $3x10^{-8}$, $5x10^{-7}$, and $8x10^{-13}$ mg/m^3, respectively. Carcinogenic risk estimates associated with direct inhalation of these emissions (averaged over a typical lifetime of 70 years) corresponded to a range of associated risks from $2x10^{-8}$/annum to $3x10^{-8}$/annum. The Royal Commission on Environmental Pollution[21] states that there is a consensus among regulatory authorities in the UK and USA that annual incremental risks of death greater than 1 in 10 000(10^{-4}) are too high to be acceptable; and that a risk of 1 in 1 000 000(10^{-6}) represents a reasonable upper level, below which measures to achieve a further reduction in the risk would not be justified in terms of benefit gained. These criteria are also acknowledged by the Health and Safety Executive[22]. In this study, associated risks from the inhalation of carcinogenic emissions of 1 in 33 000 000 to 1 in 50 000 000 are considerably less than the accepted risk level.

An assessment of carcinogenic effects via indirect exposure pathways – ingestion of contaminated soil, dermal absorption and consumption of vegetable produce grown in contaminated surface soils – revealed conservative annual risk estimates of $2x10^{-9}$, $1x10^{-13}$ and $5x10^{-8}$ respectively. Again, with reference to the acceptability criteria, potential carcinogenic risks from these routes were deemed to be negligible.

Application 2: Groundwater Contamination Arising From Transportation Accidents

QRA has recently been used to assess risks to a public groundwater supply (here, the receptor) from contaminant spillages arising from the transportation or industrial accidents within an identified catchment area. The study was undertaken against a background of the ongoing publication of aquifer vulnerability maps for England and Wales. In this instance, the impact (a 'derogation event') was defined as a 'failure' of the UK Water Quality Regulations in untreated abstracted water, which could lead to a potential loss of the resource. As such, this study was essentially an asset management rather than a conventional health-risk assessment, although the concept of 'wholesomeness' of water supply within the Regulations could be considered to exclude any substance present within water at a concentration or value which is detrimental to public health.

The methodology considered risks from transportation or industrial accidents. Local or national

TABLE IV. ESTIMATED DEROGATION PROBABILITIES QUANTIFIED FOR RAIL ACCIDENTS

No. of derogations	Probability of derogation over defined periods							
	10 years		20 years		50 years		100 years	
	Lower bound	Upper bound	Lower bound	Upper bound	Lower bound	Upper bound	Lower bound	Upper bound
>=1	0.005	0.181	0.01	0.33	0.025	0.632	0.049	0.865
>=2	0	0.018	0	0.062	0	0.264	0.001	0.594
>=3	0	0.001	0	0.008	0	0.08	0	0.323
>=4	0	0	0	0.001	0	0.019	0	0.143
>=5	0	0	0	0	0	0.004	0	0.053

statistical data relating to vehicular or rail movements, or industrial accidents involving hazardous materials were compared with local businesses in and around the catchment. This was combined with a sensitivity analysis to define generic groupings of the most likely contaminants, and hence assign probabilities of spillages occurring for each group and spill size (hazard identification). The processes controlling the fate and transportation of spilt contaminants were next considered (exposure assessment), including the degree of protection afforded to groundwater by geological strata and the unsaturated zone. On reaching the water table, the movement of contaminants within groundwater will be subject to various attenuating processes which, acting over a sufficient flowpath length or time, may render the spillage incapable of causing a derogation. This was estimated deterministically using an analytical solution for each group of contaminants and spillage volumes, incorporating observed contaminant degradation rates from published groundwater studies. The results were used to produce an aquifer vulnerability map relevant to each spillage event.

Based on the map, spillage frequencies were then defined using either the length (and category) of road or rail line, or number of industrial facilities located within each area. An estimate of overall frequency of derogation over specific lengths of time were then derived, under the assumption that it follows a Poisson distribution‡. An example of the probability distribution determined for derogation events due to rail spillages, incorporating upper and lower bands for the most likely range of events, is shown in Table IV.

The study sought to compare the overall risk of a derogation event against a recommended acceptable risk, although no such criterion has yet been established for the UK water industry, through a comparison with other 'benchmark' risk criteria. The apparent risk was considerably in excess of this recommended figure, and the most likely spillage scenarios contributing to this risk were identified. As a consequence, clear recommendations could be made for the implementation of a risk management plan to assess specific risk contributory factors, and consider the cost benefits of implementing different risk mitigation measures.

‡where the probability of a Poisson random variable, $P(r) = e^{-\mu} \mu^r / r!$; where $\mu > 0$ is the expected mean and $r = 0, 1, 2, \ldots$ etc.

COMMUNICATING RISKS

The above approaches and applications to risk assessment demonstrate it to be a valuable and flexible management tool for resolving environmental problems. However, all risk-assessment processes must remain cognizant of the stakeholders who, ultimately, will use the information. The emotive nature of perceived environmental risks is such that careful communication of the findings is a necessity, particularly where a highly technical approach such as QRA has been applied. Considering the breadth of interests which may use the risk assessment effective communication to many categories of stakeholder, each with their own requirements, is often an inevitability (Table V).

The ability to meet this wide range of concerns and expectations is based on building confidence and consistency in the methodologies employed. Inherent uncertainties must be declared clearly at the outset, and the use and implications of worst case or most probable scenarios should be explained carefully. The business and financial community are entirely familiar with the judgement of risks to make sound decisions, but may not feel comfortable with environmental issues where financial implications or liabilities appear open-ended. The implications of any residual risk must therefore be specified in a way that allows the value of the resource to be adjusted, capital provisions made for appropriate remedial or abatement technologies, or refinancing to support process changes. This conversion of identified actions or

TABLE V. VARYING NEEDS AND USES OF RISK ASSESSMENT OUTPUT

Example stakeholder	Example requirement
Owner / occupier	Liability assessment; legal responsibilities
Statutory authority	Comparisons with statutory responsibilities and guidance; need for enforcement action
Lender / funder	Security of capital; financial risks
Purchaser / developer	Constraints on investment / development; suitability for intended use
Insurer	Financial and business risk implications; liability assessment
Shareholder	Business performance and balance sheet provisions
Local community	Public health impacts; risk of property blight

remedial work to financial quantification of the risk is essential, allowing businesses to manage environmental risks alongside more familiar issues.

It is increasingly likely that any report on risk assessment will immediately or subsequently reach the public domain. It is also a subject which attracts considerable public interest particularly when, for example, discussing contamination which is perhaps not widely perceived to be present, or which draws attention to liabilities and third-party responsibilities with financial consequences. Under these pressures, many reports suffer from unwise terminology and/or presentation – resulting in an escalation of perceived risk rather than a removal of uncertainty and unfounded fears. To avoid negative impacts, it is necessary to focus attention on defining issues clearly and setting results in an appropriate wider context. Recognition of the low tolerance of involuntary environmental risks[23] is important; indeed, where uncertainties remain, recommendations founded on the precautionary principle are the only recommendations which are likely to find support from the industrial, financial, and regulatory communities.

CONCLUSIONS

1. An overall objective of risk assessment must be to provide clear, defensible statements on environmental risk which (a) reflect the situation under study, (b) are protective of public and environmental health, and (c) are coherent to a range of professionals from scientific, engineering, financial, legal and commercial backgrounds.
2. Risk-assessment strategies must be selected appropriately, and a staged approach provides a balance between a pragmatic assessment of risk and the resolution of ill-defined or high-risk situations.
3. Uncertainties are inherent to discussions of risk because chemical concentrations in the multimedia environment, human behavioural characteristics, and the effects of toxic agents cannot be regarded as absolute.
4. Whilst environmental risk assessments should be justly conservative to protect public health, they should not extend to unrealistic scenarios which over-estimate even reasonable upper-bound risks by orders of magnitude. Over-conservative approaches can engender a misunderstanding of environmental risk and, in the extreme, can undermine contributions from other sources of exposure, or deflect expenditure from more worthy needs.
5. The absence of standardized methods of applying all forms of risk assessment in the UK, at present, maintains a degree of uncertainty for those procuring studies. This should be borne in mind by risk assessors who must ensure that the results are communicated clearly, with appropriate qualifications where necessary.

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(10) COUNCIL OF EUROPEAN COMMUNITIES. Regulation on the evaluation and control of the risks of existing substances (EEC/793/93). *Official Journal.* L84/36, 5 April 1993.

(11) COUNCIL OF EUROPEAN COMMUNITIES. Directive laying down the principles for the assessment of risks to man and the environment of substances notified in accordance with Council Directive 67/548/EEC, (EEC/93/67). *Official Journal* L227/36, 8 September 1993.

(12) ENVIRONMENTAL NEWS DATA SERVICES. New International Forum on Chemical Risk Management, *ENDS Report,* UK, 232, 42-43.

(13) MCKONE, T.E., AND BOGEN, K.T. Predicting the uncertainties in risk assessment. *Envir. Sci. Technol.*, 1991, **25,** (10), 1674-1680.

(14) ASPINWALL & COMPANY. *Channel Tunnel Rail Link: Assessment of Land Contamination Effects.* Aspinwall & Company, Shrewsbury, UK. 1994.

(15) INTER-DEPARTMENTAL COMMITTEE ON THE REDEVELOPMENT OF CONTAMINATED LAND. *Guidance on the Assessment and Redevelopment of Contaminated Land.* ICRCL 59/83, (2nd edn.), EPTS5P187-5RH3. 1987.

(16) MYERS, K., *et al.* Hazard ranking criteria for contaminated sites. *Land Contam. & Reclam.*, 1994, **2,** (1), 13-18.

(17) NATIONAL RIVERS AUTHORITY. P*olicy and Practice for the Protection of Groundwater.* NRA. 1992.

(18) COHRSSEN, J.J., AND CORVELLO, V.T. *Risk Analysis: A Guide to the Principles and Methods for Analysing Health and Environmental Risks.* United States Council on Environmental Quality, Executive Office of the President, NTIS, Springfield, VA, USA. 1989.

(19) UNITED STATES ENVIRONMENTAL PROTECTION AGENCY. *Risk Assessment Guidance for Superfund, Volume 1: Human Health Evaluation Manual (Part A), Interim Final,* Washington, DC, USA. 1989.

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(21) ROYAL COMMISSION ON ENVIRONMENTAL POLLUTION. *Incineration of Waste.* 17th Report. HMSO, London, 1993.

(22) HEALTH AND SAFETY EXECUTIVE. *Risk Criteria for Landuse Planning in the Vicinity of Major Industrial Hazards.* HMSO, London. 1989.

(23) SLOVIC, P., *et al.* Facts and fears: understanding perceived risk. In: *Societal Risk Assessment: How Safe is Safe Enough?* (Schwing, R.C., and Albers, A.(Eds.)) Plenum Press, NY, USA. 1980.

Table 1 Continued

Category 3: slight contamination	*Principal type of contamination‡*
Timber products manufacture	O
Animal processing works	O
Glass manufacture	I
Road haulage yards	O
Building trades products manufacture	I
Printing works	O
Research laboratories	O
Airports & airfields	O
Vehicle manufacture	O
Railway yards/sidings	O
Toiletries, detergents, disinfectants, *etc.*, manufacture	O
Electricity sub-stations	O
Dry cleaners	O

*This categorization is for illustrative purposes. It will give a broad indication only of whether the business concerned involves a contaminative use and, if so, the degree of seriousness of that contaminative use, and nature of the contamination arising from a contaminative use.
†Whether a business falls within a particular category will depend on a number of further factors, such as: whether the previous business use of the site has given rise to contamination; the length of time for which the site has been used for the business purpose; the overall sensitivity of the site with respect to its broader environmental setting; assessment of the extent to which the business follows good environmental practices and management controls; the extent of the manufacturing or processing activity which is carried on by the business and the site; assessment of the influence of the underlying geology and its hydrogeological characteristics.
‡'O' signifies organic contamination; 'I' signifies inorganic contamination.

incidents in the 1980s and early 1990s (Figure 1). At this time, investigation for soil and groundwater contamination was merely costed for in the purchase of land for redevelopment, and prior investigation was frequently patchy or non-existent. Three events which were influential in focusing concern about contaminated land are summarized in Table 2.[1,3,4]

These and other sites were described to the House of Commons Environment Committee in 1989 and their report, published in 1990,[5] called for registers of contaminated land to be established. This greatly influenced DoE thinking on the Environmental Protection Act, which was at the final drafting stage. The DoE had previously aimed to provide guidance to developers through advisory limits for concentrations of contaminants through publications from the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL). The idea of registering known or potentially contaminated land was more interventionist

[3] Derbyshire County Council (DCC), *Report of the Non-statutory Public Inquiry into the Gas Explosion at Loscoe, Derbyshire 24 March 1986*, DCC, Derby, 1988, vols. 1 and 2.
[4] M. Sury and A. Slingsby, *Proceedings of the 2nd International Conference on Construction on Polluted and Marginal Land*, Brunel University, London, 1992, pp. 379–384.
[5] House of Commons Environment Committee, *Contaminated Land*, HMSO, London, 1990, vols. I, II and III.

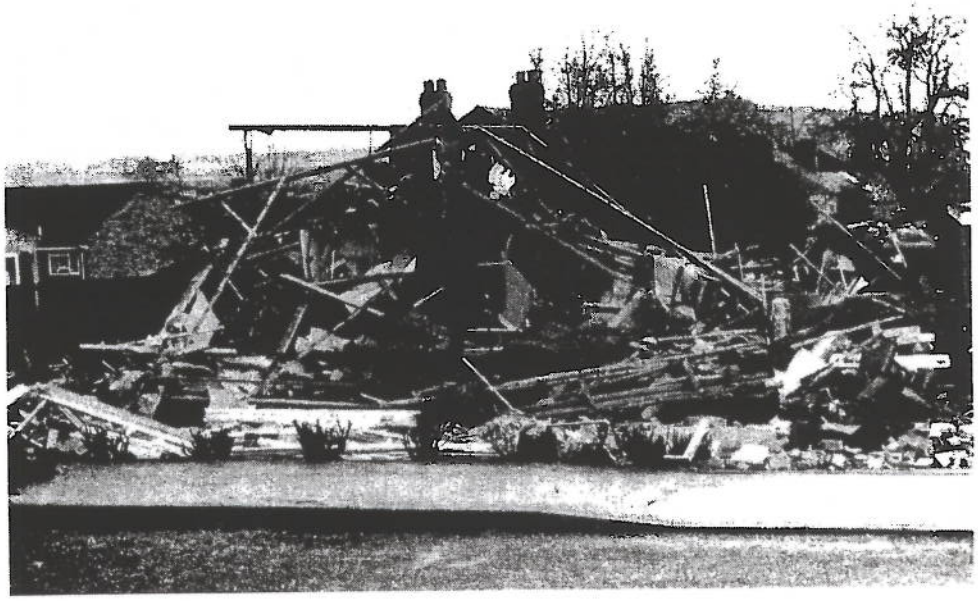


Figure 1 Bungalow demolished by landfill gas explosion. (Courtesy of the Derbyshire Constabulary)

and, if not handled extremely carefully, could blight urban areas where redevelopment and investment is most needed.

In 1990, the DoE published the Government's response to the Environment Committee.[6] Linked to this were three actions which injected momentum into the field of contaminated land assessment:

1. A provision (section 143) was made in the Environment Protection Act 1990 for regulations requiring local authorities to compile registers of potentially contaminated land.
2. The DoE initiated a process of consultation on registers and contaminated land policy.
3. The DoE began to expand its research programme to provide broader guidance on contaminated land.

Once a proposal for registers of potentially contaminated land was incorporated in legislation, a lengthy and active debate was triggered. The Government sought to focus and inform this debate by a series of consultation papers as new policy was developed. The DoE also informed itself through international liaison where alternative approaches have been offered, many of these coming under national criticism over expense or quality of environmental protection. An interpretation of the key points emerging during this debate is offered in Table 3. In understanding the current legislative position on contaminated land it is important to have regard to this recent period of debate and uncertainty, with the emergence of a true risk-based approach founded on firm scientific and

[6] Department of the Environment, *The Government's Response to the First Report from the House of Commons Select Committee on the Environment on Contaminated Land*, HMSO, London, 1990.

Table 2 Example incidents at contaminated land sites

Site	*Date of incident*	*Description of problem*	*Costs/implications*
Clarke Avenue, Loscoe, Derbyshire[3]	March 1986	Explosion due to landfill gas migration demolished bungalow, badly injuring the occupants	£325–375k;[1] continued difficulties with mortgage lending and insurance
Ilford, Essex[4]	Late 1980s	Low level radioactivity found on former chemical site being redeveloped for housing	£10 million approx.; extensive remediation and delays to site development
Lumsden Road, Portsmouth, Hampshire[1]	1991	120 families rehoused after Ministry of Defence development of 1950s/1960s constructed on former Royal Navy waste site found contaminated with asbestos and heavy metals	£6.12 million,[1] including rehousing, medical screening, demolition, remediation and rebuilding

toxicological principles. Further detail on the current regulatory framework and its foundation on risk assessment is given in Section 3.

Current Consequences

The current position with contaminated land is largely attributable to the response from Government, and more widely to the concerns highlighted at the beginning of this decade. These have led to a radical and rapid change in the technical approach to evaluating and remediating contaminated land. The routine introduction of risk assessment, a phased and chemically orientated approach to site investigation, and the selection of remediation strategies from more technologies than simple cap and cover systems are all rapidly developing areas described below in Sections 3–5. Underpinning these developments have been the changes in the legislative position, the growth in research based guidance, particularly from DoE, and the availability of specialist expertise from environmental consultants (see Section 6).

From a technical viewpoint, recent developments have been extremely beneficial. The complexity of evaluating contamination has been thoroughly exposed, and the risk associated with facile and inadequate approaches prevailing in the market place has been much reduced. The prospect of new guidance values for key contaminants which take account of the availability, toxicity, pathway and impact of the contaminant will be a significant improvement over existing ICRCL guidance. However, the draft guideline values only address human health. Separate and additional assessment techniques are required for ecological, phytotoxic and physical damage potential. The link has also been

Table 3 Key issues arising from UK contaminated land policy development since 1990

Date	*Action*	*Description*	*Consequence*
May 1991	Consultation Paper on Public Registers[7]	Proposals to introduce local authority administered registers of potentially contaminated land: 'land subject to contaminating uses'; 40 such uses identified	Initiated wide debate on use of registers and contaminated land in general; concerns over blight and application of 'polluter pays' principle expressed
July 1992	Revised Proposals for Public Registers	List of contaminating uses reduced to eight, representing perhaps 10–15% of area of 1991 proposals[1]	Concerns over land values and blight shown to be fundamental to principle of registers, not to their scope. Objectives of register: received wide support; their consequence did not
March 1993	Registers withdrawn; Government Policy Review initiated	An alternative to registers was sought to achieve improvement in knowledge and planning for contaminated land redevelopment and remediation	Many relevant professions now actively engaged in finding an acceptable policy solution
March 1994	*Paying for our Past*, Consultation Paper issued	Included a focus on the dilemma of the 'polluter pays' principle *versus* the large historical legacy of contaminated land	Enhanced recognition that a risk-based approach was needed to prioritize the few sites which caused actual environmental harm
November 1994	*Framework for Contaminated Land* published[8]	Reaffirmed UK 'suitable for use' approach which requires remedial action only where contamination poses unacceptable risks to health or the environment, taking into account land use and setting	Identified need to build on existing statutory nuisance powers as primary basis for dealing with contaminated land

Table 3 Continued

Date	*Action*	*Description*	*Consequence*
1995	*A Guide to Risk Assessment and Risk Management for Environmental Protection* published[9]	Risk Assessment promoted as key method of approach and later in the year new draft guideline values for the human health assessment of contaminants in land are developed based on toxicological and exposure pathway risk assessments	Risk-based approaches promoted by wide range of professions and development authorities start to become more consistent and authoritative
1995	s57 of Environment Act inserts new Part IIA into Environmental Protection Act on Contaminated Land	The new legislation aims to clarify which land should be regarded as contaminated, who should pay for necessary remediation, and remove blight through suspicion of future regulatory control	The new provisions are complex, requiring support from extensive statutory guidance
September 1996	Draft Statutory Guidance on Contaminated Land published for consultation[10]	The guidance provides specific definitions under the terms of the 1995 Act, and addresses the inspection (by local authorities), definition and remediation of contaminated land as well as apportionment of liabilities for, and recovery of, the costs of remediation	Continued active consultation (until December 1996) and highlighting of link to extensive technical guidance published by the DoE and others to support the identification, classification and remediation of contaminated sites

[7] Department of the Environment (DoE) and Welsh Office, *Public Registers of Land which may be Contaminated: A Consultation Paper*, DoE, London, 1991.

[8] Department of the Environment (DoE), *Framework for Contaminated Land: Outcome of the Government's Policy, and Review, and Conclusions from the Consultation Paper 'Paying for our Past'*, HMSO, London, 1994.

[9] Department of the Environment (DoE), *A Guide to Risk Assessment and Risk Management for Environmental Protection*, HMSO, London, 1995.

[10] Department of the Environment (DoE), Welsh Office and Scottish Office, *Consultation on Draft Statutory Guidance on Contaminated Land*, DoE, London, 1996, vols. 1 and 2.

made between the soil and water environments,[11] so that contaminated land assessment and remediation should succeed in addressing all potential impacts in one overall risk-based approach. Such an integrated approach places new demands on the quality of the advice available on contaminated land. Awareness of the rapidly developing technological base is required, whether in investigation, risk assessment or remediation. A common understanding and language must be used to transfer knowledge clearly between chemists, engineers, environmental scientists, chartered surveyors, developers and lawyers, to name a few of those whose skills are needed to deal successfully with contaminated land. It is against this background of escalating demand that this article has been produced.

2 Identifying Contamination

To contaminate is defined as 'to make impure or pollute' in the Oxford English Dictionary. For the purposes of dealing with land, contamination is now taking on a dual meaning. The first is defined by legislation in the Environment Act 1995, and relates to the potential to cause significant harm to humans or pollution of controlled waters. In a wider sense, however, contamination may be viewed as a condition whereby soil or water contains above background concentrations of substances which are not normally there. These can be both chemical and physical, but for the purposes of this review, chemical contamination is most relevant.

Defining soil as contaminated is not merely a question of whether a chemical substance, say cadmium or phenol, is present, but whether it is present in sufficient quantity to cause harm. In relation to the Environment Act 1995, harm is defined, *inter alia*, as death, serious injury, disease, genetic mutation or birth defects. A great deal of cadmium or phenols are needed in soil to cause death and, furthermore, death will only occur if the soil is ingested in large quantities. So this raises the question of whether the mere presence of a chemical in soil at high concentrations is contamination. The answer in the UK is that such soil is contaminated, but the land would only be defined as 'contaminated land' under the regulatory regime if harm was occurring or likely to occur.

Clearly then, contamination of soil or water may exist, but if it is not causing harm it is possible to consider leaving it alone until such time as a particular site needs to be developed or reclaimed.

Contamination can create a range of hazards, depending on its composition and nature. It may be present in solid, liquid or gas phases, and may be physical, chemical or biological. Contaminants that are hazardous to humans are not necessarily hazardous to building materials or flora. Hazards may include:

- carcinogenicity
- toxicity
- asphyxiation
- corrosivity
- phytotoxicity

[11] Department of the Environment (DoE), *A Framework for Assessing the Impact of Contaminated Land on Groundwater and Surface Water*, CLR1, DoE, London, 1994, vols. 1 and 2.

- combustibility
- explosivity
- radioactivity

The process of assessing whether the existence of contamination matters is termed risk assessment. This is discussed more fully in the next section. Of prime importance in carrying out a risk assessment is the need to identify what or who is at risk, and these risk groups are termed targets or receptors. They comprise the following:

(i) People
- adults
- children
- site workers (temporary and permanent)
- permanent residents
- visitors
- neighbours

(ii) Water resources
- surface water
- groundwater

(iii) Flora and fauna
- sites of special scientific interest (SSSIs)
- livestock and wild animals, birds, *etc.*
- landscaping

(iv) Buildings
- foundations
- services
- structures

It should be remembered that not all the above receptors will exist at all locations, and part of the risk assessment process will be to define site-specific receptors.

3 Risk Assessment

Principles

With introduction of the new regulatory regime for contaminated land in section 57 of the Environment Act 1995, the UK has endorsed a risk-based framework within which contaminated land can be identified, assessed and managed.[8] This framework adopts a rationale and terminology from accepted international approaches to the regulation of environmental media and it embodies the fundamental distinctions between toxicity, hazard and risk that exist throughout environmental science. These terms are defined below:

- toxicity: the potential of a material to produce injury in biological systems
- hazard: the nature of the adverse effect posed by the toxic material
- risk: the probability of suffering harm or loss under specific circumstances

The term 'risk' has a multitude of uses and is not to be confused with 'hazard'. In the context of contamined land, the term 'risk' is used widely across disciplines when referring to issues such as first and third party financial liability, risks to human health and the environment, the perceived consequences of chemical exposure and the operational risk of project over-run. There is always a requirement, therefore, to state clearly what form of risk is under consideration and what its components are.

In terms of contaminated land, risks to human health and the environment can be regarded as being comprised of the following components:

- a source: a toxic substance or group of toxic substances with the potential to cause harm
- a pathway: a route by which a receptor could be exposed to, or affected by, the toxic substance(s)
- a receptor: a particular entity which is being harmed or adversely affected by the toxic substance(s)

Hazards arising from chemical exposure are characterized specifically by the nature of the adverse effect, the receptor and the target they affect; like physical hazards, they can only be realized where there is a 'linkage' between the source, the pathway and the receptor. The probability of a hazard being realized, *i.e.* the risk, depends on the context of this linkage, including site-specific factors such as the contaminant concentration in the exposure medium, its bioavailability, the ease of access to the exposure pathway and the duration of exposure. The consequences of the risk under consideration depend on site-specific factors such as the toxicological potency of the contaminant being considered, the specific adverse effect on the receptor, the duration of exposure and the sensitivity of the receptor (*e.g.* child *versus* adult, sites of special scientific interest (SSSIs) *versus* unprotected ecosystems of low sensitivity).

Risk Assessment. The process of risk assessment can be defined as simply 'an evaluation of the probability of harm'[12] and, in the context of contaminated land, is concerned with gathering and interpreting information on the characteristics of sources, pathways and receptors at a specific site and understanding the uncertainties inherent to the ensuing assessment of risk. The requirements of the risk assessment set the scope of a site investigation and, together, these activities form the scientific part of the contaminated land investigation. In practice, this involves characterization of the environmental chemistry of the contaminants, relevant properties of the soil(s) encountered and the wider site characteristics that influence contaminant fate and transport.

The environmental properties of chemicals encountered at contaminated land sites (Table 4)[13] determine the distribution, fate and transport of the contamination and play a major role in determining:

[12] L. D. Hooper, F. W. Oehme and G. R. Krieger, in *Hazardous Materials Toxicology*, ed. J. B. Sullivan, Jr., and G. R. Kreiger, Williams and Wilkins, Baltimore, 1992, pp. 65–76.

[13] S. J. T. Pollard, R. E. Hoffmann and S. E. Hrudey, *Can. J. Civil Eng.*, 1993, **20**, 787.

Table 4 Environmental fate and transport properties of selected contaminants

Compound	*Aqueous solubility* ($mg l^{-1}$)	*Vapour pressure* (Pa)	K_{oc}*	*Dominant partition medium*
Benzene	1780	1.3×10^{4}	65	Air
Phenol	8.2×10^{4}	71	14	Water
Hexachlorodibenzo-*p*-dioxin	1.3×10^{-4}	1.9×10^{-6}	2.6×10^{7}	Soil
Benzo[*a*]pyrene	3.8×10^{-3}	7.3×10^{-7}	5.5×10^{6}	Soil

*Organic carbon–water partition coefficient.

(i) the suite of chemical analyses undertaken as part of the site investigation
(ii) the exposure assessment component of the risk assessment
(iii) the screening of remedial technologies

Because soil is itself a multi-media environment comprising solid, liquid, gaseous and biotic components, understanding the relative distribution and flux of contaminants between these components is an essential prerequisite to the site investigation, risk assessment and remedial plan. For example, the 4–6 ring polynuclear aromatic hydrocarbons (PAHs) possess very high soil organic carbon–water partition coefficients and remain predominantly adsorbed to the solid soil matrix. Therefore, where high molecular weight PAHs are of concern, analytical efforts focus on soil-bound PAH; the exposure assessment centres on pathways that involve the ingestion and inhalation of soil particles; and the remedial plan considers specific technologies that treat the soil matrix, such as soil-phase bioremediation.

The process of risk assessment[14] can be viewed as consisting of four key stages:

- hazard identification (what are the hazards presented by toxic substances at the site?)
- exposure assessment (what are the key environmental pathways and exposure routes by which the toxic substances can reach the receptors and, if required, what are the concentrations of substances at the point of exposure?)
- dose–response assessment (how potent are the toxic substances that can reach the receptor?)
- risk characterization (what level of risk can be assigned to each source–pathway–receptor linkage?)

Methodologies for contaminated land risk assessment vary widely between practitioners and jurisdictions but can essentially be categorized as qualitative, semi-quantitative and quantitative in their approach. In most cases, a qualitative assessment of risk is sufficient to identify the key issues at a contaminated site, providing it includes the full range of toxic contaminants encountered, takes account of direct and indirect exposure pathways and considers relevant receptors on and off the site.

[14] S. J. T. Pollard, D. O. Harrop, P. Crowcroft, S. H. Mallett, S. R. Jeffries and P. J. Young, *J. Chart. Inst. Water Environ. Manage.*, 1995, **9**, 621.

Where the source–pathway–receptor linkage is established, the qualitative approach can usefully provide an initial ranking of risks as insignificant, low, medium and high, depending on the site-specific factors mentioned above. These obviously are subjective designations and would require their own criteria in order to achieve uniformity of approach between sites (Table 5). Within the context of a tiered approach to risk assessment, semi-quantitative and quantitative risk assessment (QRA) methodologies are reserved for situations where greater resolution is required between risks in order to select between risk management options. QRA has become a highly specialized tool that relies heavily on the expert understanding and interpretation of baseline toxicological data. It can be applied only where contaminated sites are very well characterized and hazards are well defined (*e.g.* sites with radioactivity).

Risk Management. Risk management involves 'the evaluation of alternative options taking into account available economic, regulatory, political, social, scientific and technological information in order to select the most appropriate means of reducing risk' (adapted from La Grega *et al.*[15]). In practice, risks are managed by isolating or removing contaminant sources, intercepting exposure pathways or isolating or removing receptors; the guiding principle is to break the source–pathway–receptor linkage. The process of risk management employs the scientific output of the risk assessment, but considers other factors such as the financial and technical feasibility of remedial technologies, planning constraints and risk perception issues.

Environmental Criteria Development

Two recurrent themes with respect to contaminated land over the last 20 years have been 'when is a site contaminated?' and 'how clean is clean?'. Regulatory approaches to addressing these questions have, historically, relied on the development of environmental assessment criteria for soils and groundwaters, against which analytically determined site concentrations can be assessed. It is usual to take into account analytical detection limits and background concentrations in establishing such criteria. Three approaches have been dominant:

(i) the 'trigger' and 'action' guideline concentrations such as those developed by the UK Inter-departmental Committee on the Redevelopment of Contaminated Land (ICRCL), which considers two tiers of intervention: the 'trigger' value indicating when further investigation is necessary, and the 'action' value indicating where some form of remedial action is likely for the proposed end use of the site
(ii) the 'ABC' guideline values historically adopted by the Dutch Government and Ontario Ministry of Environment which represented background (A), intermediate (B) and heavy (C) levels of contamination for soil and groundwater

[15] M. D. LaGrega, P. L. Buckingham, J. C. Evans and the Environmental Resources Management Group, in *Hazardous Waste Management*, McGraw-Hill, Maidenhead, 1994, pp. 837–882.

Table 5 Example of a site-specific qualitative risk assessment matrix

Source	*Hazard*	*Pathway*	*Receptor*	*Site-specific risk*
Chromium(III)	Non-carcinogenic toxicity	Incidental ingestion	Humans, site fauna	Low to medium
		Inhalation	Humans, site fauna	Low to medium
		Dermal contact	Humans, site fauna	Low to medium
		Leaching	Watercourse	High
		Leaching	On-site buildings	Low
Chromium(VI)	Non-carcinogenic toxicity	Incidental ingestion	Humans, site fauna	Medium
		Inhalation	Humans, site fauna	Medium
		Dermal contact	Humans, site fauna	Medium
		Leaching	Watercourse	High
		Leaching	On-site buildings	Low to medium
	Carcinogenic toxicity	Inhalation	Humans, site fauna	Medium
Zinc	Phytotoxicity	Root uptake	Site flora	Low to medium
Suspended solids	Increased turbidity	Direct run-off	Watercourse	High
Methane	Explosion	Permeable strata	Buildings	High

(iii) the health risk assessment approach to site remediation enforced by the United States Environment Protection Agency (US EPA) under the 'Superfund' legislation which sets individual criteria, as 'applicable, relevant and appropriate requirements (ARAR)' determined on the basis of a site-specific risk assessment and adopted as site-specific clean-up requirements

Risk-based Criteria. Dissatisfaction with these historical approaches to environmental criteria development[16] is now leading to the establishment of risk-based environmental assessment criteria for soils and groundwaters that combine the simple screening function of numerical criteria within a tiered risk-based rationale. One example of this approach is the American Society for Testing and Materials' (ASTM) guide for 'Risk-Based Corrective Action at Petroleum Release Sites' (RBCA).[17] Here, the first tier of environmental criteria

[16] S. E. Hrudey and S. J. Pollard, *Environ. Rev.*, 1993, **1**, 55.

[17] American Society for Testing and Materials (ASTM), *Emergency Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites*, ASTM, Philadelphia, 1994.

(air, soil and groundwater concentrations) for screening petroleum-contaminated sites are a set of risk-based screening levels. Sites with media concentrations in excess of these levels require higher levels of site characterization with site-specific second and third tier criteria being developed to achieve accepted *de minimis* levels of risk.

This general approach has also been adopted by the Dutch Government in the 1994 Soil Protection Act, with the exposure assessment model 'CSOIL' being used to derive new, risk-based intervention values for soil and groundwater at contaminated sites.[18] The UK DoE strategy has also been similar, with the 'CLEA' exposure assessment model being used to derive new, risk-based criteria to replace the ICRCL trigger concentrations. A useful discussion of the UK approach is provided in the Royal Commission on Environmental Pollution (RCEP) 19th Report on the Sustainable Use of Soil.[19]

Notwithstanding these improvements to the regulatory approach, problems remain with the limited ability of measurements of total concentrations to reflect the different behaviours and toxicities of combined or dissociated forms of contaminants, or of isomers of individual contaminants within soil.[16] Likewise, continued use of criteria based on solvent-extractable matter such as toluene-extractable matter, as surrogates for the organic characterization of contaminated soils, ignores the different solubilities of organic compounds across a wide range of solvent polarities. Analytical efforts in such cases need to progress beyond a rudimentary screen of solvent-extractable matter if they are to characterize contaminant-specific risks.[20]

Recent Regulatory Framework

The contaminated land provisions in the UK introduced in the 1995 Environment Act insert a new Part IIA into the Environmental Protection Act 1990 (EPA 1990) consisting of sections 78A to 78YC. The background to the legislation and a summary of the provisions are available.[21] In brief, the Act provides a new regime for the control of threats to health and the environment from land contamination and enacts the policy objectives set out in the UK Government's 1994 paper 'Framework for Contaminated Land' (Department of the Environment, 1994).[8] The key features of the new legislation are:

- a new definition of contaminated land
- endorsement of the 'suitable for use' approach: the new regime deals with unacceptable risks that arise from the current use of the land; change of use issues continue to be addressed by the existing planning process

[18] F. A. Swartjes and R. van den Berg, *Remediation of Contaminated Soil and Groundwater: Proposals for Criteria and Priority Setting*, Royal Institute of Technology Workshop on Contaminated Soils, Department of Chemical Engineering, Stockholm, 1993.

[19] Royal Commission on Environmental Pollution (RCEP), *Sustainable Use of Soil*, 19th Report of the RCEP, HMSO, London, 1996, pp. 130–133.

[20] S. J. T. Pollard, S. L. Kenefick, S. E. Hrudey, B. J. Fuhr, L. R. Holloway and M. Rawluk, in *Analysis of Soil Contaminated with Petroleum Constituents*, ed. T. O'Shay and K. B. Hoddinott, ASTM, Philadelphia, 1994, pp. 39–52.

[21] O. McIntyre, *J. Property Dev.*, 1996, **1**, 5.

- the primary regulatory role rests with the local authorities, reflecting their existing role with respect to statutory nuisance and as planning authorities; the Environment Agencies will act as the enforcing authority for a new designation of 'special' sites
- both enforcing authorities are required to keep a public register of regulatory action
- contaminated land is to be identified on the basis of a risk assessment that uses the source–pathway–receptor approach in the first instance
- where feasible, the 'polluter pays' principle will be applied and persons who caused or knowingly permitted contamination will bear the responsibility for paying for remediation required by a remediation notice; where the polluter cannot be found, responsibility will pass on to the owner/occupier
- the Environment Agencies will provide local authorities with site-specific guidance, regulate special sites, publish periodic reports on the status of contaminated land, sponsor technical research and act as centres of expertise on the subject

The provisions are currently anticipated to come into effect in 1997 and are regarded as addressing much of the uncertainty that previously existed over issues of land contamination. They aim to ensure that actions on contaminated land are directly linked to a technically well-founded assessment of risk. Land will be determined as contaminated only where connectivity between the source, pathway and receptor is established and there is at least one of the following:

(i) evidence of significant harm, or
(ii) the significant possibility of significant harm, or
(iii) the pollution of controlled waters, or
(iv) the likelihood of pollution of controlled waters

In this manner, the perceived automatic blight associated with the 'potentially contaminative use' approach put forward by Section 143 (EPA 1990) registers is addressed, action is prioritized on unacceptable actual or potential risks to human health and the environment, and sites are improved as and when hazards need to be dealt with.[8]

Application to the Water Environment

The Environment Agency in England and Wales is empowered to take 'anti-pollution works' under section 161 of the Water Resources Act 1991 to deal with the polluting effect of contaminated land on controlled waters and recover the costs from the responsible person. The Scottish Environmental Protection Agency (SEPA) has similar powers under sections 46A–C of the Control of Pollution Act 1974, as subsequently amended.

'Pollution of controlled waters' is defined in the Environment Act 1995 contaminated land provisions as meaning the entry into controlled waters of any poisonous, noxious or polluting matter or any solid waste matter. In their implementation of the new regime, local authorities are to apply a similar

approach to that currently used by the Agencies in determining whether the pollution of controlled waters is, or is likely to be, caused. In the latter case, these approaches place a strong emphasis on determining contaminant concentration and availability (combined form, inherent aqueous solubility), mobility (soil adsorptive capacity, porosity and permeability, effective rainfall), the presence of intervening sub-strata, and the presence or absence of existing risk management measures. Determination of these factors relies in part on the results of appropriate leaching tests that establish the propensity of *in situ* contaminants to move through the soil. The importance of these tests is likely to increase substantially under the new contaminated land regime.

Uncertainty Issues

Implementation of the new contaminated land regime in the UK will do much to address the uncertainties associated with the subject in the sense of providing a consolidated piece of legislation and defining responsibilities to deal with the issue. Site-specific uncertainties, however, will always be present, given the complexity of the soil environment. These need to be acknowledged at the outset of an investigation so that effort and resources are focused on issues that improve the overall quality of the information gathered in support of the risk assessment.

Analytical precision and accuracy are issues that require continual scrutiny throughout site assessment and remediation, and many of these issues are now being addressed through various inter-laboratory proficiency schemes. A similar level of attention must be paid to the representativeness of sampling methodologies and sampling techniques. QRA methodologies are constrained by the quality of the baseline toxicological information on which they rely and the relevance of the numerous assumptions they employ in the preparation of risk estimates. Acknowledging such uncertainties is not to negate analytical chemistry or risk science but allows appropriate use of the output from these disciplines for the particular audience, whether a regulator, land owner, financier or member of the public.

4 An Approach to Site Investigation

Site investigation provides the means by which the basic data blocks for risk assessment are assembled. When designing an investigation, it should always be remembered that the outputs must serve several purposes:

- definition of sources of contamination
  - location of contaminant
  - nature of contaminant
  - concentration
  - total loading
- identification of pathways
  - site topography
  - soil/rock permeability

joint/bedding systems
man-made pathways (shafts, pipe backfill, *etc.*)
surface drainage channels
- location of sensitive receptors
  depth to groundwater
  proximity of surface water

At the same time as determining data for contamination assessment, it may also be appropriate to consider geotechnical issues, such as ground stability, which could affect the nature of remediation measures.

Investigations are most effective when phased. The most common phasing consists of the following steps:

(i) desk study
(ii) main intrusive investigation
(iii) supplementary intrusive investigation

Monitoring of piezometers and standpipes can take place in parallel with intrusive investigations, and the benefit of monitoring over a period of time should not be underestimated. Figure 2 sets out the framework for undertaking investigations of potentially contaminated land.

Desk studies will include historical research of a range of sources to obtain the maximum available information on the site and the previous industrial uses. Sources may include Ordnance Survey maps, previous site owners, regulatory authorities such as the Environment Agency, landfill operators and planning and environmental health authorities. In addition, geological, hydrological and hydrogeological records should be searched.

On completion of the desk study, the main investigations can be designed, either as a single comprehensive survey or as a series of stages targeting specific high-risk areas or problems. The investigation may use a range of techniques, some of which involve non-intrusive activities and others which require physical sampling on site. These techniques are summarized below:

- Non-intrusive
  site walkover
  surface gas emission testing
  geophysical testing
  false colour infrared photography
  thermography
  tracer gas testing
- Intrusive
  boreholes
  trial pits and trenches
  probing techniques
  static cone penetrometer
  window sampling
  gas and water monitoring wells

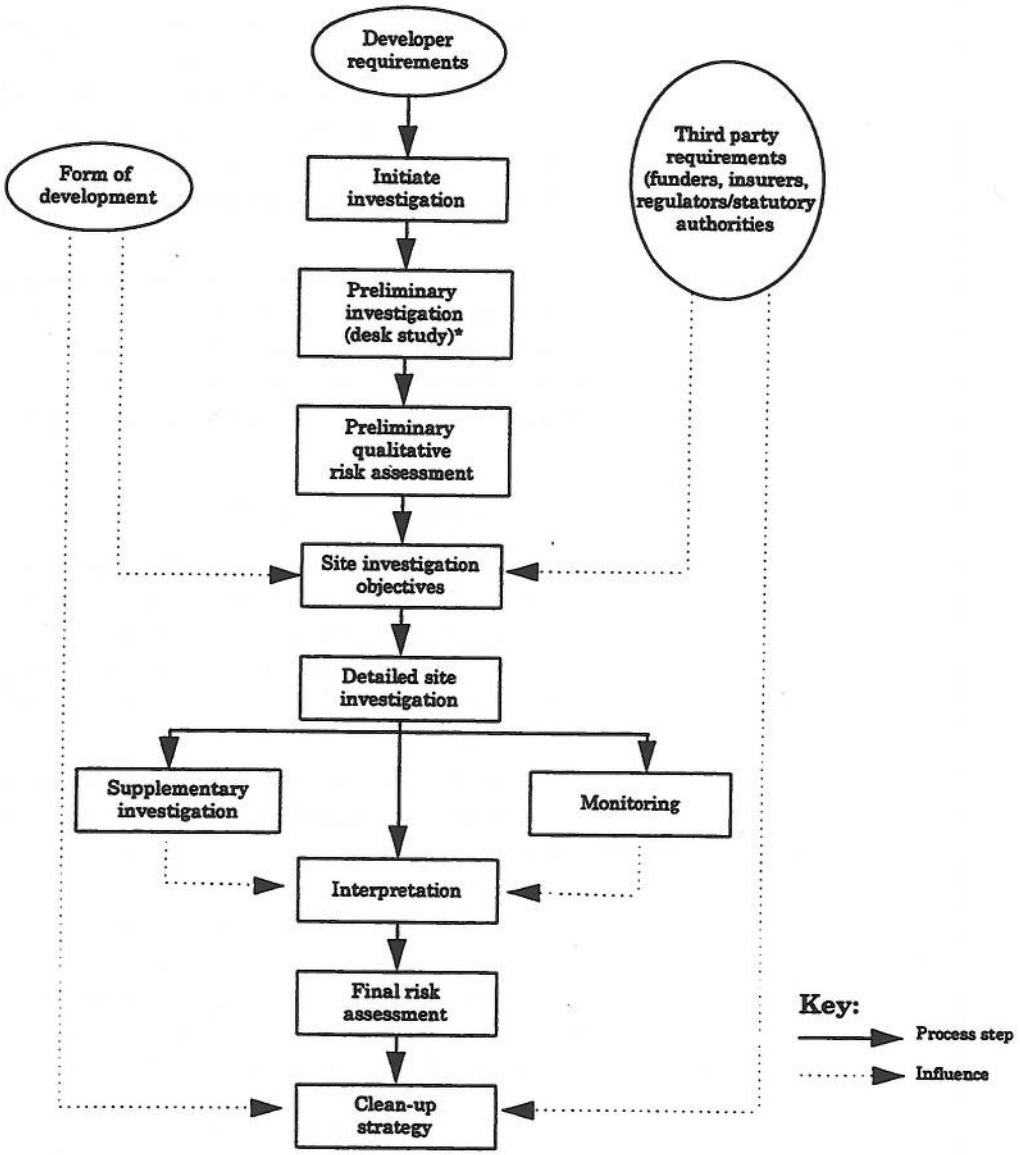


Figure 2 Investigation process for contaminated land

All opportunities for data collection should be seized upon, and data should be collated and assessed in a systematic manner. For example, when installing monitoring wells, the borehole should be fully logged and described to provide a complete record of the strata. This will aid both decisions about the depth to which screen sections should be installed, and a wider understanding of the site conditions and potential migration pathways.

The extent of investigation of a site is very much a matter for professional judgement based upon an understanding of the history of site usage (derived from the desk study) and the proposed future use. The degree of confidence which can be placed upon the results of an investigation are a function of the following variables:

- the number of soil, water and gas samples taken
- the number of samples tested
- the number of exploratory holes from which the samples are taken
- the spatial layout of exploratory holes
- the extent of any *in situ* testing
- the frequency and duration of subsequent monitoring

Whilst it would be easy to design an investigation with a very large number of sampling and testing locations, this would be a costly and inefficient approach, and investigations should always seek to balance the degree of confidence required against the total cost of the work. Much work is being carried out on sampling strategies[22] and this provides a rational basis for designing investigations.

5 Remediation Strategy

If risk assessment establishes that there is an unacceptable risk of a pollution event or hazard exposure to a sensitive target, then it will be advisable to undertake remedial measures or change operational practices to minimize future risk. In the context of contaminated land, this may mean carrying out additional work during redevelopment to achieve one or more of the following objectives:

- eliminate the hazard by total removal/treatment
- control the hazard by encapsulation or separation
- cut off pathways for contaminant movements by use of barriers or sealing systems
- remove or protect sensitive targets

If redevelopment is not proposed, it may still be necessary to carry out work on land to guard against future liability, and this may be particularly the case for sites which have ongoing active industrial use. Furthermore, if the work is to be undertaken without any prospect of enhanced value, then a further stage to risk assessment is sometimes considered which compares the magnitude and likelihood of financial penalties against the cost of clean-up. This balance is not just a financial one, however, as legal penalties associated with environmental damage in recent legislation also include prison terms and disqualification of directors. Thus any person considering just the financial aspects of damage to the environment should also take legal advice on the additional risks that he or she runs.

When determining the best course of action for remedial/control works, the following factors must be taken into account:

- engineering feasibility
- economics
- health and safety

[22] Department of the Environment (DoE), *Sampling Strategies for Contaminated Land*, The Centre for Research into the Built Environment, The Nottingham Trent University, CLR4, DoE, London, 1994.

- environmental impact
- current and future standards/codes of practice
- legislation

Engineering feasibility must be considered for any physical solution which is deemed necessary at a contaminated site. This means that the solution must be practical and buildable, and appropriate to the ground conditions. Schemes which require separation of contaminated soil from clean when the two are visually indistinguishable must be designed with the time delays of chemical testing in mind. Cover systems should combine natural and synthetic layers as appropriate, and the thickness of layers must take into account both their theoretical performance and the practicalities of laying specified materials to a given thickness.

Economics are fundamental to the progression of a scheme, and having established through the risk assessment that there is a requirement for clean-up, then cost must be controlled to ensure that the development scheme can generate sufficient funds to cover the additional reclamation costs. This condition applies for both the public and private sector.

When designing the clean-up strategy, both health and safety and environmental impact issues must be considered such that when a solution is finally chosen, it can be demonstrated to have considered all issues in addition to basic cost. The chosen solution should balance all environmental impacts against cost and final site condition to provide the required reduction in risk, the minimization of environmental impacts and a reasonable cost, thus following the strategy of the Environmental Protection Act of Best Available Technology Not Entailing Excessive Cost (BATNEEC). Furthermore, the Construction Design and Management (CDM) Regulations (1994) require that hazards to the construction workforce are addressed by the Client, the Designer and the Principal Contractor, and this is particularly an issue for contaminated land.

Techniques for dealing with contaminated land in the UK have evolved over the last 30 years from relatively cosmetic solutions of thin soil covers, designed to support minimal vegetation, through to more sophisticated treatment technologies or engineered encapsulation solutions. There are three broad categories of solution which are currently available:

- risk avoidance methods
- engineering methods
- process-based methods

Risk avoidance options include changing land use, site layout and location of services and other infrastructure, thus reducing the risks to particular targets through changing the pathway and isolation of the target. They are not usually feasible where development already exists and are limited to the type of receptor they will protect. Furthermore, if a particular site is designated for, say, housing under a Local Plan, then a change of use may be very difficult to achieve. Assuming that all viable risk avoidance techniques have been adopted, then either engineering or process-based methods or a combination of both must be adopted to deal with the remaining risk.

Engineering methods are based upon conventional civil engineering techniques and are used to remove or isolate the sources of contamination or modify the pathway. They broadly comprise:

- excavation (may be followed by off-site or on-site disposal)
- in-ground barriers such as cut off/vent trenches and slurry walls
- covering and capping systems
- hydraulic measures such as pumped control of contaminated groundwater

Whereas engineering methods do not alter the state of contamination, process-based methods may be defined as treatment to remove, stabilize or destroy contaminants. The unit processes developed for cleaning contaminated soils can be divided into categories, depending on their general operating principles. The categorization is derived from work into waste treatment processes and is as follows:

- biological
- chemical
- physical
- solidification
- thermal

When considering a remediation strategy for a site, six factors have been highlighted as requiring consideration. Of these six, economics is generally the deciding factor when other issues have been taken into account and perhaps two or three options are left. One option which entails twice the expenditure of another is unlikely to be taken up unless the benefits of the more expensive option can be seen to be worth the increased cost. For example, capping contaminated soil with engineered layers of clean material may be feasible, have minimal impact on the environment, accord with Codes of Practice and legislation and not create any health and safety problems. However, the contamination will remain on site, and some parties such as banks or funding institutions may view this as unacceptable and require total elimination of all contaminants from site, either by off-site landfill or treatment. A much higher cost may attach to this second option which reflects this 'whiter than white' approach, but this higher cost may tip the scales in terms of the economics of the overall development.

Whatever solution is chosen, it is absolutely essential to ensure a high standard of implementation; this may be done *via* both the normal controls of a construction contract and the quality assurance procedures which most companies now embrace British and European Quality Standards. The documentation of the works is important to demonstrate to future site owners and tenants or those who fund purchase of the land that the remediation has been successful in meeting targets and objectives set. Verification of the remediation *via* a systematic sampling and testing programme is often the best way of demonstrating the achievement of the set objectives.

6 Use of Consultants

The role and performance of consultants is increasingly important in delivering technically sound decisions in contaminated land management. The development of an optimum relationship between client and consultant has been hampered in the past by variable quality in the market place. However, there is strong evidence that access to appropriate consultancy advice is now a critical factor in business becoming comfortable that the challenges of contaminated sites have technical and affordable solutions.

At present, no professional institution can properly lay claim to contaminated land as its special sphere of interest. Good consultancy in contaminated land requires inputs from a number of separate disciplines. It is unlikely that a single individual consultant would ever have all the detailed professional knowledge, expertise and technical skills to be able to deal with the more complex situations that can arise regarding contaminated sites. However, a good appreciation of the concerns of other specialists/professionals will usually be required, and is of increasing importance as consultants assume greater responsibility for project specification and management.

Historically, consultants dealing with contaminated land have come from a range of disciplines and backgrounds. This is likely to remain the case, and should be welcomed because of the multidisciplinary and complex nature of the problems that may be encountered. A number of organizations have been formed to assist in communication of cross-discipline issues. Examples include the Environmental Consultancy Group (ECG) of the Environmental Industries Commission (EIC), formerly the Association of Environmental Consultancies (AEC), the Association of Geotechnical and Geoenvironmental Specialists (AGS), and the Forum on Contamination in Land (FOCIL) (Table 6). These groups have a key role in telling clients who wish to use consultants what is on offer and how to engage specialist advice in a cost-effective and beneficial way.

An example of the information now being produced to explain and define the role of consultancy in contaminated land is the forthcoming DoE report on Quality Assurance in Environmental Consultancy.[23] This addresses the responsibilities and expectations of a competent consultant practising in the field of contaminated land. In addition, many organizations with practical or legal responsibilities for contaminated land have also been developing guidance to improve the realization of expectations, including the usual circumstances when consultancy support is involved. Examples include the Institute of Environmental Health Officers,[24] the National Federation of Housing Associations,[25] Scottish Enterprise,[26,27] the Welsh Development

[23] *Quality Assurance in Environmental Consultancy: A Quality Approach for Contaminated Land Consultancy*, report by Association of Environmental Consultancies in Association with the Laboratory of the Government Chemist, DoE, London, in preparation.

[24] Institution of Environmental Health Officers (IEHO), *Contaminated Land: Development of Contaminated Land—Professional Guidance*, IEHO, London, 1989.

[25] National Federation of Housing Associations (NFHA), *Contaminated Land: Issues for Housing Associations*, NFHA, London, 1995.

[26] Scottish Enterprise (SE), *How to Investigate Contaminated Land: Requirements for Contaminated Land Site Investigations*, SE, Glasgow, 1994.

Table 6 Contact points for advice in consultancy capabilities in contaminated land

The Association of Geotechnical and Geoenvironmental Specialists *39 Upper Elmers End Road* *Beckenham* *Kent* *BR3 3QY*	**The Environmental Industries Commission** *6 Donaldson Road* *London* *NW6 6NB*
Environmental Contacts: A Guide for Business *DTI Environmental Publications* *ADMAIL 528* *London* *SW1W 8YT*	**Environment Industry Yearbook** *Environment Press Ltd* *26 Brock Street* *Bath* *BA1 2LN*
Environment Business *Information for Industry Ltd* *521 Old York Road* *London* *SW18 1TG*	**The Forum on Contamination in Land (FOCIL)** *c/o Royal Institute of Chartered Surveyors* *12 Great George Street* *Parliament Square* *London* *SW1P 3AD*

Agency[28] and the Construction Industry Research and Information Association.[29]

It can be concluded that the sophistication of and understanding between client and consultant has changed and improved rapidly, in response to the technical and legal development of the subject area. Very few organizations which own, develop or administer contaminated land have the expertise to address all foreseeable issues adequately. Indeed, efficient contaminated land work must rely on such a breadth of professional and technical experience it is rarely cost effective for organizations to be self-sufficient. Those with the greatest track record in dealing with historical legacies of contamination, for example in the chemicals, oil and gas, waste and metal industries, are the largest users of specialist consultancy support.

The essence of effective consulting support is quality assured and clearly presented reports and documentation. Even where specialist investigation or remedial techniques are being implemented, the value of the site work is dependent on effective reporting of findings and actions carried out. Many third parties, whether they be regulator, developer, purchaser, auditor or the local public, will require to understand what has been done to manage a contaminated

[27] Scottish Enterprise (SE), *How to Approach Contaminated Land: A Framework for the Assessment of Contaminated Land and Selection of Remedial Options*, SE, Glasgow, 1994.

[28] Welsh Development Agency (WDA), *Manual on Remediation of Contaminated Land*, WDA, Cardiff, 1993.

[29] Construction Industry Research and Information Association (CIRIA), *Remedial Treatment for Contaminated Land*, SP101–SP111, CIRIA, London, 1995, vols. I–XI.

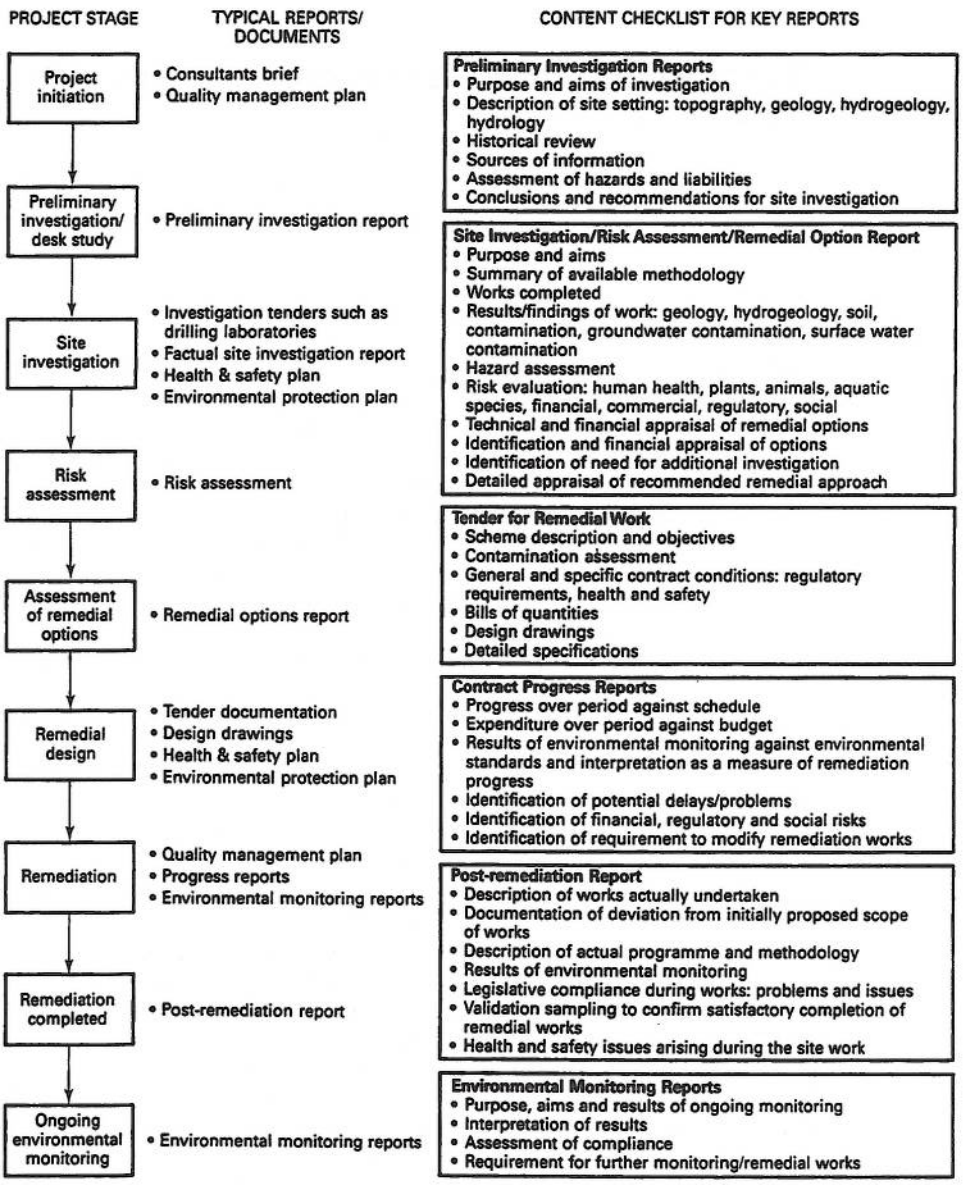


Figure 3 Consultant reports for site-based projects[23]

site. Usually, these requirements are met by appropriate reports. Confidence in advice and action is dependent on good communication. Figure 3 lists the reports which are characteristic of site-based projects. The following articles aim to provide more detail on the processes and techniques which are applied to deliver such site-based projects from initial data gathering through risk assessment to successful implementation of all necessary remediation.

Quantitative Risk Assessment for Incineration: Is It Appropriate for the UK?

D. O. Harrop, BSc, PhD, FRGS* and S. J. T. Pollard, BSc, PhD, MRSC, CChem *(Member)***

Abstract

The economic benefits of waste-to-energy plants are well known, but what are the environmental concerns? Public anxiety with regard to the development of incineration plants has focused attention on the need for informed and transparent assessment procedures based on sound science, to ensure that the impact of such developments is acceptable from an environmental perspective.

Key words: **Incineration; model; risk assessment; waste.**

Introduction

'Environmental impact assessment' (EIA) refers to the evaluation of the impacts likely to arise from a development which may adversely affect the environment. The EIA process provides decision-makers with an indication of the likely consequences of their actions. If properly employed, the EIA process allows informed decisions to be made on planning applications for potentially environmentally significant developments. EIA is therefore an anticipatory, participatory environmental management tool[1]. For these reasons, EIA has been applied to a plethora of development projects of varying scales. One sphere of development which has utilized the benefits of EIA has been incineration. Inevitably, in the case of most incinerator projects, there has been a tendency for the planning authority to request an EIA and, in a growing number of situations, a 'quantitative risk assessment' (QRA) of emissions from the plant, so that potential impacts on human health and the environment are fully addressed.

The concept of 'risk', which has now become a ubiquitous term, combines the probability of an adverse event (a hazard) occurring, with an analysis of the severity of the subsequent consequences. Risk assessment can be defined as the process of assimilating and analysing the available scientific information associated with a hazard or set of hazards[2]. Pollard *et al*[3] have previously discussed a number of approaches to risk assessment applied within environmental management, and these can be considered in a general sense as being qualitative, semi-quantitative or quantitative in nature[4].

*Director, CORDaH, Aberdeen Science and Technology Park, Bridge of Don, Aberdeen, UK.

**Policy Advisor, Scottish Environment Protection Agency, Stirling, UK.

Assessing the Impacts of Incineration Plants

Practitioners encountering EIA for the first time may see environmental assessment as a relatively simple and straightforward task. In practice, however, there is often a lack of knowledge concerning the nature and extent of impacts arising from incinerator developments because of their location in different environmental settings. The impacts from an incinerator in one location may be quite different from those arising from an identical installation in another environment. As a result, the identification of impacts is complex and should be continued throughout the EIA study as more data become available to the project. Nevertheless, from the outset of the project there is a need to anticipate potential impacts at the project initiation stage.

The initial identification of the most likely and important impacts is called the 'scoping stage'. Basically, the scoping stage of the project involves dialogue between (i) those implementing the EIA, (ii) those responsible for the design, construction and operation of the incinerator, and (iii) representatives of government departments and regulating agencies who have an interest in the development. There is a range of EIA methods to aid the individual in the identification of potential impacts. These methods are robust structured mechanisms for the identification, collection and organization of environmental data[5]. Fig. 1 shows an incineration plant detailing, qualitatively, those environmental issues of concern in relation to project-related activities.

The Royal Commission on Environmental Pollution – Incineration of Waste[6] identified the principal environmental impacts emanating from an incineration development as including (a) emissions to air and their associated health implications, (b) visual intrusion, (c) nuisance (odour, noise and smuts and char), (d) vehicular movements, (e) effects on flora and fauna, and (f) socio-economic effects. Depending upon the environmental sensitivity of the development site, water impacts may also necessitate consideration.

Ultimately, environmental concerns will depend upon the proposed environmental setting. The Department of the Environment EIA procedures guide[7] and the statutory regulations identify other issues which may need consideration. They identify the 'specified information' needs for an 'environmental impact statement' (EIS) which include (i) a description of the proposed development, comprising information about the size and the design and size or scale of the development, (ii) data necessary to identify and assess the main effects which the development is likely to have on the environment, and (iii) a description of the likely significance (direct and indirect) on the environment of

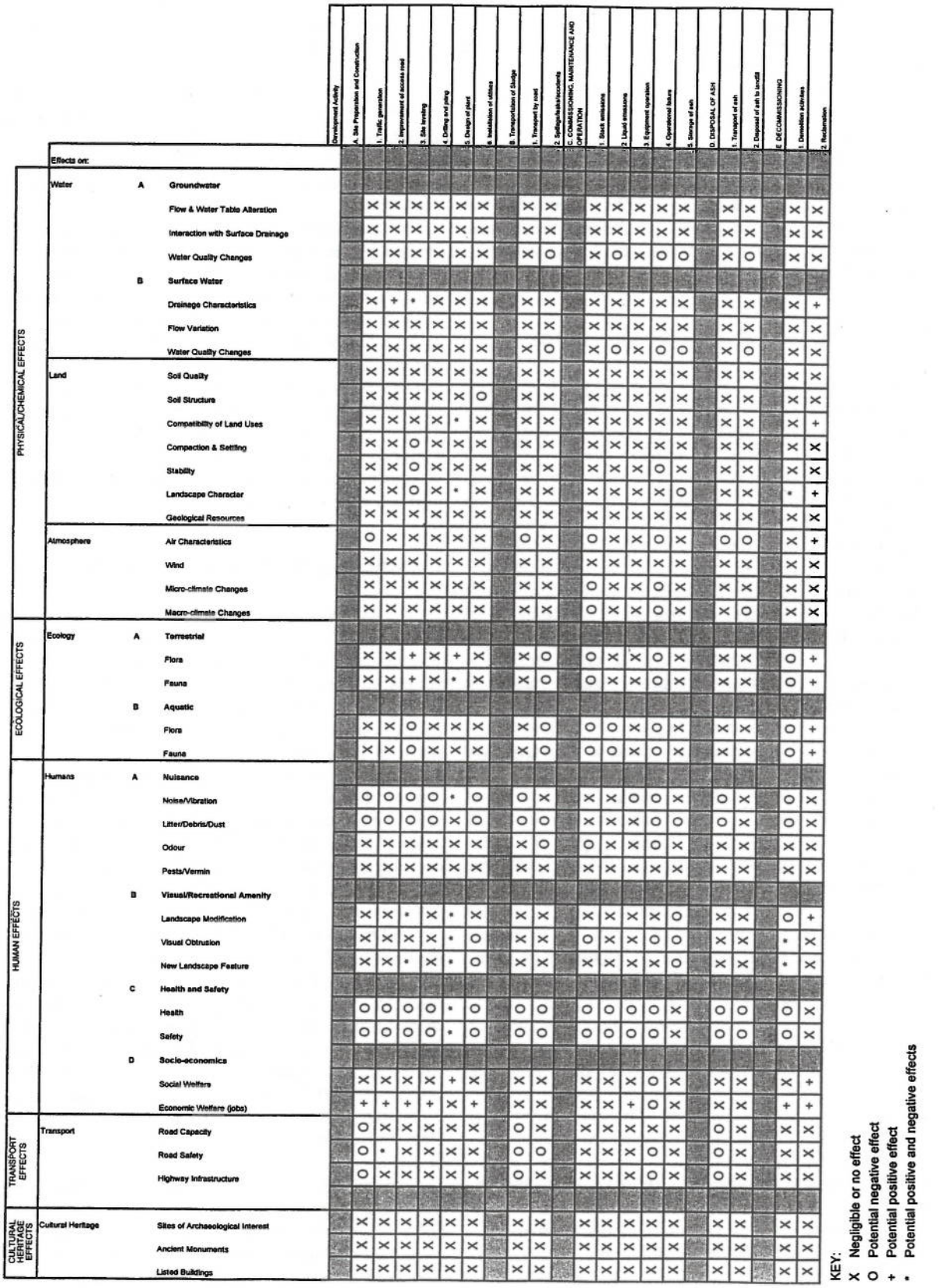


Fig. 1. Scoping matrix for proposed incineration plant (after Harrop 1994[8])

the development with reference to its impact on human beings, flora and fauna, soil, water, air, climate, the landscape, the interaction of any of the foregoing, material assets and cultural heritage. Where significant adverse effects are identified with respect to these environmental criteria, a description of the mitigation measures to avoid, reduce or remedy the impact should be provided. The need to ensure that each environmental criterion is properly assessed has resulted in the use of disparate scientific techniques to quantify or quality the level of impact, so there is always a need for an iterative review to ensure that impacts are assessed on a 'level playing field'.

In general, stack gas emissions and their effects on human health have received and occupied the greatest attention to date in submitted EISs; therefore, due consideration is normally given to assessing the impacts on ambient air quality and the associated risks to human health and the environment.

Air Quality Impact Assessment (AQIA)

AQIA involves not only identification, prediction and evaluation of critical variables such as source emissions and meteorological conditions, but also potential changes in air quality as a result of emissions from a proposed incinerator project. It can be used as a screening device for setting priorities for pollution control, or it can be implemented to test alternative project designs at an early stage in the planning design and to aid the identification of the most suitable site in terms of mitigating environmental impacts. Through its application, it will identify and quantify environmental impacts, and through plant design and planning mitigate for them to ensure that a development's impact on a locality is acceptable[8]. An AQIA comprises three stages as described below[8].

The AQIA assessment begins with a knowledge of the existing situation because incremental impacts can only be assessed in the context of baseline conditions. These will depend upon (a) ambient air pollution concentrations; (b) pollutant sources and their specific location; (c) meteorology; (d) local topography; (e) physical conditions affecting pollutant dispersion; and (f) sensitive receptors and their specific location. In general, it is important to understand what air pollutants are present in the area under consideration and in what quantities, where the pollutants came from, how they will be dispersed and where they are destined. There is no substitute for genuine data in this regard, and these information requirements are fundamental to the study.

The next step of an AQIA is to determine the character of incinerator emissions which will be released from the development. This will include (i) the nature of pollutants, (ii) emission concentrations, (iii) emission rates, (iv) efflux velocities, (v) efflux temperatures, and (vi) source morphology (stack height, diameter, etc.).

The third stage is the assessment of air-quality impacts resulting from the identified source emissions from the proposed development. The assessment is generally based on a comparison of the 'ambient air-quality standards' (AAQS) for the pollutant of concern to the cumulative concentrations (background and predicted incremental concentrations) of that pollutant. This phase of the AQIA also functions as a preliminary screen for the QRA, identifying (at an early stage) those contaminants for which a more rigorous appraisal is required. In order to avoid exceeding the AAQS, mitigation measures should be incorporated into the project at the design stage.

An effective method in AQIA procedures is atmospheric dispersion modelling[9]. The objective of modelling is to relate, mathematically, the effect of source emissions on ground-level pollutant concentrations, and to establish whether permissible levels are, or are not, being exceeded once background concentrations are included.

A large number of models are available to predict the impact of flue-gas emissions from an incinerator. Perhaps the two which have received most attention in the UK are the United States Environmental Protection Agency (US EPA) Industrial Source Complex (ISC) model[10] and the UK developed ADMS model[11]. Both models are widely used in the UK to predict exposure concentrations. The predictions are precursors to QRA. The rudiments of modelling are discussed elsewhere[12], as are the merits of individual models[13] and the application and the use of dispersion modelling techniques for Environmental Protection Act (EPA) 1990 authorization purposes[14].

Quantitative Risk Assessment Within EIA

As a management tool, QRA attempts to express risks mathematically by modelling exposures to source(s) present, aggregating exposures over all relevant exposure routes and key sources, and expressing estimated risks for individual receptors or groups of receptors. Throughout preparation and communication of a QRA, it is essential to keep in focus the overall objective of the risk assessment in the context of the EIA to avoid mis-use of the output. As currently practised within EIAs in the UK, the application of QRA has been to re-inforce the third phase of the AQIA procedures, often focusing on carcinogenic exposures and, where necessary, allowing an assessment of indirect exposures (i.e. those associated with exposure pathways other than inhalation).

The objective of the QRA is to evaluate the potential *incremental* adverse effects which could arise from the facility under the specific conditions of the exposure scenario. This is normally performed with reference to communities (or other receptors) downwind of the facility at the point of maximum ground-level pollutant concentrations, modelled from the AQIA. In selected cases, the QRA may extend to an assessment of ecological impacts, although (in most cases to date in the UK) such ecological risk appraisals have been qualitative in nature.

In general, the practice of QRA in the UK at present is based upon experience in the USA. The application of QRA specifically for the estimation of health risks at incineration plants evolved out of interpretation of the US Clean Air Act (s. 112) which required the US EPA to 'protect the public health with an ample margin of

safety'. The Clean Air Act Amendments of 1990 formally instated risk assessment as the basis of quantifying this 'margin of safety' and for subsequent regulatory decisions regarding air quality in the US[15]. The risk-assessment methodology devised by the US EPA, and now adapted for use in the UK, is under continual refinement and re-evaluation as more data become available on which factors drive environmental risk. The methodology remains a subject of considerable debate among regulatory bodies in the USA and UK, and has recently received a thorough evaluation by the US National Research Council[15]. In some quarters, considerable reservations have been expressed in the UK over the appropriateness of QRA for environmental-assessment purposes. Knowledge of these concerns is important because they form the basis for challenging the underlying assumptions in any QRA.

Key Components of QRA for Waste-to-Energy Plants

The methodology of QRA studies for waste-to-energy plants comprises the following key stages:

(i) Hazard identification (or data collection and evaluation);
(ii) Exposure assessment (or hazard analysis);
(iii) Dose (concentration) – response (effect) assessment (toxicity assessment); and
(iv) Risk characterization (or risk evaluation).

In the context of incineration plants these stages comprise:

(a) Identification of chemical contaminants within stack emissions which could result in adverse human-health effects (acute and chronic);
(b) Identification of the physio-chemical and toxicological properties of key contaminants;
(c) Characterization of potential human receptors as recipients of chemical exposure, including identification and characterization of the hypothetical 'maximally exposed individual' (MEI);
(d) Identification and evaluation of all potential human exposure pathways for the site and all receptors under consideration;
(e) Appraisal of the above pathways and receptors and identification of critical exposure pathways for the site and all receptors under consideration;
(f) Estimation of the amount of exposure (dose) for the above receptors under specified conditions of exposure;
(g) Estimation of the carcinogenic and non-carcinogenic risks associated with these levels of exposure;
(h) Evaluation and discussion of uncertainties associated with the risk assessment; and
(i) Implications of the risk assessment for risk management and process design.

As with any mathematical estimation model, QRA has its limitations; these invariably act to qualify the estimates of risk and place constraints on the means and manner in which the risk can be estimated, expressed, communicated and ultimately managed. Because any risk assessment involves professional-value judgements to be made regarding data input, it must be realized that there remains an element of subjectivity regarding the output. This is particularly the case where emissions and incremental exposures from proposed incineration facilities have to be modelled as opposed to being measured at an operational facility.

The level of uncertainty and subjectivity within QRA is vital to the current UK debate over its validity. In the absence of site-specific data, uncertainty regarding data input is controlled by using accepted air-quality models and referring to literature values and accepted best practice in their selection. It must be acknowledged that the quality of the risk-assessment output relies heavily on the confidence associated with the modelling methodology, the validity of baseline toxicology, and the professional defence of default values applied in the absence of measured data.

Given the level of modelled or assumed data used in the preparation of QRAs for proposed incineration plants, an assessment of the principal uncertainties and their impact on final-risk estimates is an inherent part of the risk-assessment process. This represents current best practice and can assist in making the risk assessment transparent to the planning authority and its consultants.

Is QRA Appropriate for EIAs in the UK?

Considering the constraints on obtaining site-specific data for proposed incineration facilities and the unresolvable limitations of the baseline toxicology, it is vital that the use of QRA is reviewed critically for EIA applications.

The underlying premise of QRA is that very low environmental exposures can be translated mathematically into expressions of the probability of adverse effects occurring and their associated significance. It is usual to assess both potential carcinogenic and non-carcinogenic effects (so-called toxic 'end-points'). This is conventionally undertaken with reference to available baseline toxicology and the use of excess lifetime cancer risks and hazard quotients, respectively. A comparison of the risk estimates and hazard quotients obtained with reference to accepted tolerability criteria and background risk levels provides an account of the incremental risk and its significance attributable to the proposed facility. The assessment of carcinogenic and non-carcinogenic risk relies fundamentally and heavily on interpretation of the baseline toxicology. Because most of the data on chemical exposure has been gathered on animals (rather than humans) at high doses (rather than low), and at doses deliberately sufficient to illicit a toxic response, there is an over-riding need for extreme caution in the interpretation and presentation of QRA output. Therefore risk-assessment output is not absolute and does not represent the actual probability, say, of contracting cancer. Instead, the output is indicative and should be used responsibly to highlight the relative distribution of risk among exposure pathways and between individual receptors so that risk-management measures, where required, can be prioritized and

designed accordingly. The paradox between the apparent level of sophistication implied by QRA methodologies, and the considerable uncertainties inherent to risk estimates, often becomes all too clear in the communication of risk estimates to a local public.

Present debate on the fundamental science has focused on (i) the validity of a 'no-threshold' assumption for the onset of chemical carcinogenesis (in the absence of observed effects from low-level exposures), and (ii) attempts to derive 'tolerable' risk levels for environmental hazards which balance public-health protection and the economic cost of the level of benefit gained.

It has been argued that QRA methodologies are inappropriate because they cannot resolve the considerable uncertainties associated with establishing safe levels of exposure for genotoxic carcinogens[16]. Application of low-dose extrapolation to derive a *de minimus* risk level has defensibility problems[17, 18] and has not been entirely successful in yielding safe levels of exposure to carcinogens. In the long-term, it is important to invest in the powers of environmental epidemiology to provide direct estimates of risk on human receptors, but such approaches provide only retrospective views, are complicated by high background rates of cancer, and are still limited at very low levels of exposure by the practical and ethical constraints of studying human subjects[19, 20].

It can be argued that until more data become available, informed application of QRA represents a defensible means of prioritizing risk-management decisions, provided that risk estimates are not seen as absolute and the application of QRA in itself is not mistakenly viewed as 'guaranteeing safety'. Responsible use of QRA must mean including recent toxicological data and explaining where and why default assumptions are used. For example, the exposure assessment stage requires a number of default values and generic factors to be incorporated into the exposure estimations in the absence of a complete data set. This is consistent with accepted risk-assessment methodologies, and it is usual to detail the limitations associated with these assumptions for the purposes of outlining their contribution to the output of the risk assessment. Uncertainties in the exposure assessment include (but are not restricted to) the following inputs:

(i) Characteristics of the proposed plant location;
(ii) Site-specific meteorological data;
(iii) Model uncertainty; and
(iv) Receptor characteristics.

In the absence of UK specific receptor characteristics, default values for the receptors have often been obtained from the US EPA exposure factors handbook (a peer-reviewed collection of human exposure characteristics compiled from literature studies on the US population). Similarly, within the risk characterization stage, it is widely recognized that a determining factor in the overall variance of carcinogenic risk lies in the derivation of the dose-response factor for human exposures at low levels of environmental exposure, and the use of accepted values relies heavily on consensus among expert toxicologists as to the relevance and weighting put on available scientific data.

At present in the UK, few QRA studies have extended beyond the use of exposure concentrations as a means for dealing with the dose received. In reality, 'effective' doses are those reaching and having an impact at the cellular level in the target organ. The approach to dealing with the administration, metabolism, distribution and excretion of contaminants *in vivo* (the pharmacokinetic aspects) has been rudimentary and conservative. For example, bio-availabilities of 1.0 are often assumed for inhaled contaminants in the first instance, in the absence of toxicological data on the desorption and alveolar transfer factors across the lung. This assumption is conservative and is made so as to be protective of public health, regarding limitations in the estimation of windblown dust.

In summary, within the baseline experimental toxicology, many sources of uncertainty exist and these include[21]:

(a) The selection of the critical end-point (adverse effect) for humans for a toxic agent identified from experimental studies with animals;
(b) Extrapolation of the end-point to humans (chemicals may exert different effects on humans at different levels of exposure);
(c) The selection of the sex, species, strain and sensitivity of species and strain in the animal data;
(d) Extrapolation of the human 'dose' from the animal data and the scaling basis for conducting the extrapolation (body weight, body surface area, metabolic capabilities, etc.);
(e) Extrapolating low-dose chronic reference doses for non-carcinogens from high dose data;
(f) Derivation of the carcinogenic slope factor (q_1^*) using the linearized multi-stage model;
(g) The absence of mechanistic considerations with reference to the pharmacokinetic behaviour of contaminants *in vivo* for the human receptor; and
(h) Route-to-route extrapolation where practised from oral exposure reference doses for non-carcinogens.

These uncertainties exert considerable influence on the final expression of risk, and the existing dose-response information provided in the literature does not account for the complexity of these factors. Conservative assumptions are made in the presence of uncertainty, but liberal use of the precautionary principle can have severe implications for cost-benefit analysis; therefore an inventory of assumptions is useful in keeping check on the level of over-estimation made in the interests of protecting environmental health. In general, current approaches for potential carcinogenic effects are regarded as providing adequate protection to human receptors (Table 1).

To date, QRA has been used in a limited, although growing, number of EIAs. Table 1 indicates that, using current methodologies, the level of risk from incineration plants is very small. The Royal Commission on Environmental Pollution[6] stated that there is a consensus among regulatory authorities in the UK and the USA that annual incremental risks of death greater than 1 in 10 000 are too high to be acceptable; and that a risk of 1 in 1 000 000 represents a reasonable upper bound beyond which measures to achieve a further reduction in

Table 1. QRA Predictions for Incineration Plant in UK

Type of incinerator	Excess carcinogenic risk (per annum) (range where available)
Waste-to-energy	1 in 33 000 000 to 55 000 000 (Bexley) 1 in 26 000 000 (Belfast) 1 in 26 900 000 (Thameside) 1 in 15 900 00 (Knostrop)
Sewage sludge	1 in 2 400 000 to 5 500 000 (Belfast) 1 in 12 500 000 to 58 000 000 (Calder Valley)
Clinical waste Industrial waste	1 in 9 000 000 to 38 900 000 (Knostrop) 1 in 7 800 000 to 12 100 000 (Teesside)

Note: The values given in Table 1 have been taken from a series of EISs undertaken by ERM and Aspinwall & Company. The detail of assessment undertaken for each study was variable (e.g. inhalation exposure, ingestion or total exposure assessments, realistic or worst case scenarios, etc.), therefore direct comparisons between studies should be avoided. The values given are indicative of possible exposure levels and are not absolute. For specific details the respective EISs should be carefully consulted.

the risk would not be justified in terms of benefit gained. The predictions in Table 1 are well within these criteria. However, despite these reassurances, the local public's concern can remain undiminished. Evidence suggests that only with greater public participation at every stage can risk perception issues be properly addressed.

Conclusions

1. The application of air-dispersion modelling studies as a precursor to QRA necessitates the need for improved and accurate approaches to modelling. Available evidence indicates that the development of these modelling approaches is somewhat more developed than those of QRA, although there is no room for complacency.
2. Incineration and potential risks to public health are often inextricably linked in the public mind. Therefore it is paramount that due consideration is given to assessing the effects of these facilities on the public in an informed and reliable manner.
3. As most incineration developments have required an EIA, the output of QRA and EIA studies has become linked with the common objective of assessing the significance of impact. Many practitioners of environmental assessment have adopted the procedures of QRA into EA as good practice. Therefore, when discussing QRA and incineration, it is also prudent to be mindful of the procedures for EIA.

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Human health risk assessments for contaminated sites: a retrospective view and forward look

Simon Pollard

Abstract

The approach to taking decisions on the management of land contamination has changed markedly since the SCI's first conference on the matter in 1979. Change has been rapid with policy makers, regulators, practitioners and researchers having to keep pace with new technologies, assessment criteria and diagnostic methods for their measurement, techniques for risk analysis and frameworks that support decision-makers in their efforts to regenerate historically contaminated land. This said, there are remarkable similarities between the agendas of 1979 and 2004: (i) the concerns over risks to public health, their magnitude, assessment and contextual significance; (ii) the role, implementation and use of regulatory guidance on risk management; and (iii) the influences of the emerging stakeholder society on issues of risk. This keynote will review the themes on human health risk assessment developed at the 1979 conference, summarise the professional achievements since and cast a forward look to the next 25 years.

Key words: contaminated land, health, risk assessment

INTRODUCTION

'Risk assessment'. The term is so widely used in the 21st century one might argue it has become a parody of itself. The BBC News web provides a snapshot of the risk society in which we live – asbestos in school buildings, increased life assurance for people with obesity, 'irritable desk syndrome', children's right to play (BBC News 2002), the alleged risks to bird populations from the EU's transport strategy. Environmental risk issues are frequently at the foreground of public concern. With the regeneration of brownfield land for housing high on the political agenda, the risks to public health from historic contamination is a central issue for most regeneration strategies, plans and projects.

This paper was presented at the SCI/RSC conference, Contaminated land: achievements and aspirations, held at Loughborough University in September 2004. The proceedings are available from EPP Publications.

Author

Professor Simon Pollard, Integrated Waste Management Centre, School of Industrial and Manufacturing Science, Cranfield University, Cranfield MK43 0AL, UK. Email s.pollard@cranfield.ac.uk

Our approach to assessing the risks from land contamination has changed markedly since the 1979, even if practices in risk management have trailed somewhat behind. But have we gone 'over-the-top' as some commentators argue? Have our decisions become better? Do we now understand more about contaminated sites? And are our actions protective of public health as a result of our full blown foray into the field of risk assessment and management?

ACHIEVEMENTS

The proceedings of the 1979 SCI Conference on the Reclamation of Contaminated Land (SCI 1980) provide a valuable starting point for a 2004 retrospective. Whilst over the intervening years we have moved from simple hazard assessment through to tools for the quantitative estimate of risk and on to the 'sustainability appraisal' of regeneration programmes, there are remarkable similarities between the agendas of 1979 and 2004 (Table 1).

Since the 1979 conference, we have investigated the issues emerging at the time in depth. Substantial advances in diagnostic technology have brought us rou-

Table 1. Summary of discussions on the assessment and acceptability of health risks (after SCI 1980)

Issue	Flavour of discussion
Risk estimation – uncertainties in the assessment of probabilities and magnitude of risks from chemical exposure	Individual chemicals may differ by 7 orders of magnitude in their toxicological potency and exposure may vary by 8 orders of magnitude between individuals. Caution over the quantitative expression of risk estimates.
Dose-response assessment	The difficulties of high to low dose extrapolation for human exposure to metals. Value of epidemiological studies, notwithstanding the risk of these studies producing negative outcomes. Impact of factors such as developmental and dietary status on tolerance to chemical exposures.
Absorption-distribution-metabolism-excretion	Value of bioavailability testing (metals).
Risk communication and the risk assessment-risk management interface	Translating scientific understanding and information to risk management on the ground, to workers at contaminated sites. The necessity of good risk communication to workers undertaking site work. The need to be honest about uncertainties, disagreements between experts and competing theories.
Carcinogenic risk from environmental exposure	Corrected misunderstanding of the 'environmental' causes of cancer; i.e. those attributable to extrinsic (and not necessarily via environmental exposure) rather than genetic factors. The relative role of scientific, social and economic contributions to the setting of standards.
Trust in experts, precaution and the stakeholder society, risk acceptance	'No longer will the public accept the statements made by experts and specialists without critical analysis and assessment'. Influential role of the media. Rise in the prominence of the precautionary principle and the stakeholder society [...] 'technical information should be freely available and open to challenge'. 'Risk assessment, [risk *sic*] acceptance and public confidence are not the same'. Who decides what risk is acceptable?
Comparative and relative risks	Examples discussed of workplace hazards in the mining industry, of alcohol abuse, of road accidents. Risk aversion by reference to air crashes *vs.* workplace accidents occurring on a daily basis.

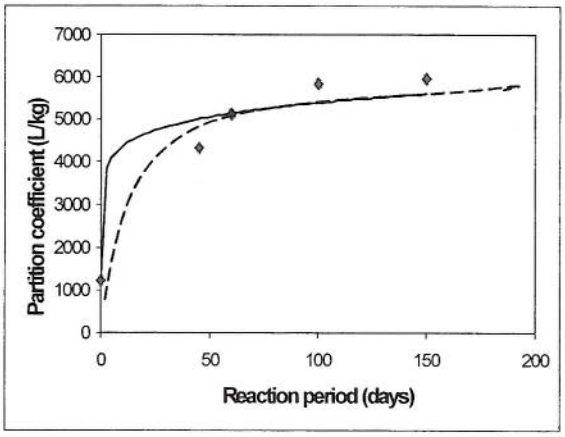


FIGURE 1. AGEING INCREASES THE PARTITION COEFFICIENT OF CADMIUM IN SOILS (AFTER NAIDU *ET AL.* 2003)

tine gas chromatography/mass spectrometric analysis and field-based immunoassay for improved site investigation and source term characterisation; understanding of the ageing effects of contaminants in soils and the associated influences on contaminant partitioning (Figures 1 and 2) provides new insights into the risks from contaminant residuals; exposure assessment has become internationally formalised in the assessment models adopted by regulators and industry sectors; and research into individual routes of human exposure has been extensive (US EPA 1992; Paustenbach 2000). Paustenbach (2000) has summarised the lessons from 50 years of human exposure assessment (Table 2) and provides an valuable reference for much of the ongoing work on contaminated land risk assessment. Looking beyond exposure to the toxicology of contaminants,

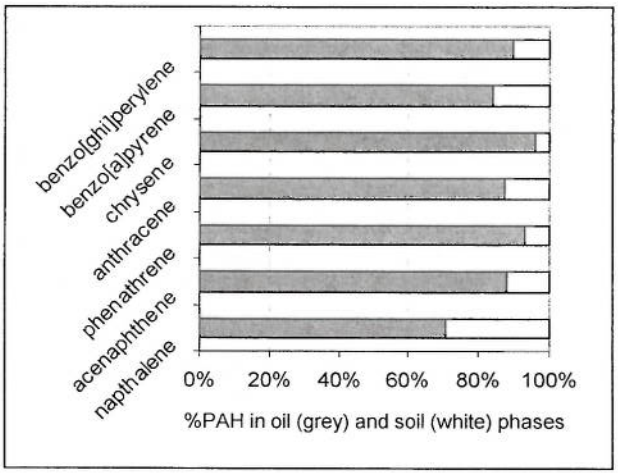


FIGURE 2. DISTRIBUTION OF SELECTED PAHS IN CREOSOTE-CONTAMINATED SOILS (AFTER ZEMANEK *ET AL.* 1997)

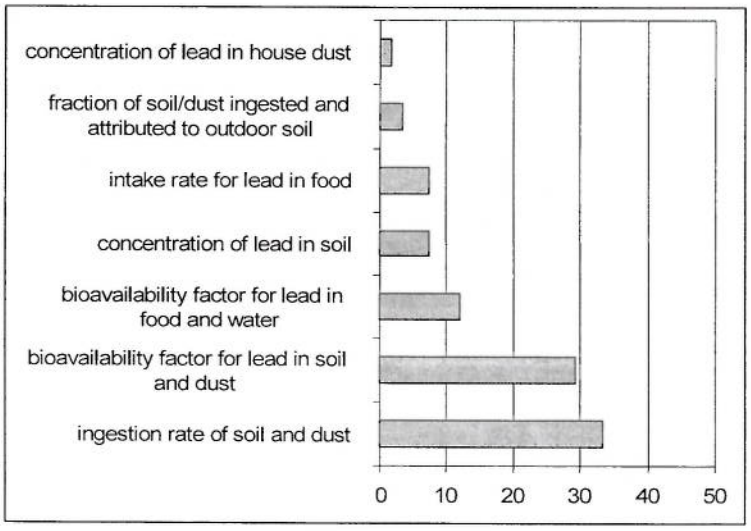


FIGURE 3. CONTRIBUTION TO % VARIANCE IN TOTAL LEAD UPTAKE FROM KEY MODEL PARAMETERS IN A PROBABILISTIC BLOOD LEAD PREDICTION MODEL (AFTER LEE *ET AL.* 1995)

research into the bioavailability of contaminants in soils and dusts, and their influence on predicted blood levels of, say lead, is now allowing us to assess the relative variance associated with the default assumptions used conservatively within exposure models (Figure 3) and consequently help direct future research effort. Probabilistic risk analysis has become a 'bench-top' reality allowing us to undertake sophisticated sensitivity analysis and isolate key risk drivers for further characterisation.

Sometimes incorrectly criticised as remote from the practical context of on-site decision-making, these and other achievements in the supporting science base provide a firmer and more evidence-based foundation for the development of good conceptual models, appropriate analytical reporting (Figure 4) and the responsible assessment and meaningful communication of risk estimates. Informed by these advances from the environmental, analytical, engineering, medical and social sciences, risk-based decision-making has undergone a radical transformation. Hazard-based assessments have been replaced by risk-based tools that inform proportionate and targeted responses to land contamination. Risk-based decision-making frameworks in 2004 pro-

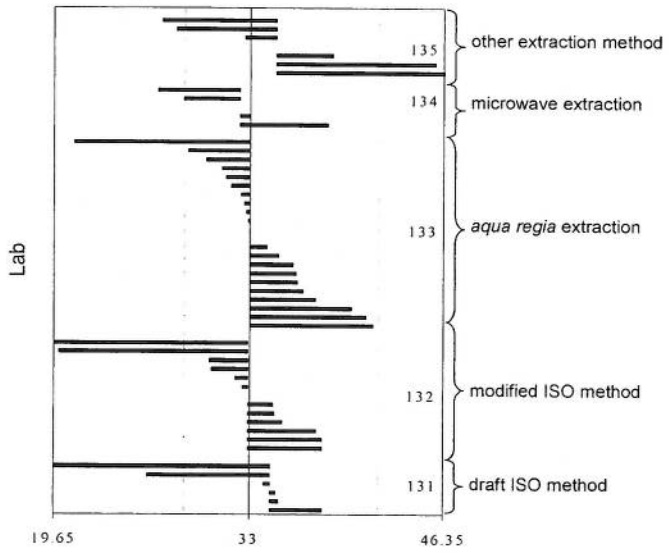


FIGURE 4. DISTRIBUTION OF AS IN A HOMOGENISED SOIL OBTAINED BY A RANGE OF LABORATORIES (INDIVIDUAL BARS) AND ANALYTICAL METHODS (GROUPS 131 – 135; BRACKETED) ABOUT A GRAND MEDIAN OF 33 MG/KG DRY WEIGHT (AFTER BOLEY AND WOODS 2000)

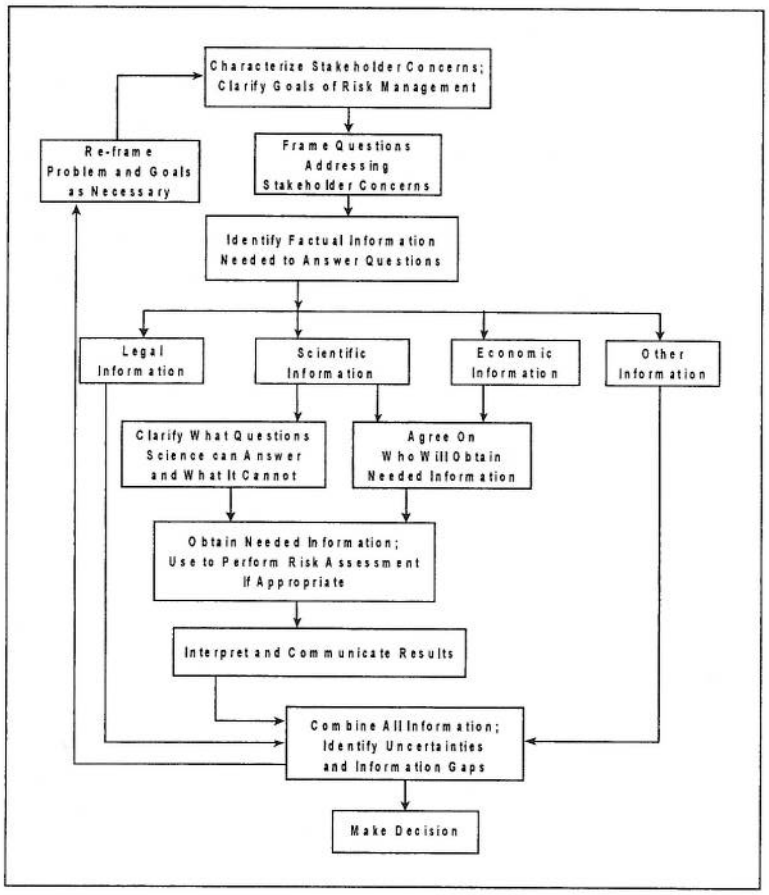


FIGURE 5. PROPOSED DECISION FRAMEWORK FOR ENVIRONMENTAL DECISIONS (AFTER CHARNLEY 2000)

Table 2. Lessons from 50 years of exposure assessment (after Paustenbach 2000)

Issue	Lesson
Implications of conservatism in exposure assessment	Too much emphasis on 'so-called' maximally exposed individuals resulting in misinterpretations by some scientists and lawyers and consequently poor decisions by risk managers.
Special and critical groups	Whilst our focus has been on protecting 95% of the population through quantitative exposure assessment, increased emphasis has been on special groups, such as subsistence fishermen, dairy farmers, indigenous peoples with high fish/meat diets, that might be exposed to high doses (95%–99%). Whilst high dose populations need to be understood, typical exposure levels for the majority of the populations should be the primary focus. Interest has risen in the characterisation of risks to children.
Deterministic and probabilistic exposure assessments	Do not allow the repeated use of conservative exposure assumptions to dictate the results of the assessment. Monte Carlo techniques are valuable in addressing the problems of conservative, deterministic estimates of exposure.
Communicating uncertainty	Risk managers (decision-makers) and the public want to understand the statistical confidence in risk estimates. Sensitivity analysis is valuable in illustrating the role of critical exposure variables and risk assessments benefit from an analysis of both variability and uncertainty.
Handling uncertainty	We have improved our methods for handling data statistically and in particular for analytical data below the detection limit. Use of the detection limit or one-half of the detection limit at sites that may only be 2–10% contaminated can lead to erroneous decisions on risk.
Quantitative exposure assessment	We now understand the value of quantifying indirect exposure pathways. One pathway that has emerged as important is the ingestion of particulate dust deposited on soil and plants where animals graze.
Child exposures	Children are not miniature adults in their exposure patterns. Their intake of certain foods, percentage of time spent outdoors, proximity to carpets indoors and inhalation rates per unit body weight are all different to adults.
Biological monitoring	Environmental and medical diagnostics have progressed rapidly. We can now detect very small concentrations of chemicals in blood, urine, hair, faeces, breath and fat. These advances may allow us to validate our exposure models in future years.
Risk significance	It has become clear that most significant risks from chemicals occur in the workplace. Notwithstanding the advances in health and safety practice and regulation, exposures are often 100 times those in the community will ever face.
Indoor vs. ambient exposures	For most persons, chemical and bacterial exposure in the home pose a greater risk than those via ambient air or through the ingestion of water. Many studies show that in-home exposures are about 2–20 times greater that those in the ambient environment. This has led to calls for concentrated efforts on personal monitoring, especially of the indoor environment.

mote a greater balance between the scientific, practical and democratic requirements of environmental decisions (Figure 5) within a context of sustainable development and pave the way for a more inclusive and participatory approach to risk assessment (Environment Agency 2003*a*). To further assist our decisions, volumes of technical guidance and supporting documentation exist on site investigation, remediation and decision-making for contaminated land. In England and Wales, the Environment Agency's recent Model Procedures (Environment Agency 2003*b*) make reference to eighty supporting documents, familiarity with which is assumed for sound judgements on land contamination.

Yet, within this information rich environment, the critical questions posed at the 1979 conference remain: what are the risks? are they acceptable? how do we make decisions that engender confidence in the face of uncertainty?

In 2004, we operate a highly precautionary approach to contaminated land risk management. The most powerful of environmental epidemiological studies (Figure 6), rarely have sufficient records or site-specific data on exposure to conclude anything other than weak and inconclusive evidence for associations between exposure to contaminated soil and adverse health outcomes (Paddle and Harrington 2000). Soil assessment criteria and guideline values incorporate substantial margins of safety on account of the uncertainties inherent to high-to-low dose, route-to-route and animal-to-human dose-response assessment. Notwithstanding the advances in coding exposure assessment equations into computer models, the default exposure factors inherent to these models often still

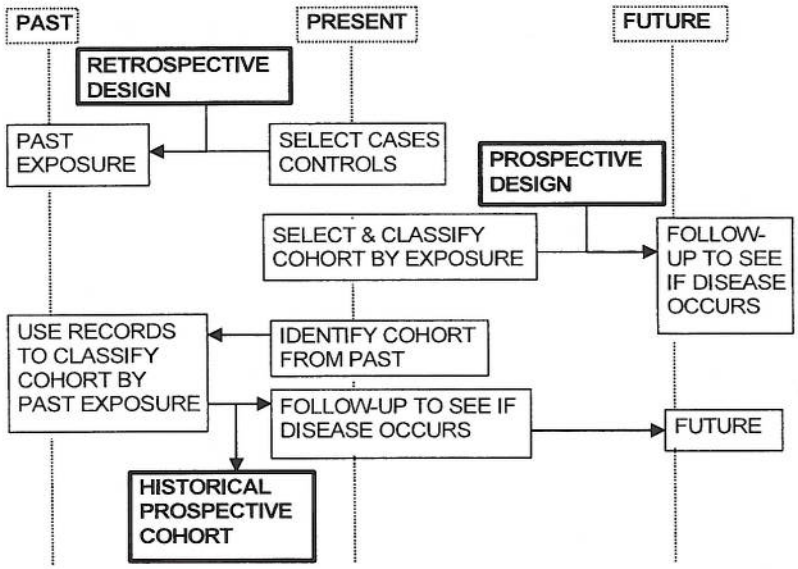


FIGURE 6. A TYPOLOGY OF EPIDEMIOLOGICAL STUDY DESIGNS (AFTER RUSHTON 2001)

assume worst case amounts and durations of exposure with consequent implications for soil assessment criteria, remedial objectives and cost. Faced with substantial residual and irresolvable uncertainty on exposure, one might be tempted to question whether we are approaching the limits to which additional scientific enquiry can provide further insight, and thus reach for the precautionary principle as a policy substitute.

However, we must harness the continuing developments in the science base and target our research on issues that will further improve risk-based decision-making in practice. The integration of risk assessment needs with statistical sampling strategies; a better understanding of the temporal risks associated with contaminant residuals; and the optimisation of remediation performance by reference to risk are all current themes that will help improve the way in which risk assessments are used to informed contaminated land management.

ASPIRATIONS

In considering our aspirations for the future, which require advances in interdisciplinary and transdisciplinary science and practice, we might reflect on the questions put to the expert health effects panel at the 1979 conference (SCI 1980):

'As the complexity of risk assessment increases, the chances that public perception of the acceptability of risk will be aligned with the conclusions of 'scientific' risk assessment recede. This leads to three questions on which the panel are invited to comment:

(a) Do they [the panel] see any basis for a synthesis of the differing views on risk assessment/acceptability of risk?
(b) Do they see any possibility of improving public understanding of the complexities involved in this subject, so that public discussion can proceed on a more rational basis?
(c) If the answer to the second question is "No", what do they see as the implications for public policy? Should we give up the attempt to get the complexities understood, and simply rely on the experts' "objective" assessment of risk?'

The questions are as valid in 2004 now risk assessments have become complex. Our aspirations are for sound and efficient decisions about land contamination, particularly in the context of brownfield regeneration, that have the confidence and trust of a broad range of stakeholders. We want risk assessments to *inform* our decisions on sustainable remediation and risk management, but not become an end in themselves or to paralyse our capacity to make decisions. Increasingly, as tools and assessment criteria develop for receptors other than human health and the water environment – for ecological receptors, buildings and property for example – we will need to grapple with comparative risk analysis (Linkov and Ramadan 2004), requiring the parallel assessment and valuation of different environmental components at risk. Beyond this, and operat-

ing in a risk policy environment that is becoming increasingly integrated, the management of risks to public health from land contamination will compete for funds alongside other environmental and public health priorities (Jones and Klein 1999), and perhaps with issues where the evidence for causality is more clear cut. Where does this leave risk assessment and its role within decision-making for contaminated sites and policy development?

In 25 years time, the landscape of human health risk assessment for contaminated sites will become more integrated (with other receptors and with other decision tools for assessing health impact), more comparative (with other risks) and more multidimensional (socioeconomic and financial issues, greater participation). These developments from competing decision tools, philosophies of approach and risks will require risk analysts to be more explicit about the specific benefits of taking a risk assessment based approach. The challenges posed in the above questions from the 1979 conference will become sharper.

Synthesis of views on risk assessment and risk acceptability

There are clearly different expectations of risk acceptability among the various stakeholders, and, when talking 'risk', we must be prepared to confront issues of trust, confidence in science and the views of experts, and ultimately 'outrage' (Sandman 1989). Moving beyond well-rehearsed debates on risk criteria, data uncertainty, and the quality of consulting advice on risk, for the next 25 years we might try an alternative tack to being driven solely by risks of less than one in a million. We might learn from other sectors and begin to think in terms of the 'levels of service' that our decisions on the risks from land contamination provide to stakeholders, rather than continuing to press an 'objective' rationale for the acceptance of risk. For example, the international water utility sector has set itself the goal of providing wholesome, affordable and safe drinking water that has the trust of customers (AWWA *et al.* 2001). We might develop something similar – 'safe, desirable and sustainable developments (on previously contaminated land) that have the trust of communities and those that live in them'. Whilst public confidence, acceptance and risk are indeed not the same (SCI 1980), a shift of focus to those that bear the risks in our communication and a new approach to involving others in decisions on risk (Figure 4) is desperately overdue (Petts *et al.* 2003).

Communicating risk in the face of complexity – public understanding and stakeholder engagement

In 2004, concerns over the poor public understanding of science and risk have been superseded by a more mature appreciation of the multidimensional aspects of risk in a stakeholder society. Publics are increasingly sophisticated in their understanding of risk and often handle uncertainty with relative ease. Making decisions that are informed by risk assessment legitimate needs to focus on how risks are assessed, managed and communicated and how stakeholders engage with the process as a whole (Table 3).

Risk management frameworks can provide route maps for stakeholders on the process of decision-making. The success of these processes and the principles that underpin them (Table 3), whether for decisions on land contamination or other environmental pressures, depends on time, openness, the equal position of all parties and a willingness to learn. What are now termed 'socially robust decisions' make a presumption of access to resources, flexibility in the decision-making process and an inherent capacity and desire for change (Homan *et al.* 2001; Brookes *et al.* 2001). In 25 years time, we will see our aspirational frameworks for greater participation in risk management (e.g. Figure 5) become routine. Getting there will require new skills in the social sciences and a tremendous effort in implementation, dedicated resourcing and the embedding of these frameworks within the sector.

Expertise and the stakeholder society

Given the above, in 25 years time, question (c) of the 1979 questions may well have become redundant. Substantial technical advances in risk assessment will have taken place for which there will be well-established means of communication. Making meaningful comparisons of risks to public health from chemical exposures will require a greater harmonisation of risk assessment approaches and the co-ordination of common toxicological and exposure data across the various exposure contexts in which they are applied. Our improved understanding of the *in vivo* fate and behaviour of environmental contaminants and of patterns of gene expression will contribute to our knowledge of the toxicity of environmental chemicals and allow us to refine our exposure models and target our site investigation work. We will be working more closely with colleagues in the medical sciences to realise these aspirations for contaminated land problems.

Table 3. Principles for good risk management (after HM Treasury and Cabinet Office 2003)

Openness and transparency	Make available risk assessments that affect the public; how decisions are reached and how risks handled, including where new policy developments pose a risk to the public. Where facts are uncertain or unknown, make clear what the gaps are and, where relevant, what is being done to address the gaps. Being open about mistakes and what is being done to rectify them.
Involvement	Actively involve significant stakeholders, including members of the public throughout risk identification, assessment and management to support timely and targeted action. Two-way communication to be used in all stages of policy development, risk assessment and management. Differences in interpretation to be clarified through open discussion. Seek to balance conflicting views to best serve the public interest and explain how views obtained through consultation have been reflected in decisions.
Acting proportionately and consistently	Base all decisions about risk on what best serves the public interest. Action to be proportionate to the level of protection needed and targeted to the risk. Seek a consistent approach to the assessment of risks and opportunities and to the evaluation of costs and benefits of options for dealing with risk. Application of the precautionary principle where there is good reason to believe that irreversible harm may occur and where it is impossible to assess the risk with confidence. Revisit decisions as knowledge changes.
Evidenced-based decisions	All relevant evidence, from a range of perspectives, is considered and, where possible, quantified before decisions are taken on risk. Seek impartial and informed advice that can be independently verified. Seek to build a shared understanding of the risks and the options for their management. Avoid the absence of evidence alone to prove the absence of a threat and acknowledge alternative interpretations of available evidence. Make clear how evidence has informed decisions and keep them under review.
Responsibility	Ensure, where possible that those that impose risks on others also bear responsibility for controlling risks and for the consequences of inadequate control. Aim to give individuals a choice about how to manage risks that affect them, where feasible and in their interest, and where this does not expose others to disproportionate risk or cost. Seek to clarify where responsibility for managing risks rests and that those responsible have the authority and information to act.

CONCLUSION

The luxury of a forward look is best tempered by reflections on the reality of the present. Notwithstanding the advances of the last 25 years outlined in this paper, we have not been as smart as we might have been in transferring and implementing new knowledge within the marketplace. We may now assess risks in a more sophisticated fashion, but what counts is the capacity to implement the outcome of risk assessment. Unfortunately, children still find their way on to waste sites and become exposed to mercury, for example, in a similar way to that which caused in the initial outcry for the development of waste legislation in the UK in the early 1970s (OETG 2003). We need to ensure risk assessment is seen as part of risk management, that it informs good decision-making and that advances in the science base are harnessed by risk analysts into methodological improvements that result in better and implementable decisions. We can be both optimistic and confident that in 25 years' time many of our aspirations will have been met and that the new focus on inter- and transdisciplinary science will deliver both sought after improvements and new challenges for risk assessment practice.

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REVIEW PAPER

RISK ANALYSIS AND MANAGEMENT IN THE WATER UTILITY SECTOR
A Review of Drivers, Tools and Techniques

S. J. T. POLLARD[1]*, J. E. STRUTT[2], B. H. MACGILLIVRAY[1], P. D. HAMILTON[1] and S. E. HRUDEY[3]

[1]*Integrated Waste Management Centre, Cranfield University, Cranfield, Beds, UK*
[2]*Reliability Engineering and Risk Management Centre, Cranfield University, Cranfield, Beds, UK*
[3]*Environmental Health Sciences, Department of Public Health Sciences, University of Alberta, Edmonton, Alberta, Canada*

The provision of wholesome, affordable and safe drinking water that has the trust of customers is the goal of the international water utility sector. Risk management, in terms of protecting the public health from pathogenic and chemical hazards has driven and continues to drive developments within the sector. In common with much of industry, the water sector is formalizing and making explicit approaches to risk management and decision-making that have formerly been implicit. Here, we review the risk management frameworks and risk analysis tools and techniques used within the water sector, considering their application at the strategic, programme and operational levels of decision-making. Our analysis extends the application beyond that of public health to issues of financial risk management, reliability and risk-based maintenance and the application of business risk maturity models.

Keywords: risk; management; assessment; water; utility; decision-making

INTRODUCTION

Providing wholesome, affordable and safe drinking water that has the trust of customers is the overarching goal of the water utility sector. The sector has publicly stated (AWWA *et al.*, 2001) that achieving this requires, at a minimum, that water is safe in microbiological and chemical terms, that it is acceptable to consumers in terms of taste, odour and appearance, and that the supply is reliable in terms of quality and quantity.

Delivering safety, acceptability and reliability within a multi-stakeholder, institutional and business context in which expectations are rising is challenging. Privatization, sector globalization, increased competition, emerging technologies, increasingly stringent regulatory control and the trend towards financial self-sufficiency are all serving to transform the water sector, and posing new risks and opportunities (Westerhoff, 2003; Huber, 2000; Westerhoff and Lane, 1996; Kucera, 1993). Many within the industry are now promoting an enterprise-wide approach to risk management as a means to ease and indeed exploit this transition (e.g. Lifton and Smeaton, 2003). This requires:

(1) integrated frameworks for the management of internal (e.g. from ageing infrastructure) and external (e.g. from market processes or competitor actions) risks to the utility;
(2) the support of board-level, executive management and operational staff as well as that of external stakeholders; and
(3) the effective communication of risk and engagement within decision-making processes both within companies and with external stakeholders.

Developing organizational cultures responsive and not necessarily wholly averse to risk is itself a challenge. Recent international reports (Stern and Fineberg, 1996; Economic and Social Research Council Global Environmental Change Programme, 2000; Prime Minister's Strategy Unit, 2002; Royal Academy of Engineering, 2003; Australian Academy of Technological Sciences and Engineering, 2002) have commented on the relationship between risk management and organizational performance and culture. Critical aspects include:

- the importance of openness, transparency, engagement, proportionality, precaution, evidence and responsibility to good decision-making;
- the critical role of taking a long-term perspective in assessing the potential indirect consequences of management actions; and
- a widely-held view that 'hard' quantitative risk analysis tools used in isolation of transparent decision-making does little to gain public confidence and can result in the long-term erosion of trust.

*Correspondence to: Professor S. J. T. Pollard, Integrated Waste Management Centre, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK.
E-mail: s.pollard@cranfield.ac.uk

Although the techniques of risk identification, analysis and management have been commonly applied within other process industries, their explicit and routine use within the water utility sector has historically been less widespread (Egerton, 1996). There is considerable scope for learning from the experiences of related utility sectors, for example the offshore (UK Offshore Oil Operators Association, 1999), energy supply and nuclear industries (European Commission, 2000), and from companies at the cutting edge of risk management. These combined experiences will prove invaluable to the water sector as it considers the risk analysis strategies and decision-making frameworks it might adopt for more defensible and rewarding utility decisions.

The transition to an explicit risk management philosophy within the water utility sector is reflected in recent revisions to the World Health Organization's (WHO) Guidelines for Drinking Water Quality (Fewtrell and Bartram, 2001; WHO, 2002, 2003). This is placing an emphasis on the development and implementation of water safety plans for water quality management and, within these, application of risk frameworks such as the 'hazard analysis and critical control points' (HACCP) approach (Dewettinck *et al.*, 2001; Hellier, 2000) as a basis for prioritizing risk management measures within the water supply chain from catchment to tap. The approaches place primary emphasis on achieving effective operational performance than a narrow focus of monitoring finished water quality (end-product testing) against numerical water quality standards. The latter approach is fundamentally reactive rather than preventative and is inherently less reliable given the limitations of monitoring in proportion and frequency (Hrudey, 2003).

RISK GOVERNANCE

Commentators increasingly refer to activity that integrates risk management across legal, financial, environmental and other risks as 'risk governance' (European Commission, 2000): 'governance', because the frameworks proposed extend to the broader institutional arrangements and responsibilities for managing risk (e.g. National Health and Medical Research Council, 2001; Council of Standards of Australia, 1999). Clarity over the accountabilities, both between and within organizations, is essential if risk management is to translate into practical procedures that deliver sustainable improvements in service and decision-making to the drinking water community. A critical aspect is the capabilities of institutions in managing risk. These can be thought of as the processes, people, reports, methodologies and technologies (collectively, 'risk infrastructure') acquired or developed to systematically identify, source, measure, manage and monitor risks (DeLoach, 2000). Although mostly qualitative, attempts have been made to categorize and rank institutional risk management expertise. For example, Sharp *et al.* (2002) describe a 'maturity' model in which organizations progress from being 'learner organizations' with *ad hoc* approaches to risk and reliability management through to 'adaptive organizations', which have an adaptive, responsive and proactive approach.

The structural hierarchy that exists even within 'flat' organizations requires that risks are actively managed at



Figure 1. The risk hierarchy (after Prime Minister's Strategy Unit, 2002).

the strategic, programme and operational levels of an organization (Figure 1). Typically, there are split accountabilities for these risks such that the chief financial officer/financial director and board have overall responsibility, supported by an internal audit or control function for the management of strategic risks; executive management for programme level risks (e.g. asset management, maintenance planning) and operational (e.g. site) managers for operational risks (e.g. plant performance). Many companies have risk management committees in place that monitor and report on priority risk areas within the company, principally in response to requirements on internal control. Beyond these company boundaries, there are important risk interfaces with other institutions including the regulators (e.g. licenses to operate) and the capital markets (e.g. raising finance).

An important interface concerns the financing of infrastructure spend and the raising of capital. Over and above the levy of rates at the local level to support investment on the maintenance of water and wastewater treatment systems, capital spend within public sector utilities is supported through the tax base and granted via a series of government-aided revenue streams or funds. For example, in the US, the Clean Water State Revolving Fund (set up under the 1987 Clean Water Act) provides financial support to individual states to pay for sewage treatment works, and the Drinking Water State Revolving Fund (1996 Safe Drinking Water Act) supports capital investments in water treatment facilities. Within private sector utilities, capital (Figure 2) is typically raised from the markets, e.g. as shares or a bank loan and invested in a firm's operations (e.g. a treatment plant). These investments are treated as costs and include all capital and operational expenditure. Operation develops revenue, and if this income exceeds expenditure it is returned back to the investors or reinvested into the company. The latter is acceptable if it leads to an increase or securing of the current value of the share price (Strutt, 2003).

In the UK, the water regulators [the Office of Water Services for England and Wales (Ofwat), the Drinking

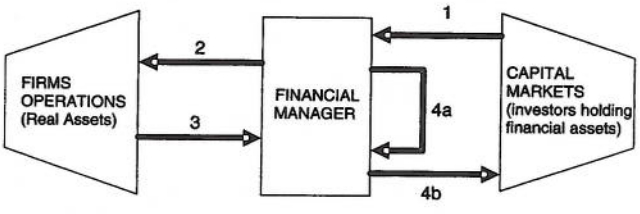


Figure 2. Water utilities and financial risk (after Strutt, 2003).

Water Inspectorate (DWI) and the Environment Agency (EA)] have raised the prominence of risk management for assessing company performance. Following the 1999 periodic review of the industry, Ofwat released 'Maintaining serviceability to customers (MD161)' to managing directors of all water and sewerage companies and water-only companies, underlining Ofwat's desire to formalize risk management within the asset planning process. The procedures developed by the UK water sector are of equal merit to public sector utilities abroad in that

> each company needs to demonstrate how the flow of services to customers can be maintained at least cost in terms of both capital maintenance and operating expenditure, recognizing the trade-off between cost and risk, whilst ensuring compliance with statutory duties.

Ofwat's position has since been further clarified under the 'common framework' outlining the requirements for the 2004 Periodic review, embedding risk management firmly in the process. The DWI in their letter (IL15/2002), 'Distribution Operation and Maintenance Strategies (DOMS), DWI requirements and expectations' expands the need for water utilities to demonstrably and explicitly manage the risks from their operational activities.

Utility managers manage cash flow, whether raised through public or private sector means, by optimizing expenditure and income in the context of providing good, safe drinking water. Events inevitably occur that reduce income and cause increased expenditure. For example, failures in the infrastructure/distribution network causing leaks lead to increased expenditure on leak detection and pipe repair,, refurbishment or asset replacement. Public health incidents requiring emergency response and water advisories often incur substantial costs. The techniques of risk management are applied for at least one, and usually several of the following categories of risk:

(1) *Financial risk.* These are risks arising principally from the financial operations and management of the business. From an internal perspective, both capital and operating costs are reduced by carrying out assessments during the design stage of a scheme, whilst operating and maintenance costs can be optimised on existing plant. External financial risks are derived from market processes (e.g. currency rate fluctuations) and are of rapidly increasing significance to water utilities, given the increasing need for self-financing and the twin trends of privatization and globalization.
(2) *Commercial risk.* Formerly considered immune to such risks owing to their public sector monopoly, utilities are no longer insulated from competition or financial instability. They face an increasingly demanding public with powers to make significant changes if unsatisfied (Westerhoff, 2003; Westerhoff and Lane, 1996). A serious accident can depress the share price in publicly quoted companies, persuading boards to make management changes.
(3) *Public health risk.* Failure or inadequacy of the treatment and distribution process can result in an interruption of supply or derogation in water quality (microbiological or chemical). The underlying causes may include source contamination, human error, mechanical failure or network intrusion. The consequences can be immediate; there is often very little time to reduce exposure and the impacts can affect a large number of people simultaneously. The financial costs to the community of the fatal Walkerton outbreak, for example, were in excess of Cdn$65 million, with one-time costs to Ontario estimated at more than Cdn$100 million (O'Connor, 2002). The loss of consumer confidence has been enormous (Hrudey and Leiss, 2003).
(4) *Environmental risk.* Equipment failure or human error can lead to environmental impacts, including discharges to the atmosphere, ground or the water environment. These may occur directly or as a result of actions to mitigate the results of the failure, such as discharges of polluted water from a tank. Similarly, environmental change can affect water quality. The relationship between watershed management, source quality and water quality at the tap is inevitably one characterized by a need for sound risk management.
(5) *Reputation risk.* For most water utilities and regulators, the biggest fear is the loss of consumer confidence. If an organization has target levels in its customer charter, considerable time and effort can be taken up by customer service functions explaining to customers and the media when incidents occur. The Sydney Water crisis of 1998 (McClellan, 1998) was estimated to have cost Sydney Water Corporation over $37 million in directs costs with contingency costs estimated at over $100 million, for an episode with no health consequences (Quill, 1999).
(6) *Compliance/legal risk.* Legislation sets out minimum standards for water quality, the handling and storage of treatment chemicals, the discharge of wastes and the health and safety of the operational staff and the people living nearby. Aside from the inherent risk of failure to comply with legislation (with all its associated consequences), there is the risk arising from uncertainty regarding the future actions of the regulator/legislator. Even when there is no legislation covering some aspects, there can be claims of negligence against operating companies and litigation for civil damages have been prominent features following both the Walkerton outbreak (settled out of court) and the Sydney Water Crises (largely dismissed, costs still incurred).

Assessing risk across these and other categories then becomes essential for optimizing operations and cost/benefit trade-offs. A typical issue is the optimization of workforce planning (e.g. asset inspection or maintenance scheduling). In risk-based resourcing, human (and financial) resources are targeted towards addressing higher risk activities (Pollard *et al.*, 2002; Figure 3). The presumption is that moving to risk-based resourcing (focusing on poorly performing assets, the failure consequences from which are higher) yields greater risk reduction per unit resource of maintenance. Many water companies have risk ranking procedures in place to inform maintenance scheduling. Principles have been developed for the proper design (Long and Fischoff, 2000) of ranking systems following earlier criticism over the implications of bias within these systems.

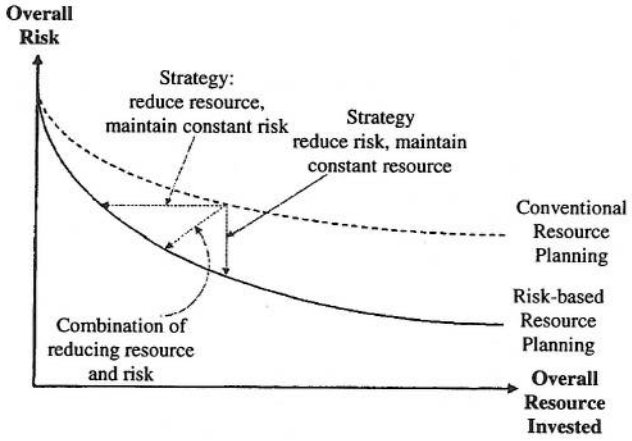


Figure 3. Risk-based workforce planning (after Pollard *et al.*, 2002).



Figure 4. Risk Management Framework (after US Presidential/Congressional Commission on Risk Assessment and Risk Management, 1997).

RISK MANAGEMENT

Decisions on managing risk, if they are to be effective, need to be active rather than reactive and well structured (Pollard and Guy, 2001). Risk management frameworks set out the relationship between the processes of risk identification, evaluation and management (Jardine *et al.*, 2003). They can be regarded as 'route maps' for decision makers. The principles for water utility risk management have been outlined for the Australian water industry to illustrate the value of developing a preventative quality management approach (Hrudey, 2001). One of these, 'turning hindsight into foresight', has been developed as a compilation and analysis of case studies of drinking water outbreaks in developed countries (Hrudey and Hrudey, 2004).

Classical linear approaches to risk management have been replaced by iterative frameworks that adopt the management processes of 'assess–plan–do–monitor–revise' and that aim to engage stakeholders in decision-making. Their application has resulted in a reappraisal of risk analysis in which the relationship between the analysis of risk and the audience is recognized as central to defensible decisions. The US Presidential/Congressional Commission on Risk Assessment and Risk Management (1997) was among the first of government responses to take a fresh look at the issue of risk management. The framework (Figure 4) recognizes the continuous improvement necessary for organizations to develop a mature capacity in risk management and the central role of stakeholders to the decision-making process. It emphasises the importance of (a) good problem definition, (b) management feedback in making decisions, and (c) the central role of stakeholders within the decision-making process. Here, risk analysis is viewed not as an end in its own right, but as a means of selecting and prioritizing options for risk management, that themselves require evaluation after implementation, all set within a context of making better decisions. These frameworks can, however, inadvertently cloud the explicit role of science and evidence within decision-making. The 'process' and 'content' of decisions must be viewed as equally important to the outcome, thus developments since the US Presidential Commission are focusing on making more explicit the role for scientific evidence within democratic decision-making processes (e.g. USEPA, 1999; Charnley, 2000).

TOOLS AND TECHNIQUES FOR RISK ANALYSIS AT THE OPERATIONAL, PROGRAMME AND STRATEGIC LEVEL

Risk analysis plays a role alongside other decision tools for risk management. Not all risks require detailed analysis to be managed. In many industries there are accepted standards of performance and codes of practice (e.g. engineering standards; accepted best practice; Figure 5) that, if adhered to, provide high degrees of control. These are applied where uncertainties and system vulnerabilities are well understood. However, complex, uncertain and novel systems, and situations with a deviation from routine operation, may require risk analysis, so as to better understand what drives the risk from or to the plant, process or operation, thereby allowing management measures for the reduction of unacceptable risks to be targeted.

Tools and techniques for the analysis of these different types of risk vary by their sophistication and design. A wide range of approaches are available (Table 1) from distribution modelling for the analysis of contaminants and pathogens within catchments, to probabilistic fault tree models for the analysis of potential engineering failures at the works level. The implementation of a portfolio of risk techniques within a water utility is contingent on institutional capacity, data quality and the requirements of the decision that the risk analysis is informing.

Operational Risk Analysis

Here we are concerned with the assessment of risks associated with specific operations at plant level—for example, the risk of failure of a device or process component, or the risk of exceeding a particular water quality standard. A common technique used is a semiquantitative risk ranking of hazards according to their likelihood and consequence. Leverett (2000) describes the ranking of risks from and to routine and non-routine process operations within four risk categories: health and safety, water quality, water quantity and environmental. Analysis and prioritization assists treatment managers in identifying

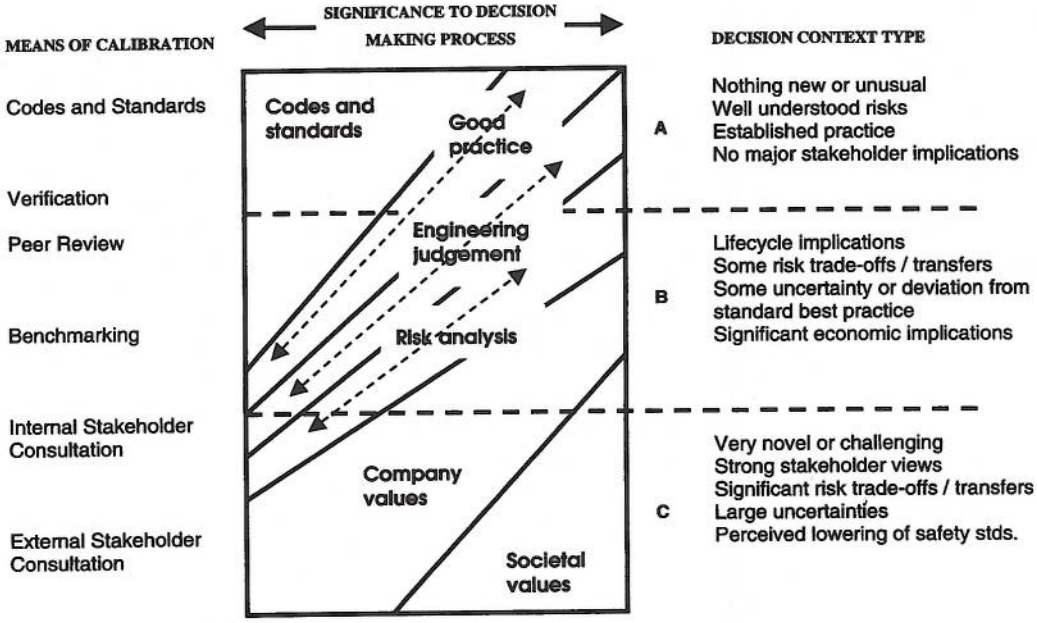


Figure 5. Decision framework for the offshore oil industry (after UK Offshore Oil Operators Association, 1999).

and mitigating previously unforeseen risks to operations, and the planning of projects such as the shut-down and maintenance of a strategic treated water reservoir. A similar ranking approach has been used to identify health and safety hazards at treatment works, e.g. with respect to hazardous chemical usage (Wirth and Siebert, 2000). Typically, risk ranking is used to screen risks as part of a more involved tiered risk assessment programme. The National Health and Medical Research Council (NHMRC), the body responsible for issuing drinking water guidelines to Australian water utilities, in their 'Framework for management of drinking water quality' (National Health and Medical Research Council, 2001, Rizak *et al.*, 2003) describe the incorporation of several risk assessment techniques within a single quality management system. In addition to risk ranking, the framework advocates the

Table 1. Risk analysis strategies for operational, programme level and strategic risks in the water utility sector.

Level	Example	Tools used	Reference
Operational	Assessing reservoir safety—operations and structural condition	Fault and event tree analysis	Parr and Cullen (1988)
	Health and safety hazard assessment—chemical use at water and wastewater treatment works	Risk ranking Hazard and operability studies (HAZOP) What if, checklists Failure mode and effect analysis (FMEA) Fault-tree analysis	Wirth and Siebert (2000)
	Process risk assessment and project contingency planning	Risk ranking	Leverett (2003)
	Individual pathogen risk assessment	Simulation (e.g. Monte Carlo)	Teunis *et al.* (1997) Masago *et al.* (2002)
Programme	Risk-based asset management	GIS-based infrastructure risk models	Doyle and Grabinsky (2003) Booth and Rogers (2001)
	Process risk assessment to help formulate asset management strategy	Risk ranking Failure mode and effect analysis (FMEA)	Abell and Askey (2001)
	Prioritising expenditure on mains rehabilitation	Three tiered risk assessment: (1) Risk ranking (2) Generic quantitative risk assessment model (KANEW) (3) Monitoring programme with tailored QRA	Radovanovic and Marlin (2003)
Strategic	Investment risk analysis—portfolio management for public utilities	Multi-attribute analysis Scenario planning and analysis	Rothstein and Kiyosaki (2003)
	Financial risks of public–private partnerships for infrastructure projects	Simple expected cost analysis Sensitivity analysis Monte Carlo simulation	Grimsey and Lewis (2002)

application of a HACCP (hazard analysis critical control points) methodology, namely the determination of 'critical control points' whereupon risks can be monitored and reduced. The NHMRC framework proposes that utilities should adopt a multiple barrier approach to risk management (Hrudey and Hrudey, 2003; Deere *et al.*, 2001), ensuring multiple levels of protection against specific contaminant threats. NHMRC presents an example of this from two treatment works, both with very different water sources: (a) a heavily protected catchment (Melbourne) and (b) a large river fed by multi-use catchments (Adelaide). In the Melbourne system, applied barriers include protected catchments, large catchment reservoirs, and effective chlorination, whereas in the Adelaide system the barriers are more heavily weighted towards treatment and downstream controls. Risk analysis has long been the basis for the derivation of water quality guidelines for drinking water (WHO, 2002). The substance-specific health risk assessments that have historically informed the guidelines may, however, be somewhat distanced from the immediate operational context of individual utilities. The recent draft of the third edition of the WHO drinking water guidelines (WHO, 2003) provides explicit reference to chemical and pathogenic risk management for water quality control. Risk analysis tools are available for informing utility decisions on risk management.

The New Zealand Ministry of Health (NZMOH) has developed a pragmatic programme for encouraging public health management plans (NZMOH, 2001). Their approach was developed with full awareness of HACCP but a conscious decision was made to focus on 'events' defined as incidents or situations that may lead to hazards being introduced into, or not being removed from, the water (Nokes and Taylor, 2003). In developing this approach, four barriers were identified that, if maintained effective, will adequately control hazards:

- prevention of contamination entering the raw water of the supply;
- removal of particles from the water;
- inactivation of microorganisms in the water; and
- maintenance of the quality of the water during distribution.

The NZMOH approach targets smaller systems and particularly valuable for systems with limited technical resources.

Teunis *et al.* (1997) and Masago *et al.* (2002) describe the application of quantitative microbial risk assessment in an operational context, in determining the risk posed by pathogens from specific source waters. The process begins with the definition of the relationship between pathogen source levels and the consumed dose, followed by the construction of a deterministic model mathematically describing this relationship. The relevant dose–response relationship is applied in order to determine the 'unconditional' probability of infection—unconditional because at this stage no consideration has been given to the distribution spread of the outcome. In order to determine this spread, the first step is to generate the range of values for the input variables and specify their probability distributions. The authors input these values into a Monte Carlo simulation, which through a process of iterative sampling provides a frequency distribution for the probability of infection. Similar approaches can be adopted for determining the risk of exceeding water quality compliance standards at a particular plant. In assessing the potential threats to water supplies from ongoing or accidental releases within catchments, Halfacree (1998) describes the use of PRAIRIE, a PC-based software tool for assessing chemical pollution risks to water bodies. The main elements are an aquatic dispersion model; hydrological, substance and standards databases; and a tabular/graphical output facility. The model has a deterministic mode (used to 'screen out' low risk sites) and a probabilistic mode (for more detailed analysis of high risk sites). The output results (e.g. frequency vs concentration curves) are compared with pre-determined criteria to inform regulatory actions on risk management from hazardous activities within a sensitive catchment.

Risk analysis at the operational level is further concerned with the reliability of the system components, for example in determining the risk of failure of a particular treatment step. The analysis may be summarized (Egerton, 1996):

- What can go wrong with the system?
- What are the effects and consequences of failure?
- How often will that failure occur?

For unreliable or heavily used equipment, an analysis of the historical data is often sufficient for determining frequencies of failure. In the absence of such data, there exist a number of techniques for assessing the frequency and consequences of system failure, including fault tree analysis (e.g. Parr and Cullen, 1988) and failure mode and effect analysis (e.g. Demotier *et al.*, 2002).

Programme Level Risk Analysis

At the programme level, we are concerned primarily with techniques used to evaluate the risks posed by a similar hazard at a variety of locations (e.g. mains bursts, progressive failure of filter media—in asset management, for example) or with the wide variety of risks existing within a watershed. The availability of geographic information systems has facilitated the ease by which such assessments can be performed. Programme level risk assessments are typically concerned with the implementation of strategies across multiple sites and geographic regions (catchment/watershed planning).

Risk analysis of infrastructure assets is widespread within the sector, and is a critical tool in asset management. Approaches range from the simple coupling of GIS techniques with infrastructure data in order to visually track utility assets and examine their associated risk factors (e.g. Doyle and Grabinsky, 2003; Booth and Rogers, 2001) to the complex integration of data intensive GIS with hydraulic simulations in order to assess the risk of distribution system intrusion (e.g. Lindley and Buchberger, 2002). On a national scale, the US Natural Resources Defence Council (NRDC, 2003) recently reported on the risk to drinking water quality from aging pipes and process plant across the USA with individual city 'rankings' being informed by water quality data, USEPA compliance records and water utility annual reports. Similar risk ranking techniques have been used internationally to inform threat assessments of water

systems in light of recent terrorist activities (e.g. Anonymous, 2001).

The assessment of hazards to the quality of water resources within a catchment or watershed is increasingly subject to formal risk assessment and can be expected as part of routine water safety plans (Umweltbudesamt, 2003; WHO, 2003; UKWIR, 2003). In Europe, the DPSIR approach to identifying key hazards within a watershed, by reference to the driving forces (e.g. population growth), pressures (sewer discharge), state (increased nutrient load), impacts (anthropogenic eutrophication) and policy response (discharge control) is being adopted under the European Water Framework Directive (IMPRESS Management, 2002). Here, risk assessments are intended to inform a programme of activities targeted at raising the ecological status of the watershed. Various tools are available for the analysis of catchment risks. For example, Wickham and Wade (2002) have developed a watershed risk model of nitrogen and phosphorus export based on the surrounding land cover class, whilst Verro *et al.* (2002) describe a GIS-based mass balance model for use in risk assessments of agricultural chemicals. Given the plethora of potential catchment management issues in any improvement programme, there is a need to prioritize risk management within the watershed by concentrating on those measures that reduce the significant likelihood of severe impacts being realised. Lytton *et al.* (2003) describe a generic methodology based on the source—pathway—receptor model (Environment Agency, 2000) that enables the evaluation and ranking of potential pollution risks to groundwater abstractions. This ranking is designed to be used in prioritizing risk management or mitigation procedures.

Programme level risk analysis invariably involves trading costs and benefits, such as in risk-based resourcing previously described (Figure 3). When designed well, piloted and implemented with feedback, these systems can provide a sound basis for distinguishing greater risks from lesser ones, and for investing resources in risk management that are proportional to the risks posed (Pollard *et al.*, 2002). However, these systems, whether for driving maintenance schedules, monitoring regimes or workforce planning, may also incur risk unless the consequences of resource trade-offs are themselves assessed. An example relevant to drinking water safety arose from the actions of the Saskatchewan Department of Environment and Resource Management (SERM) prior to the North Battleford *Cryptosporidoisis* outbreak in April 2001. This provincial department held legislative responsibility for the drinking water programme in Saskatchewan and, when faced with budget cuts in the mid 1990s, it drastically reduced the already limited field inspection and enforcement of municipal drinking water facilities. This culminated in a SERM proposal to eliminate its drinking water programme altogether that was tentatively approved by the Treasury Board in 2000/2001 and justified as being based on risk-based decision-making. The subsequent North Battleford outbreak, infecting between 5800 and 7100 persons in the immediate community plus a large numbers of visitors from three other provinces, led to a public inquiry into the outbreak and the provincial drinking water regulatory system. Justice Laing concluded in his Inquiry report:

> that the current risk-based model employed by SERM since 1996 is arrived at on the basis of economics, and has nothing to do with how best to safeguard the health of the population, all of whom consume water. (Laing, 2002).

For a provincial regulator to use 'risk' as a basis for eliminating altogether inspections and field support at a time when a substantial number of utilities were out of compliance with the drinking water guidelines appears to be a serious distortion of the concept of risk as the basis for decision-making.

Strategic Risk Analysis

Risks at the strategic level include project, commercial and financial risks, such as those associated with infrastructure investment; merger and acquisition activity; company reputation; outsourcing; and the long term viability of investment decisions. Louis and Rogers (2001) provide a strategic risk analysis of three investment strategies and describe a multi-objective planning model that seeks to optimize operational capacity and economic, environmental and social gains. The project and investment risks associated with public-private partnerships are reviewed by Grimsey and Lewis (2002). Using the financing of Stirling Water, a Scottish design–build–operate contractor as an illustrative example, they discuss the complexity of the contractual arrangements within such partnerships and use a quantitative analysis of returns on investment to characterize the robustness of cash flows from each of the senior lenders to this public–private venture. Rothstein and Kiyosaki (2003) describe the application of portfolio management theory to utility investments in order to provide a balance of risk and return that is consistent with the utility's strategic goals and objectives. This approach, facilitated by tools including multi-attribute analysis and scenario planning, involves: (a) determining the set of investments available to the water utility and their characteristics in terms of risks (both monetary and non-monetary), returns and resource requirements; (b) prioritizing investment opportunities across functional areas (i.e. looking beyond departmental barriers within organisations); and (c) selecting investment options by virtue of their alignment with established corporate goals and objectives.

Group risk managers also need to consider risks external to their operations. Water utilities are becoming increasingly exposed to commercial and market risks (Rothstein and Kiyosaki, 2003; Westerhoff and Lane, 1996), exposing them to a climate of operational uncertainty, including currency and interest rate fluctuations, competitive dynamics (the interactions between utilities in a liberalised market), and stock market volatility. In this context, recognizing the link between risk and opportunity becomes crucial. Tools and techniques to evaluate these risks include value at risk models, which examine gross or notional assets at risk (e.g. currency exposure) from a change in a key market variable (exchange rates); and scenario/simulation modelling, which can offer insights into how aspects of the market may evolve. As privatization and globalization take root within the water utility sector, in concert with an increasingly demanding regulatory and consumer

environment (Westerhoff, 2003), the evaluation and management of these risks will become increasingly important.

IMPLEMENTING AND IMPROVING RISK MANAGEMENT IN ORGANIZATIONS

Making credible and defensible decisions in organizations requires an institutional capacity to be predictive rather than reactive when managing risk and an aptitude to learn from experience. Implementing risk analysis strategies and decision-making frameworks requires clear, straightforward procedures that can be understood, agreed and operated by all levels in an organization. 'Keeping it as simple as it needs to be' has been a mantra of risk analysts (Morgan and Henrion, 1990). The implementation of a working framework should not be seen as the end-point of risk management (DeLoach, 2000). Businesses must strive to continuously re-assess and improve their capabilities for dealing with risk. Senior management must be able to define their risk management capabilities (both current and desired) and assess the costs and benefits of improvement (DeLoach, 2000). An increasingly applied tool that can assist in achieving this goal is the capability maturity model. Initially developed for the improvement of software processes (Paulk *et al.*, 1993), the model has been adapted and applied for use more broadly (IACCM, 2003), for example in the oil and gas sector (Sharp *et al.*, 2002). Risk mature organisations have the following key processes in place (Strutt, 2003):

(1) *Core risk management processes*, including (i) setting and allocation of safety risk and reliability requirements, (ii) performance of risk analyses including reliability and safety studies to inform decisions, (iii) design and operation of plant to meet specified risk and reliability requirements, and (iv) risk assurance to the customers, stakeholders and regulators.
(2) *Typical organizational implementation processes* include (i) the verification of management processes and validation of risk models and data, (ii) project risk management (ensures risks managed to cost and delivery schedules), (iii) emergency response management, (iv) reliability, qualification and safety testing (provides assurance of performance), (v) measurement and analysis of data (assurance of what is achieved in service), (vi) procedures for the management of change (identifying key differences), and (vii) supply chain management (sometimes failures and incidents have their causes in products supplied down the supply chain).
(3) *Institutional support.* Finally, there is an expectation that the implementation of a risk management framework will be supported by organizational learning, education and training and research and development.

Capability maturity models have a set of well-defined attributes that can be used to benchmark organizations within a sector. A company's capability in risk management can be evaluated by reference to these attributes and well-defined 'scores' representing a scale from poor to best practice in the demonstration of that attribute. 'Spider diagrams' (Figure 6) allow comparisons between organizations and cross-sector similarities to be established, showing where further improvements can be made. Using these models, it is possible to rank an organization's progression from a learner to exemplar of best practice in risk management. Sharp *et al.* (2002) describe five levels of maturity. At level 5 (highest), the organization is at 'best practice', capable of learning and adapting itself. It not only uses experience to correct any problems, but also to change the nature of the way it operates. Level 4 organizations are 'managed organizations' controlling what they do in the way of processes with requirements, ensuring these are met through feedback. A level 3 'defined organization' can say what it does and how it goes about it, whilst level 2 can repeat what it has done before, but not necessarily define what it does or adapt previous experience to a new situation. Finally, a level 1 organization is characterized by an absence of the above qualities. Of fundamental importance is the acceptance that resources are finite, and so desired capabilities should be selectively pursued according to particular risks or risk types (DeLoach, 2000). The value of these models of course is in identifying what measures are required for an organization to progress between levels of maturity in risk analysis and management. Ultimately, of course, risk analysis as only as good as the decision it informs and risk management activity should reflect sensible and meaningful conclusions rather than theoretical perspectives that may run counter to sound judgements (Hrudey and Hrudey, 2003).

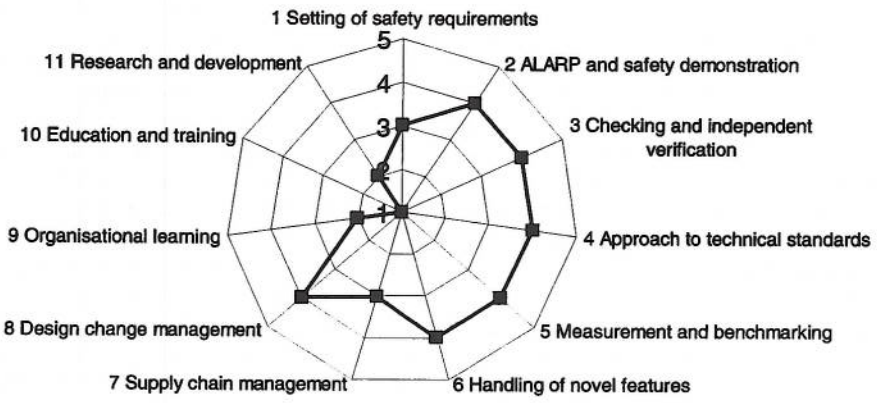


Figure 6. Illustrative spider diagram showing organisation profile (red) by reference to key aspects of safety and design (after Sharp *et al.*, 2002).

CONCLUSIONS

The water utility sector has made substantial progress to recognizing the value of risk analysis strategies and decision-making frameworks within its business, evidenced by a number of current international water sector initiatives. Embedding these systems within organizations and making them fit for purpose is the next step.

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Spray irrigation of landfill leachate: estimating potential exposures to workers and bystanders using a modified air box model and generalised source term

Duncan Gray[a], Simon J.T. Pollard[a,*], Lynn Spence[b], Richard Smith[c], Jan R. Gronow[c]

[a]*Integrated Waste Management Centre, Cranfield University, Cranfield MK43 0AL, UK*
[b]*Spence Environmental Engineering, 239 Main Street, Pleasanton, CA 94566, USA*
[c]*Environment Agency, Science Group – Waste and Remediation, Block 1, Government Buildings, Burghill Road, Westbury-on-Trym, Bristol BS10 6BF, UK*

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Modelling approaches are used to assess human exposure routes to chemicals during spray irrigation of landfill leachates.

Abstract

Generalised source term data from UK leachates and a probabilistic exposure model ($BPRISC_4$) were used to evaluate key routes of exposure from chemicals of concern during the spraying irrigation of landfill leachate. Risk estimates secured using a modified air box model are reported for a hypothetical worker exposed to selected chemicals within a generalised conceptual exposure model of spray irrigation. Consistent with pesticide spray exposure studies, the key risk driver is dermal exposure to the more toxic components of leachate. Changes in spray droplet diameter (0.02–0.2 cm) and in spray flow rate (50–1000 l/min) have little influence on dermal exposure, although the lesser routes of aerosol ingestion and inhalation are markedly affected. The risk estimates modelled using this conservative worst case exposure scenario are not of sufficient magnitude to warrant major concerns about chemical risks to workers or bystanders from this practice in the general sense. However, the modelling made use of generic concentration data for only a limited number of potential landfill leachate contaminants, such that individual practices may require assessment on the basis of their own merits.
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Keywords: Spray irrigation; Landfill leachate; Exposure; Aerosols; Dermal; Risk; Assessment

1. Introduction

The irrigation of landfill leachate by spray or pipe flow systems onto grassland, woodland or peat slopes has been widely practised in the UK, particularly in areas (Scotland, Cornwall) where: (i) high rainfall leads to the production of large volumes of dilute leachate; (ii) there are appropriate areas of land for irrigation; or (iii) where isolation from sewer watercourses makes off-site disposal difficult or expensive. The practice has been regarded as suitable for dilute, high volume leachate and for the polishing of pre-treated leachate. To be successful, it relies on a combination of physicochemical and biological processes (plant uptake, evapotranspiration, oxidation, nitrification, denitrification, absorption and

* Corresponding author. Tel.: +44 1234 754 101; fax: +44 1234 751 671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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Fig. 1. Representative spray irrigation of landfill leachate using spray guns and illustrating typical spray radii.

adsorption) for treating leachate volume and pollutant (chemical oxygen demand (COD), biochemical oxygen demand (BOD), inorganic nitrogen) load (Tyrrel et al., 2002). In Cornwall, for example (Ankers and Ruegg, 1993), leachate concentrations of up to 1500 mg BOD_5/l and 300 mg NH_4^+-N/l, have been spray irrigated to woodland at appropriate loadings that show no detrimental effects on the irrigated vegetation; the loadings having been established on the basis of extended operational experience (Cornwall County Council, 1994). Irrigation equipment used historically includes slotted pipes, rain guns, sprinklers and spray nozzles. The practice was common in the UK during the late 1970s and early 1980s, though fine spray irrigation has decreased in recent years. Currently, most operations are conducted using larger spray guns to redistribute leachate within the landfill site (Fig. 1). Application rates per unit area vary substantially (Table 1) but are typically in the order of ca. 50 (m^3/ha)/d (Knox, 2003; personal communication). Irrigation volumes applied vary widely and seasonally (Table 1) and the practice is regulated through limits on volume and nitrogen load to the receiving land through regulatory conditions on waste management licences.

Spray irrigation results in the generation of aerosols, the volatilisation of contaminants and may result in the subsequent exposure of human receptors (workers, bystanders) to hazardous components in leachate through inhalation, ingestion or dermal exposure routes. Operators of waste facilities have statutory obligations with respect to protecting workers and public health. The general approach for assessing exposures to bystanders from chemical sprays has been to assume that, since bystanders may be exposed less frequently than workers, worker exposure, providing it is found not to be significant, is generally protective of public health (ACP, 2002).

This study concerns the preliminary screening of potential exposures in hypothetical site workers to specific leachate constituents during the spray irrigation of landfill leachate, with broader public health considerations in mind. We seek to understand the potential significance (in terms of the relative order of magnitude) of exposures that might arise from this practice and the relative contributions to total exposure from a range of exposure routes and hazardous components present in typical UK landfill leachate. In this context, the study might contribute to the risk screening requirements for landfill sites recently by the regulator (Environment Agency, 2004). Our approach has been to modify and apply a shower model combined with an outdoor air box model (Foster and Chrostowski, 1986; Walden and Spence, 1997) to represent an exposure space, or volume, on site, and to use generalised data from UK leachates as the source term for estimating exposures to hypothetical and maximally exposed workers. The risk estimates and hazard quotients generated cannot be regarded as definitive quantitative predictions of health risk. Their value is in illustrating the dominant exposure routes and likely chemicals of concern and thus in highlighting where further study might best be focused. Following an initial screen, a quantitative examination of the implications of varying certain key parameters in the analysis was undertaken. Results are interpreted in the context of the literature on dermal and inhalation exposures to chemicals in outdoor sprays.

1.1. Modelling exposures from spray irrigation

The estimation of human exposure to chemicals in sprays has its origins in the quantitative models used to

Table 1
Illustrative spray irrigation conditions for UK landfill sites in Cornwall, UK

Site	Pump rates (m^3/h)	Spray regime (vols. in 2002)	Nitrogen load (kg/ha)	Leachate quality	Conditions
A	80 (wood); 50 (fields)	150,055 m^3 32,500 m^3 (Nov.); 389 m^3 (Sept.)	50 (grassland); 70 (wood)	35–45 mg/l NH_4^+-N 5–16 mg/l NO_3^--N	Old leachate; Hypro™ spray nozzle 10 mm
B	80 (wood); 50 (fields)	23,600 m^3; 7600 m^3 (Nov.); 725 m^3 (Sept.)	700 (wood); 500 (grassland)	9 mg/l NH_4^+-N 20 mg/l NO_3^--N	Weak leachate only; Hypro™ spray nozzle 10 mm
C	80 (wood); 50 (fields)	6060 m^3; 859 m^3 (Nov.); 229 m^3 (Sept.)	700 (wood); 500 (grassland)	220 mg/l NH_4^+-N; 7 mg/l NO_3^--N	Hypro™ spray nozzle 10 mm

estimate exposures to volatile organic compounds (VOCs) in shower stalls and in the development of regulatory models for the control of exposures to pesticide spray (van Hemmen, 1993; Hamey, 2001; USEPA, 2001; European Commission, 2002). The modelling of inhalation exposures to contaminants from water used during showering is reported by several workers (Andelman, 1985; McKone, 1987, 1992; Little 1992a, 1992b; Giardino et al., 1992). One model, the Integrated Household Exposure Model (IHEM; Foster and Chrostowski, 1986) examines potential household exposures to VOCs through the ingestion of drinking water, inhalation of volatiles while showering, inhalation of water while bathing and through dermal absorption while bathing. An assessment of the IHEM (Carver et al., 1991), notes it as the most conservative of a range of models, predicting shower air concentrations approximately double those of the least conservative model. The IHEM is based on the two-film, gas–liquid mass transfer theory. The rate of volatilisation across the surface of a hypothetical droplet is estimated and the volatile chemical concentration in the air is predicted using the concept of dilution within a box. The model assumes that a volatile organic chemical evaporating into the air of the shower stall (the 'box') is completely mixed and there is no build up of the volatile organic chemical at the air–water interface. It does not take time-dependent distributions or in vivo toxicological considerations following exposure into account.

Shower models have been adapted to simulate the volatilisation of contaminants during spray irrigation. Walden and Spence (1997) applied the IHEM to a US groundwater irrigation scenario in which potential exposures to BTEX (benzene, toluene, ethylbenzene, xylenes) compounds were a concern. Residential use of contaminated groundwater for watering lawns or gardens (including vegetables) was considered and exposures, including the dermal contact of children playing under the sprinkler with spray, the ingestion of groundwater by the child, and the vapour inhalation by the adult or child under, or downwind of the receptor, were modelled. The model estimates vapour emissions from spray and the aqueous concentrations of contaminants in grounding spray. Air phase concentrations are estimated assuming complete mixing of air in the box and dilution within the box volume. Volatilisation is limited by mass transfer rates.

Briefly, the overall mass transfer coefficient is calculated as (see Glossary, for symbols):

$$K_L = \left[1/k_l + RT/Hk_g\right]^{-1} \tag{1}$$

Gas and liquid phase mass transfer coefficients for contaminants can be estimated from measured values for carbon dioxide (CO_2) and water (H_2O) and the following correlations:

$$k_{g(VOC)} = k_{g(H_2O)}[18/MW_{VOC}]^{0.5} \tag{2}$$

$$k_{l(VOC)} = k_{l(CO_2)}[44/MW_{VOC}]^{0.5} \tag{3}$$

The overall mass transfer coefficient is adjusted for the shower temperature and the viscosity of water at the lower temperature:

$$K'_{L(T_s)} = K_L[T_l\mu_s/T_s\mu_l]^{-0.5} \tag{4}$$

Volatilisation is assumed to be a first order process:

$$C_{sh} = C_o\, e^{-K_L t/600d} \tag{5}$$

The total amount of contaminant that volatilises is given by:

$$M_{sh} = fv \times Q \times time_{sh} \times C_o \tag{6}$$

Finally, the concentration of the shower air can be estimated from:

$$C_{sh} = M_{sh}/V_{sh} \tag{7}$$

Walden and Spence (1997) coded the model into the peer-reviewed BPRISC$_4$ (British Petroleum Risk Integrated Software Cleanup) software program (version 4, BP, 2001). Modelling a spray irrigation scenario, the concentration of volatilised chemicals in the air is calculated using an outdoor box approach, where the 'shower' volume (V_{sh}), the volume of air in which exposure occurs, is represented by a hypothetical box. The dimensions of the box are defined by the product of the wind speed and exposure time, the width of the spray source and the height of the receptor. The rate of mass volatilisation is calculated and the air in the box is assumed to be ventilated – differing from the shower scenario, where the air is stagnant and a total volatilised mass is calculated. The model assumes that the air in the box is fully mixed, the concentration in the box is constant and the receptor is inside the box. The model only considers on-site exposures and does not consider receptors at distance from the source. The on-site exposure will be more conservative than any exposures downwind of the source.

Table 2
Leachate compositional data (after Robinson, 1995; Knox et al., 2000 and Robinson and Knox, 2001)

Chemical	Frequency of occurrence in leachate samples (%)	Assumed distribution	Mean (mg/l)	Min (mg/l)	Max (mg/l)
Aniline	17	Triangular	1.46E−03	1.00E−03	7.00E−03
Aroclor 1260	20	Triangular	8.00E−05	2.00E−05	3.40E−04
Arsenic	94	Triangular	1.60E−02	1.0E−03	1.60E−01
Benzo[*a*]pyrene	29	Triangular	5.60E−03	5.25E−03	1.22E−02
Cadmium	20	Triangular	2.00E−02	1.00E−02	3.00E−02
Chromium^{VI}	33	Triangular	9.20E−02	5.00E−02	1.24E+00
Dieldrin	7	Triangular	1.30E−04	7.00E−05	2.00E−04
Ethylbenzene	15	Triangular	1.90E−02	1.00E−02	5.90E−02
Hexachlorobenzene	17	Triangular	9.00E−05	4.00E−05	2.20E−04
Lead	8	Triangular	6.00E−02	5.00E−02	4.10E−01
Lindane	23	Triangular	3.37E−03	2.00E−05	2.03E−02
Mercury	30	Triangular	3.00E−04	1.00E−04	1.00E−03
Dichloromethane[a]	13	Triangular	4.28E−02	1.00E−03	5.04E−01
Naphthalene	70	Triangular	3.04E−03	1.00E−04	4.20E−02
Toluene	54	Triangular	8.70E−02	1.00E−02	1.29E+00
1,2,3-Trichlorobenzene	17	Triangular	5.80E−04	8.00E−05	1.29E−03
Xylenes	35	Triangular	5.90E−02	3.00E−02	2.08E−01

[a] Methylene chloride.

2. Methodology

2.1. Rationale

Caution must be exercised in conducting and interpreting quantitative risk studies (HSE, 2003). Conceptual models of exposure and the subsequent characterisation of risks rely on numerous assumptions, many of which have gross incertitude. The value of such analyses is in providing insights into system behaviour, rather than definitive point estimates of risk, for the purpose of informing an appraisal of the options for managing risk (Paustenbach, 2002a). To this end, the aim of this study was to understand the relative importance of a range of exposure routes and trace components in a generalised leachate for worker and bystander exposure during spray irrigation.

2.2. Source term data

Leachate compositional data were abstracted from Robinson (1995), Knox et al. (2000) and Robinson and Knox (2001) (Table 2). These studies reported analytical data on approximately 4000 leachate samples for 72 landfill sites throughout the UK (Robinson, 1995). Knox et al. (2000) further reported on 57 organic substances and 8 metals listed in the UK Pollution Inventory (PI), in raw and treated leachates from UK landfills. Following extension of the PI in 2002 to include a further 32 substances, these researchers sampled raw leachate and treated effluent from 24 leachate treatment plants. Thirty-six substances were tested for and of these 17 were present in more than 5% of samples (Robinson and Knox, 2001). Our assessment was limited to 17 chemicals (Table 2), selected (i) on the basis that they were identified in >5% of the leachates sampled; and (ii) on account of their accepted toxicological relevance and the availability of toxicological data. With respect to chemical classes and multivalent species, for ease, total polynuclear aromatic hydrocarbons ($\sum$PAH) were represented by benzo[*a*]pyrene alone, as a conservative surrogate. Similarly, hexavalent chromium (Cr^{VI}) represented the total chromium content of the leachate. Analytical data expressed PCBs in Aroclor 1260 equivalents and the toxicological profile for this substance was used to represent the mixture of PCB compounds. Where dose–response assessment data were not available for each exposure route, route-to-route extrapolations were invoked; oral carcinogenic slope factors and oral reference doses (RfDs) being used for dermal and inhaled exposures for organic compounds. Route extrapolations were not made for inorganics due to reported differences in absorption efficiencies for the two routes of exposure. This is acceptable within BPRISC$_4$ (BP, 2001) and is supported, for example, by regulatory guidance in the US EPA's Region 9 Preliminary Remediation Goals (EPA, 2003).

2.3. Operational assumptions for spray irrigation

There is considerable scope for variation in flow rates for the irrigation of leachate with the type of irrigation system used and loading rate of the soil, as well as with the age, type and location of the landfill site (Ankers and Ruegg, 1993; Alker et al., 2002). Estimated values for flow rate vary widely from ca. 11 l/min (Alker et al., 2002) to >800 l/min (Webb, 2003; personal communication). A nominal flow rate of 100 l/min was selected as

a reasonable assumption. A review of spray droplet distribution data from Kohl (1974), Kohl and DeBoer (1984), Edling (1985), Solomon et al. (1985), Li et al. (1994) and Kincaid et al. (1996), and the rationale given by Walden and Spence (1997) resulted in the selection of a value of 0.2 cm for the droplet diameter. The droplet residence time represents the length of time that a particular droplet is available to contribute emissions of volatile contaminants to the outdoor box. A conservative assumption of droplet residence time is 10 s, to account for volatilisation occurring from water travelling through the air to the point where it is puddled or standing before it soaks into the soil, after which volatilisation is assumed not to occur.

Localised environmental conditions influence exposure. For the probabilistic analysis, triangular distribution data for average wind speed were approximated from the UK annual mean wind speed (BWEA, 2003), values for mean, minimum and maximum being 5, 0 and 9 m/s, respectively. Finally, because volatilisation increases with temperature and spray irrigation of leachate tends to be carried out during the summer, a leachate temperature of 20 °C was used.

2.4. Receptor characteristics

Receptor assumptions are presented in Table 3. A hypothetical maximally exposed receptor is an adult worker occupationally exposed to leachate spray. In this study, receptor assumptions were based, where appropriate, on the Department for the Environment, Food and Rural Affairs' (Defra's) Contaminated Land Exposure Assessment (CLEA) model (Defra, 2002). In CLEA, the critical receptor is a female aged 15 to 69 years. $BPRISC_4$ default values of fraction of total skin surface area exposed (10%; hands and forearms) were selected, where the CLEA value is for exposed hands only. The duration of exposure by the potential receptor is highly site-specific, but should reflect a reasonable estimate of the time spent by the receptor in the outdoor box. For consideration of an adult worker on a landfill site during spray irrigation, a conservative estimate of time spent in the outdoor air box is 4 h, while the maximum would be 8 h. The number of exposure events per year is based on irrigation during the eight warmest months, for a 5 day working week, i.e. 175 days or events/year. $BPRISC_4$ default estimates of typical exposure duration for workers is 8.3 years, with a maximum of 50 years (US Bureau of Labor Statistics, 1992). These assumptions were regarded as suitable for the purposes of this screening study.

2.5. Modifications to the outdoor air box

The inhalation of aerosol in spray is a route of potential concern. $BPRISC_4$ does not code for exposures due to inhalation and ingestion of aerosols (i.e. very fine water droplets) and the model requires modification. Exposure to contaminants that may be dissolved or suspended in the leachate, and then inhaled and inwardly ingested as aerosols was assessed in the same fashion as the ingestion of irrigated groundwater in the $BPRISC_4$ model. Whilst this approach does not accurately account for aerosols taken directly into the lung airways, it does allow for exposures from larger

Table 3
Summary of baseline input parameters for $BPRISC_4$

Input parameter	Distribution	Mean	Std Dev	Min	Max
Receptor characteristics					
Body weight (kg)[a]	Normal	68.5	13.9	46.4	68.5
Lifetime (y)	Constant	70	–	–	–
Ingestion rate (ml/h)	Constant	5.2E−01	–	–	–
Inhalation rate outdoors (m^3/h)[c]	Triangular	1.23	–	4.11	1.63
Lung retention factor (unitless)	Constant	1	–	–	–
Total skin surface area (cm^2)	Constant	1.76E+04	–	–	–
Fraction skin exposed to water (unitless)	Constant	1.1E−01			
Height of breathing zone (m)	Constant	2	–	–	–
Exposure characteristics					
Time in sprinkler (h/day)	Constant	4	–	–	–
Exp. freq. irrigation (events/year)	Constant	175	–	–	–
Exposure duration leachate (years)[d]	Lognormal	8.3	8.7	0	50
Spray operational parameters					
Width of sprinkler spray (m)	Constant	10	–	–	–
Sprinkler flow rate (l/min)	Constant	100	–	–	–
Droplet diameter sprinkler (cm)	Constant	0.2	–	–	–
Droplet droptime for sprinkler (s)	Constant	10	–	–	–
Environmental parameters					
Temperature of irrigation water (°C)	Constant	20	–	–	–
Average windspeed (m/s)[b]	Triangular	5	–	0	9

[a] Body weight maximum and minimum values taken as 5th and 50th percentile values for critical adult female receptor aged 16–59 (Defra, 2002).

[b] Average wind speed approximated from BWEA (2003).

[c] Inhalation rate determined: mean of active respiration rate; minimum of passive respiration rate; and maximum as 95th percentile of active respiration rate for critical adult female receptor aged 16–59 (CLEA, 2003).

[d] Exposure duration; default values from BPRISC, based upon Bureau of Labor Statistics (1992).

aerosols trapped in the upper respiratory tract and ingested. A conservative assumption of the percentage of irrigated leachate that would aerosolise was chosen as 1% v/v (Sorber et al., 1976; Camann et al., 1978, 1988). For a 4-h exposure and a flow rate of 100 l/min, this gives an estimate of 240 l. The volume of the outdoor air box was estimated to account for the total volume of leachate irrigated. This required selecting a value for the width of the outdoor air box to reflect the diameter of the spray area. Examination of data for irrigation equipment, suggested considerable variation between wetted spray radii of different irrigation systems. Using literature data, conservative estimates of spray diameter (10 m), wind speed (2 m/s), exposure time (4 h) and receptor height (2 m), provide a value for the volume of the outdoor air box (576,000 m^3). Thus the concentration of aerosolised leachate in the air box may be estimated (0.42 ml/m^3), assuming instantaneous dispersion and no settling of the aerosol over the exposure time.

2.6. Exposure assessment and risk characterisation

Given an active respiration rate for an adult female receptor of 1.2 m^3/h, the rate of inhalation of aerosol can then be estimated at 0.52 ml/h. For a 4-h exposure time and flow rates of 50 and 1000 l/min, the rates of inhalation of aerosol are 0.26 and 5.2 ml/h, respectively. Although the model is conservative in that it assumes that aerosols are dispersed and do not settle during exposure, it cannot account for the position of the receptor relative to the source within the outdoor air box, i.e., the closer the receptor the greater the volume of aerosol the receptor is likely to inhale.

A generalised leachate was subjected to probabilistic analysis in $BPRISC_4$ using mean, minimum and maximum leachate compositional data from UK leachates (Table 2). Probability distributions of risk were generated on 10,000 iterations of the model using parameter distributions identified in Table 3. $BPRISC_4$ adopts a US approach to risk estimation and risk characterisation for long term exposures. Chronic average daily doses (CADD; glossary for abbreviations) for non-carcinogens and lifetime average daily doses (LADD) for carcinogens are estimated using (Walden and Spence, 1997; BP, 2001):

For inhalation

$$\mathrm{LADD} = C_{\mathrm{air}} \times \mathrm{InhR} \times \mathrm{AAF}_{\mathrm{inhal}} \times \mathrm{LRF} \times \mathrm{ET} \times \mathrm{EF} \times \mathrm{ED} / (365 \times \mathrm{LT} \times \mathrm{BW}) \quad (8)$$

$$\mathrm{CADD} = C_{\mathrm{air}} \times \mathrm{InhR} \times \mathrm{AAF}_{\mathrm{inhal}} \times \mathrm{LRF} \times \mathrm{ET} \times \mathrm{EF} / (365 \times \mathrm{LT} \times \mathrm{BW}) \quad (9)$$

For dermal contact

$$\mathrm{LADD} = 10^{-3} C_{\mathrm{W}} \times \mathrm{SA} \times \mathrm{FS} \times \mathrm{AAF}_{\mathrm{dermal}} \times \mathrm{ET} \times \mathrm{PC} \times \mathrm{EF} \times \mathrm{ED} / (365 \times \mathrm{LT} \times \mathrm{BW}) \quad (10)$$

$$\mathrm{CADD} = 10^{-3} C_{\mathrm{W}} \times \mathrm{SA} \times \mathrm{FS} \times \mathrm{AAF}_{\mathrm{dermal}} \times \mathrm{ET} \times \mathrm{PC} \times \mathrm{EF} / (365 \times \mathrm{LT} \times \mathrm{BW}) \quad (11)$$

For ingestion

$$\mathrm{LADD} = 10^{-3} C_{\mathrm{W}} \times \mathrm{IR}_{\mathrm{iw}} \times \mathrm{ET} \times \mathrm{AAF} \times \mathrm{EF} \times \mathrm{ED} / (365 \times \mathrm{LT} \times \mathrm{BW}) \quad (12)$$

$$\mathrm{CADD} = 10^{-3} C_{\mathrm{W}} \times \mathrm{IR}_{\mathrm{iw}} \times \mathrm{ET} \times \mathrm{AAF} \times \mathrm{EF} / (365 \times \mathrm{BW}) \quad (13)$$

For carcinogens, risks are estimated as individual excess lifetime cancer risks (IELCR):

$$\mathrm{IELCR} = \mathrm{SF} \times \mathrm{LADD} \quad (14)$$

Potential non-carcinogenic effects are evaluated using the hazard quotient (HQ) and, where relevant, the hazard index (HI):

$$\mathrm{HQ} = \mathrm{CADD} / \mathrm{RfD} \quad (15)$$

$$\mathrm{HI} = \sum \mathrm{HQ}_1 + \mathrm{HQ}_2 + \mathrm{HQ}_3 \ldots \mathrm{HQ}_n \quad (16)$$

The (US) carcinogenic slope factor and hazard quotient approach to risk characterisation above is not adopted in the UK. Occupational and dietary exposures are assessed by reference to occupational exposure limits (OELs), including maximum exposure limits (MELs) for carcinogens, and tolerable daily intakes (TDIs); and are referenced to air concentrations and dose, not risk (Illing, 2001). For pesticide sprays, an acceptable operator exposure level (AOEL – a dose) is used (ACP, 2002). Environmental exposures are conventionally characterised by reference to the drinking water and air quality guidelines (Defra, 2001), that act as risk-based quality standards, expressed as concentrations, in the exposure medium of concern. The above toxicological criteria are referenced to individual statutes and do not easily fit the range of exposures considered in this study. For screening purposes therefore, risks were assessed using the US approach and dose–response data obtained from the USEPA integrated risk information system (IRIS; USEPA, 2003a, b), a database of human health effects that may result from exposure to various

Table 4
Summary Monte Carlo estimates of IECLR by exposure route (flow rate of 100 l/min and a droplet diameter of 0.2 cm)

Route of concern	Min	Mean	95%ile	Max	Std Dev
Ingestion of leachate aerosol	6E−09	3E−07	9E−07	3E−06	3E−07
Inhalation of volatiles	5E−10	4E−08	1E−07	3E−06	8E−08
Dermal contact with irrigated leachate	1E−05	5E−04	1E−03	5E−03	5E−04

substances found in the environment. The updated $RISC_4$ (BP, 2001) software is cross-referenced to IRIS.

3. Results and discussion

3.1. Risk estimates and apportionment

Risk estimates for the spray irrigation of generalised leachate, with a nominal flow rate of 100 l/min and droplet diameter of 0.2 cm, are summarised in Tables 4–7. Taking an IECLR (expressed as a lifetime risk, not an annual) of 1E−04 (1 in ten thousand; LaGrega et al., 2001) as an upper bound guideline for exposure to carcinogens from leachate and, for screening purposes, a HQ value of 1E + 00 (i.e. 1) as an indicator level for non-threshold contaminants, we can screen for exposure routes and principal chemicals of concern within the subset of 17 candidates substances (Tables 4–7). Acknowledging the uncertainties and model artefacts inherent to such an exercise and discussed below, an examination of the risk estimates modelled using this conservative worst case exposure scenario suggests that they are not of a sufficient order of magnitude to warrant major concerns about the chemical risks to workers or bystanders from this practice in a general sense.

In terms of contribution to exposure and reviewing the 95th %ile values in Tables 4 and 5, dermal contact with spray and benzo[*a*]pyrene emerges as a key contributor to the potential carcinogenic risk. Were we to adopt a toxicological equivalency factor (TEF) approach to apportioning the toxicity of ∑PAH between individual PAH the contribution would be lowered significantly. For illustrative purposes, if the risk component attributable to benzo[*a*]pyrene is set aside, the potential carcinogenic risk is reduced substantially with the key contributions to dermal exposure from Aroclor 1260, arsenic and dichloromethane (Fig. 2) at the 95th %ile level. The HI data by route and by chemical from the Monte Carlo analysis are summarised in Tables 6 and 7, respectively. In terms of overall hazard, the major contributing routes are dermal contact and the inhalation of volatile components from spray irrigated leachate (Fig. 3). None of the indices are expressed at a level of significance (i.e. HQ > 1). From Table 7, leachate components with the highest contribution to hazard quotient are Aroclor 1260, arsenic, Cr^{VI}, lindane, mercury, dichloromethane, naphthalene, toluene and xylenes. Again, because of the toxicity/permeability coefficient of Aroclor 1260 used for all PCBs in the leachate and because the significant route of exposure is by dermal contact, its contribution to the overall hazard is artificially increased.

Table 5
Summary Monte Carlo estimates of IECLR by chemical (flow rate of 100 l/min and a droplet diameter of 0.2 cm)

Chemical	Min	Mean	95%ile	Max	Std Dev
Aniline	7E−12	3E−10	1E−09	4E−09	4E−10
Aroclor 1260	2E−08	1E−06	4E−06	2E−05	2E−06
Arsenic	3E−09	8E−07	3E−06	1E−05	1E−06
Benzo[*a*]pyrene	1E−05	5E−04	1E−03	5E−03	5E−04
Dieldrin	3E−08	9E−07	3E−06	7E−06	9E−07
Hexachlorobenzene	8E−11	8E−09	3E−08	6E−07	2E−08
Dichloromethane	2E−10	7E−08	2E−07	2E−06	9E−08

Table 6
Summary Monte Carlo estimates of hazard quotients by exposure route (flow rate of 100 l/min and a droplet diameter of 0.2 cm)

Route of concern	Min	Mean	95%ile	Max	Std Dev
Ingestion of leachate aerosol	2E−03	8E−03	1E−02	2E−02	3E−03
Inhalation of volatiles	2E−03	2E−02	5E−02	2E+00	3E−02
Dermal contact with irrigated leachate	1E−01	4E−01	7E−01	1E+00	2E−01

3.2. Sensitivity analysis

Three simulations were executed varying certain of the input parameters: (i) decreasing the droplet diameter to 0.02 cm, since volatilisation increases with a decrease in droplet size (Edling, 1985); (ii) increasing the flow rate to 1000 l/min; and (iii) decreasing the flow rate to 50 l/min,

Table 7
Summary Monte Carlo estimates of hazard quotients by chemical (flow rate of 100 l/min and a droplet diameter of 0.2 cm)

Chemical	Min	Mean	95%ile	Max	Std Dev
Aniline	3E−05	2E−04	4E−04	4E−03	2E−04
Aroclor 1260	4E−02	3E−01	6E−01	1E+00	1E−01
Arsenic	3E−04	2E−02	3E−02	5E−02	1E−02
Cadmium	1E−03	3E−03	4E−03	6E−03	7E−04
$Chromium^{VI}$	2E−03	2E−02	3E−02	5E−02	9E−03
Dieldrin	5E−03	1E−02	1E−02	2E−02	2E−03
Ethylbenzene	4E−04	1E−03	2E−03	4E−03	5E−04
Hexachlorobenzene	2E−03	8E−03	1E−02	1E−01	3E−03
Lead	2E−04	8E−04	2E−03	2E−03	4E−04
Lindane	6E−04	4E−02	8E−02	2E−01	2E−02
Mercury	3E−04	3E−03	7E−03	1E−01	4E−03
Dichloromethane	3E−05	3E−03	6E−03	6E−02	3E−03
Naphthalene	9E−05	1E−02	3E−02	6E−01	1E−02
Toluene	2E−04	9E−03	2E−02	3E−01	7E−03
1,2,3-Trichlorobenzene	4E−04	3E−03	5E−03	1E−02	1E−03
Xylenes	1E−03	4E−03	9E−03	1E−01	3E−03

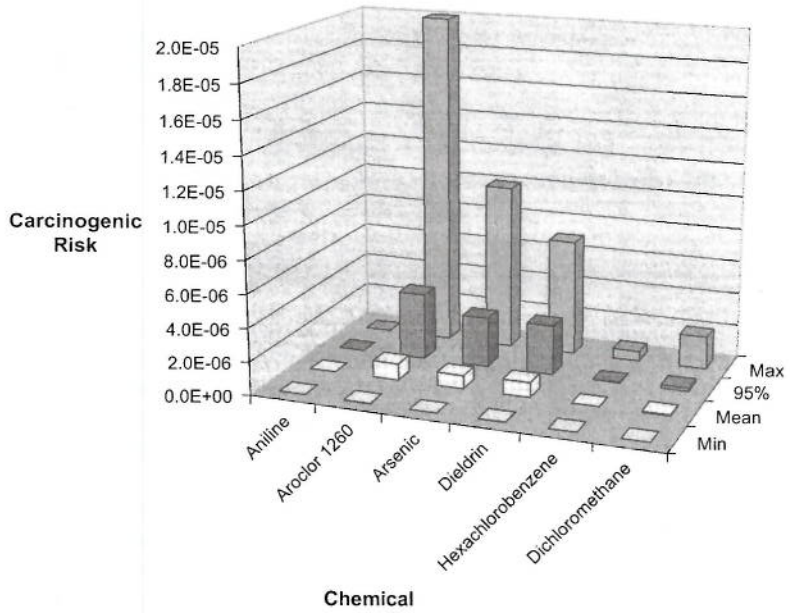


Fig. 2. Distribution of carcinogenic risk (IECLR) by chemical in spray irrigated leachate, excluding benzo[*a*]pyrene.

to reflect the variance in operational practice. An analysis of the carcinogenic risk estimates for each route is shown in Table 8 and for the hazard quotients, in Table 9. Again, dermal contact with irrigated leachate spray drives the exposure under these scenarios that assume that 10% of the receptor's skin surface area is wetted for 4 h/d.

Adjusting operational variables such as flow rate, droplet size, droplet residence time and the dimensions of the outdoor air box, appears to exhibit little effect on the level of dermal exposure. This may appear counter-intuitive. One normally expects, from Fick's law of diffusion, dermal absorption to be directly proportional to the applied concentration and the amount of chemical applied (entering the box; Paustenbach, 2002b). However, in the spray scenario, dermal exposure is not sensitive to flow rate and droplet size because it assumes that the skin is completely wet already and that there is enough water exchange (from the water already

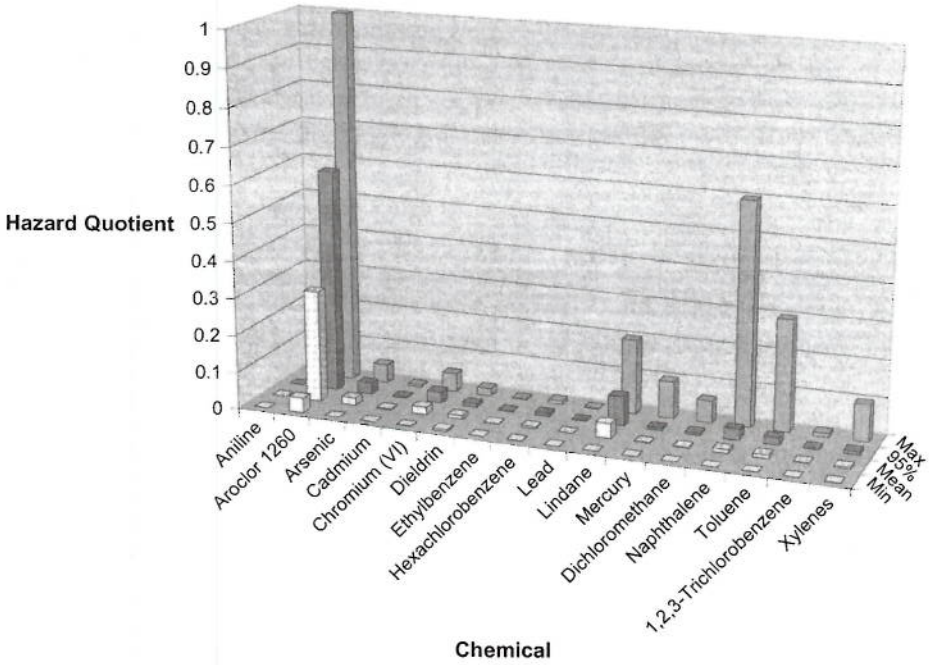


Fig. 3. Distribution of hazard quotient associated with chemicals in irrigated leachate, excluding benzo[*a*]pyrene.

Table 8
Summary estimates of IELCR varying droplet diameter and flow rate

Variable	Route of concern	Min	Mean	95%ile	Max	Std Dev
Droplet diameter = 0.02 cm	Ingestion of leachate aerosol	3E−09	3E−07	9E−07	4E−06	3E−07
	Inhalation of volatiles	3E−09	2E−07	6E−07	2E−05	4E−07
	Dermal contact with irrigated leachate	1E−05	5E−04	1E−03	4E−03	5E−04
Flow rate = 1000 l/min	Ingestion of leachate aerosol	6E−08	3E−06	9E−06	3E−05	3E−06
	Inhalation of volatiles	6E−09	4E−07	1E−06	3E−05	7E−07
	Dermal contact with irrigated leachate	1E−05	5E−04	1E−03	5E−03	5E−04
Flow rate = 50 l/min	Ingestion of leachate aerosol	3E−09	1E−07	4E−07	1E−06	1E−07
	Inhalation of volatiles	4E−10	2E−08	7E−08	2E−06	5E−08
	Dermal contact with irrigated leachate	1E−05	5E−04	1E−03	4E−03	5E−04

in contact with the skin) so that chemicals are not further depleted as they become absorbed. Under these assumptions, the only pathway-specific exposure parameters that dermal exposure to sprayed water pathway is dependent on are skin surface area in contact with water and the time spent in the water. The chemical-specific dermal permeability coefficients are also time dependent. Note this is quite different than the mechanism used for dermal absorption from chemicals in soil. By means of illustration, dermal contact was excluded as a route from the analysis and the effects of operational variables on the other two routes compared with a 'baseline' flow rate of 100 l/min (Fig. 4). These data indicate that over a reasonable range of input values, flow rate is an important input variable when estimating exposures via inhalation and ingestion as one would intuitively expect. All values for IECLR via ingestion of leachate aerosol or inhalation are proportionately less for a flow rate of 50 l/min compared with a flow rate of 1000 l/min, or reduced droplet size (and a flow rate of 100 l/min). Data for the inhalation route are closer for a droplet size of 0.02 cm compared with a flow rate of 1000 l/min, and greater in comparison to the values for the baseline flow rate of 100 l/min and droplet size of 0.2 cm, although within the same order of magnitude. The analysis suggests that droplet diameter also plays a significant role in the extent of volatilisation and subsequent exposure for the inhalation of volatile components. Minimum, mean and 95th %ile values for IECLR are greater for the ingestion of leachate aerosol than corresponding values for the inhalation of volatile contaminants, suggesting that the ingestion route is of greater significance in this scenario. Examination of data for the minimum, mean and 95th %ile values of HQ (Fig. 5) indicate a reversal of this order. Nevertheless, these effects are masked by the apparent dominance of the dermal to the total exposure.

3.3. Model artefacts

As discussed earlier, the width of the outdoor air box is assumed to be constant at 10 m. This is a conservative assumption based on examination of data for 360° rotating sprinklers, which are subject to very large variations between irrigation systems. The width of the outdoor air box is also treated as if the flow rate was from a single static sprinkler head, rather than from several sprinkler heads spaced along a distribution pipe allowing spray overlap, or from mobile spray irrigation systems. This considerably reduces the size of the outdoor air box and therefore increases the concentration of volatilised contaminants within the box. Thus our

Table 9
Summary estimates of hazard quotients varying droplet diameter and flow rate

Variable	Route of concern	Min	Mean	95%ile	Max	Std Dev
Droplet diameter = 0.02 cm	Ingestion of leachate aerosol	2E−03	8E−03	1E−02	2E−02	3E−03
	Inhalation of volatiles	4E−03	4E−02	1E−01	6E+00	1E−01
	Dermal contact with irrigated leachate	1E−01	4E−01	7E−01	1E+00	2E−01
Flow rate = 1000 l/min	Ingestion of leachate aerosol	2E−02	8E−02	1E−01	2E−01	3E−02
	Inhalation of volatiles	2E−02	2E−01	5E−01	1E+01	3E−01
	Dermal contact with irrigated leachate	9E−02	4E−01	7E−01	1E+00	2E−01
Flow rate = 50 l/min	Ingestion of leachate aerosol	1E−03	4E−03	6E−03	1E−02	1E−03
	Inhalation of volatiles	1E−03	1E−02	3E−02	9E−01	2E−02
	Dermal contact with irrigated leachate	9E−02	4E−01	7E−01	1E+00	2E−01

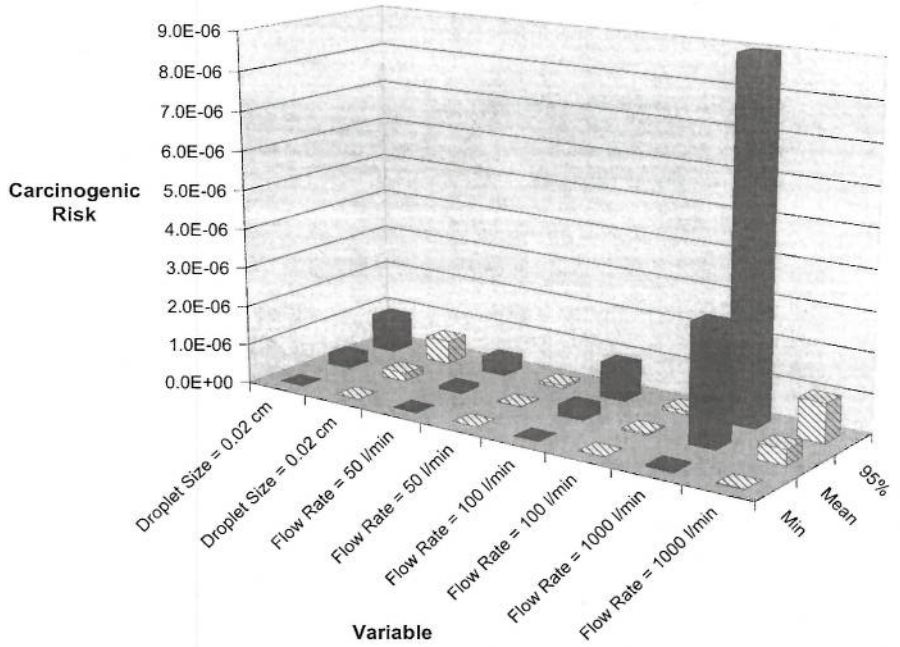


Fig. 4. Effects of variation in flow rate and droplet diameter on carcinogenic risk (IECLR) by route, excluding dermal contact. ■ = Ingestion of leachate aerosol; ▨ = Inhalation of volatiles.

assumptions about the air box are regarded as conservative. Further, the BPRISC model assumes that the spray (and/or volatile chemicals) is limited to the height of the receptor. All contaminants are assumed to stay below that height and are assumed to pass by the receptor. Therefore, a conservative assumption for height of the box is 2 m for an adult; this would be reduced for consideration of a child receptor. Use of the

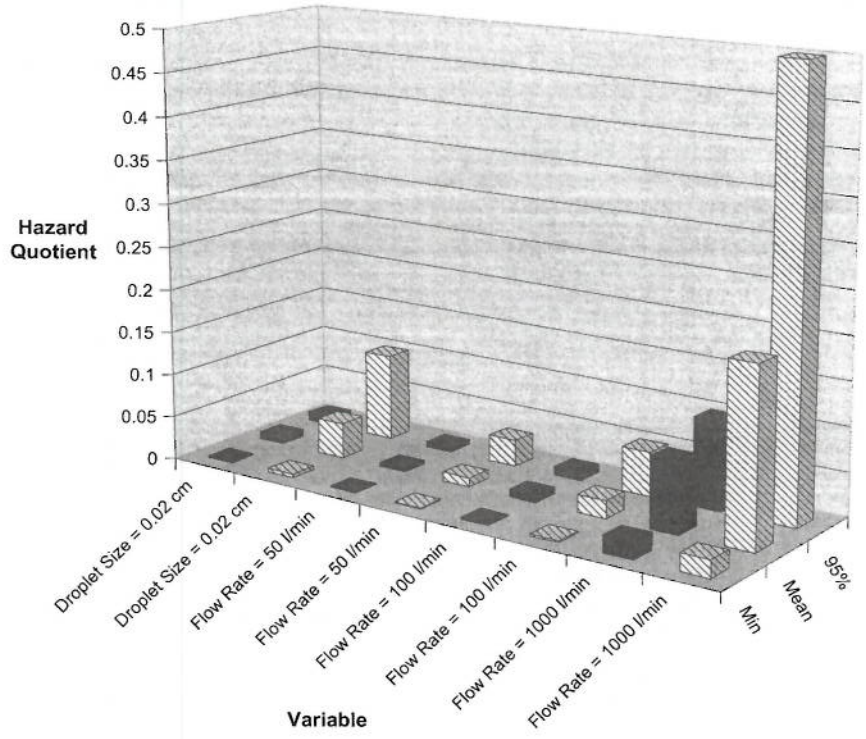


Fig. 5. Effect of variation in flow rate and droplet diameter parameters on hazard quotient by route, excluding dermal contact. ■ = Ingestion of leachate aerosol; ▨ = Inhalation of volatiles.

surrogate benzo[*a*]pyrene for ∑PAH and Aroclor 1260 for ∑PCB accounts for further artefacts in terms of the magnitude of the risk estimates in this study. This said, the pattern of exposure is consistent with other spray studies within the pesticide spray and exposure literature.

3.4. Analogous studies from pesticide spray – bystander risk assessments

In this study, the dermal contact route is a function of concentration, the dermal permeability coefficient, the fraction of skin exposed and the exposure time, and was shown to be insufficiently sensitive to other variables such as wind speed or flow rate. To confirm, simulations were conducted for each of the following variables in turn: wind speed, water temperature, droplet time, droplet diameter, flow rate and spray width and we found no appreciable difference for 95% ile risk estimates and only slight differences for the maximum values in two cases (when droplet time changed to 100 s; and where flow rate was increased to 10,000 l/min).

It is useful to consider our findings in light of research on worker and bystander exposure to pesticides, where the dermal and inhalation routes of uptake can also be important (Hamey, 2001; European Commission, 2002; ACP, 2002). Ross et al. (2001) have argued that pesticide toxicology studies have much to offer occupational risk assessments, in particular, with respect to our understanding of dermal exposure. Considering the validity of our modification of Walden and Spence (1997) to account for aerosol inhalation exposure, ACP (2002) reported two experimental studies undertaken by the former Ministry of Agriculture Fisheries and Food (Lloyd and Bell, 1983; Lloyd et al., 1987) on pesticide exposures to bystanders (persons incidentally located at or adjacent to the site of pesticide application who take no action to control exposure) downwind (8 m) of the spray drift. Harmless tracers were used. From studies of arable crop spray in high wind speeds (Lloyd and Bell, 1983; Lloyd et al., 1987) inhalation exposures of ca. 0.02 ml/m^3 (max. values 0.1 ml/m^3) and 0.002 ml/m^3 were estimated. At a distance of 5 m from conventional pesticide spray equipment, the typical levels of pesticide spray drift deposited on the ground are reportedly ca. 1% of the applied dose (ACP, 2002). Using this assumption with respect to dermal exposure, Ganzelmeier et al. (1995) estimated bystander exposure to pesticide spray 5 m from the point of application (at 200 l/ha) to be <0.4 ml/person. These analogous studies reinforce our view that an aerosol exposure estimate of 0.42 ml/m^3 is a reasonable worst case estimate.

4. Conclusions

The spray irrigation of landfill leachate is regarded by many operators as an attractive option for meeting discharge consent limits when considered alongside the costs of tankering leachate off-site for specialist treatment. Spray irrigation releases volatiles from the leachate volume and disperses leachate in the form of a fine mist that can be inhaled, ingested or deposited on the skin of site workers. To date, no estimate of these exposures to site workers or bystanders has been conducted. A risk screening exercise in this study used an accepted air box model, with modifications. Chemical exposures to a hypothetical and maximally exposed worker during the simulated spray irrigation of landfill leachate were screened and the IHEM developed to simulate the ingestion of leachate aerosol.

(i) Routes of exposure were ranked in the following order according to their contribution to carcinogenic risk: dermal contact ≫ ingestion of aerosol > inhalation of volatiles; and, hazard index: dermal contact ≫ inhalation of volatiles > ingestion of aerosol. Whilst the quantification of site-specific risk estimates from the spray irrigation of leachate may require additional study and was not the purpose of this work, it is prudent for workers to wear suitable personal protective clothing where they are likely to be in close proximity to sprayed leachate, or remain beyond the spray radius.

(ii) Increasing flow rate to 1000 l/min, and to a lesser extent reducing droplet diameter to 0.02 cm from the 'baseline' parameters of 100 l/min flow rate and 0.2 cm droplet size, resulted in increased contribution to both risk and hazard due to inhalation exposure, but had little effect on dermal exposures. Procedures to reduce irrigation flow rate and/or high populations of fine droplets, such as lower operating pressures, larger nozzles, low or downward pointing spray trajectories may serve to reduce potential exposures, by minimising volatilisation and spray mist.

(iii) The quantitative risk estimates modelled using this conservative worst case exposure scenario are not of sufficient magnitude to warrant major concerns about chemical risks to workers or bystanders from this practice in the general sense. This would also require occupational exposure limits and environmental assessment levels for these substances to be exceeded in the occupational setting. However, it should also be noted that the modelling made use of generic concentration data for only a limited number of potential landfill leachate contaminants, such that individual practices may require assessment on the basis of their own merits.

(iv) This study adopted a generalised conservative modelling approach. Processes and model features for site-specific application and that, were they better characterised within the model with site data, might lessen the conservative nature of the approach include: (a) the dispersion and aerosol deposition

within the outdoor box; (b) a more representative analysis of exposure times; (c) inclusion of various spraying regimes, e.g. under coppice canopies.

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Glossary

Eq. (1)

K_L: overall mass transfer coefficient (cm/h).
H: Henry's Law constant for contaminant (atm m^3/mol).
R: gas constant (assumed to be 8.2×10^{-5}) (atm m^3/mol K).
T: absolute temperature (293 K).
k_g: gas phase mass transfer coefficient (cm/h).
k_l: liquid phase mass transfer coefficient (cm/h).

Eqs. (2) and (3)

$k_{g(H_2O)}$: gas phase mass transfer coefficient for water (cm/h) = 3000 cm/h.
$k_{l(CO_2)}$: liquid phase mass transfer coefficient for carbon dioxide (cm/h) = 20 cm/h.
18: molecular weight of H_2O.
44: molecular weight of CO_2.
MW_{VOC}: molecular weight of contaminant.

Eq. (4)

$K'_{L(T_s)}$: adjusted overall mass transfer coefficient (cm/h).
T_l: calibration water temperature of K_L (K).
T_s: shower water temperature (K).
μ_l: water viscosity at T_l (g/m s).
μ_s: water viscosity at T_s (g/m s).

Eq. (5)

C_{sh}: concentration of contaminant in shower droplet after time t (mg/l).
C_a: concentration of contaminant in shower water (mg/l).
d: shower droplet diameter (cm).
t: shower droplet drop time (s).

Eq. (6)

M_{sh}: mass of contaminant volatilised (mg).
fv: the fraction of contaminant volatilised ($1 - e^{-K_H t}/600d$) (mg/mg).
Q: the volumetric flow rate of water (l/min).
$time_{sh}$: the duration for which the shower water is flowing (min).
C_a: the concentration of contaminant in the shower water (mg/l).

Eq. (7)

C_{sh}: air concentration in the shower (mg/m^3).
V_{sh}: volume of air in the shower (m^3).

Eqs. (8)–(13)

C_{air}: concentration of contaminant of concern in air (mg/m^3).
C_w: concentration of contaminant of concern in leachate (mg/l).
InhR: inhalation rate (m^3/h).
SA: total skin surface area (cm^2).
FS: fraction of total skin surface area exposed to irrigation water (cm^2/cm^2).
IR_{iw}: water ingestion rate (ml/h).
AAF_{inhal}: contaminant specific absorption adjustment factor for inhalation route (mg/mg); assumed to be 1.
AAF_{dermal}: contaminant specific absorption adjustment factor for dermal route (mg/mg).
LRF: lung retention factor (dimensionless); assumed to be 1.
AAF: chemical-specific oral-water absorption adjustment factor (mg/mg).
ET: exposure time/activity duration (h/day).
PC: Chemical-specific skin permeability coefficient (cm/h).
EF: exposure frequency for occupation (days/year).
ED: exposure duration (years).
365: days/year.
LT: lifetime (years).
BW: body weight (kg).

Eqs. (14) and (15)

IELCR: individual excess lifetime cancer risk for a specified chemical and exposure route (for annual risk this is divided by the exposure duration).
SF: slope factor (chemical carcinogenic toxicity) for a specified chemical and exposure route (mg/kg-day)$^{-1}$.
HQ: hazard quotient for a specific chemical and exposure route.
RfD: reference dose for a specific chemical and exposure route (mg/kg-day).
HI: hazard index.

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Managing the risks from petroleum hydrocarbons at contaminated sites: achievements and future research directions

S.J.T. Pollard, R. Duarte-Davidson, K. Askari and E. Stutt

Abstract

Decades of research into the environmental behaviour of petroleum hydrocarbon wastes, from pioneering work on petroleum microbiology, through exposure assessment to the development of analytical fingerprinting techniques, have revolutionised our understanding of the risks that these contaminants pose to human health and the environment. This said, we often fail to harness the insights from this knowledge in making risk management decisions. Here, we provide a synthesis of the research, drawing on the connections between analysis, exposure and risk management, and reappraise this knowledge in the light of current policy issues in the UK, including the application of risk frameworks for hydrocarbons in soil, the fate and behaviour of the risk-critical contaminants in hydrocarbon residuals, and the development of 'fit-for-purpose' diagnostic methods to inform risk-based decision making.

Key words: hydrocarbons, risk, human health, analysis

INTRODUCTION

The contamination of soils with petroleum hydrocarbons can occur through accidental spillage or gradual inventory loss during site operations or during site decommissioning. Exposure to the toxic components of hydrocarbon residues drives the health and environmental risk assessments that inform decisions on risk reduction and management (Pollard *et al.* 1994). The science base available to support risk-based decision-making at petroleum contaminated sites is extensive. Broadly speaking, the early studies in the late 1960s through the 1970s concentrated on characterising petroleum biotransformations (e.g. Westlake *et al.* 1974), followed in the late 1970s and 1980s by concentrated efforts to improve analytical characterisation as gas chromatography/mass spectrometry (GC/MS) methods became widespread. The 1990s focused on improved exposure assessment, the application of bioremediation technologies (Sims 1990; Dupont 1991), and on characterising the environmental fate and behaviour of risk-critical components in these complex waste matrices. More recently, the emphasis has been on the development and implementation of structured, risk-based

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Authors
S.J.T. Pollard, Integrated Waste Management Centre, Building 61, Cranfield University, Cranfield MK43 0AL, UK
R. Duarte-Davidson, Environmental Policy – Risk and Forecasting, Environment Agency, King's Meadow House, King's Meadow Road, Reading RG1 8DQ, UK
K. Askari, SLR Consulting Ltd, 1 Meadowbank Way, Eastwood, Nottingham NG16 3TT, UK
E. Stutt, MRC Institute for Environment and Health, University of Leicester, 94 Regent Road, Leicester LE1 7DD, UK

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decision frameworks for petroleum-contaminated sites that offer clarity and consistent advice to site owners, regulators and their advisers on staged and tiered approaches to risk management (MADEP 2002; Environment Agency 2003).

Risk-informed decisions demand a synthesis of scientific information, however (Environment Agency 2004), and the purpose of this paper is to summarise our understanding of these wastes in the context of recent initiatives in the UK to develop and promote a risk management framework for petroleum hydrocarbons in soils (Environment Agency 2003).

PETROLEUM HYDROCARBONS AS A SOURCE TERM

Compositional complexity

The contamination of soils by petroleum is an undesirable consequence of the refining, processing, transportation, blending, storage and use of petroleum products as fuels and feedstock at refinery, distribution, storage and auxiliary facilities. The extent of contamination and the exposure to harmful components in petroleum-contaminated soils can vary from insignificant to substantial. Site conditions, the local environmental setting, the extent and nature of contamination, and the proximity to human populations and ecological receptors, all have a bearing on the magnitude of the risks.

The physical complexity of petroleum releases to the soil environment is compounded by the chemical complexity of petroleum products. Commercial fractions of petroleum (the distillates naphtha, gasoline, kerosene, gas oil, fuel oils, asphalt, etc.) each contain hundreds of individual compounds massed together as a 'spectrum' of closely related chemicals. Each of these fractions is a characteristic subset of the initial crude oil from which it is distilled, and overlaps in its composition because there is never a perfect 'cut' or separation during fractional distillation. The notation n-C_x–n-C_y (Table 1) for these fractions describes the carbon number range of straight-chain n-alkanes in an environmental sample (API 2001).

Table 1. Typical composition of some petroleum fuels (after TPHCWG 1999)

Composition/product	Automotive gasoline	Automotive diesel (DERV)	No. 6 fuel oil
alkane carbon number range	n-C_4–n-C_{12}	n-C_8–n-C_{21}	n-C_{12}–n-C_{34}
boiling point range (°C)	40–200 (25–220)[a]	200–325 (160–390)[b]	350–700
Average composition (wt %)			
n-alkanes (straight-chain)	>12.1	13.0	1.7
total straight-chain & iso-alkanes	47.0 (30–90% vol) [a]	41.0	13.0
total cycloalkanes	3.2 (1–35% vol) [a]	37.0	15.2
alkenes	10.0 (0–20% vol) [a]	1.3	nd
benzene	1.9	0.03	nd
total xylenes	9.0	0.5	nd
total monoaromatics	19.0 (BTEXs)[c]	16	>4.0
total polynuclear aromatics	nd	0.36	>0.37
total aromatics	35.0 (5–55% vol) [a]	22	34 (78.9)[d]

nd – no data; (a) Data from CONCAWE (1992); (b) CONCAWE (1996). These values refer to fuels marketed in Europe; (c) BTXs, benzene, toluene and xylenes (commonly classified as BTEXs, which includes ethylbenzene); (d) Data from ATSDR (1999). The large disparity between the percentage figures for total aromatics is probably due to the ATSDR data, including heterocyclic (O-, N-, S-containing) aromatic compounds. The TPHCWG data on which the table are based list No. 6 fuel oil as containing 30% polar material.

Secondary processing

The secondary processing of petroleum distillates adds further complexity. Thermal and catalytic cracking is used to increase the yield and performance of petroleum products with high market demand (Table 1). Typically, the gaseous cracked products from kerosene or gas oil feedstocks are fed to a flash distillation chamber and further separated into gasoline and light gas oil, and the liquids sent to a vacuum fractionator and separated into heavy gas oil and vacuum tar or residuum (Schobert 1990).

Environmental fate processes

Once released, petroleum constituents partition, each to a differing extent, between the source of the contamination (the oil itself) and the air, soil and water phases of the contaminated soil environment (Zemanek *et al.* 1997). Importantly, constituents are co-solved in one another and may become co-solved with soil porewater or groundwater. Contamination is present then as a mixture of physical forms, with the free oil (non-aqueous phase liquid, NAPL), the residual oil in soil, an oil–water emulsion, soil vapour and dissolved phases coexisting to build a picture of extreme complexity (Hrudey and Pollard 1993). Furthermore, physical (e.g. volatilization), chemical (e.g. oxidation) and biological (e.g. biotransformation) processes 'weather' the spilled product, resulting in additional compositional changes. The result is an extremely complex chemical matrix, as illustrated by Figure 1, which shows the relative abundance of polyaromatic (and mixed alicyclic and polyaromatic) classes of compound in a small fraction of waste oil isolated from a historically contaminated petroleum refinery site.

PARTITIONING AND EXPOSURE

The physicochemical and toxicological characteristics (toxicological endpoint, relative potency) of contaminants drive the design of analytical strategies, the selection of analytical methods, our understanding of exposure, and the selection and operation of remediation technologies. Oils that have been weathered shift their chemical composition towards refractory residues of increased hydrophobicity (Westlake *et al.* 1974; Pollard *et al.* 1999). These dynamic compositional changes dramatically affect the partitioning behaviour of contaminants; for example, prior to, during and following biological treatment (Figure 2).

Risk-critical components (e.g. the higher ring polynuclear aromatic hydrocarbons (PAH)) in weathered oils are then less bioavailable because they are effectively partitioned within the source term. Sun and Boyd (1991) first estimated a concentration of residual oil within contaminated soil required for it to act as a discrete partition medium (ca. 1000 mg/kg for polychlorinated biphenyls) and suggested that a residual oil phase, as the source of priority contaminants, could be typically ten times more effective as a partition medium than soil organic matter for hydrophobic organics, although behaviour depends on the partition coefficients of individual contaminants. So, for example, Zemanek *et al.* (1997) show that between 71 and 96% w/w of PAH in weathered diesel-contaminated soils was partitioned to residual oil (at 2–6% w/w of the total soil composition) in petroleum and weathered creosote-contaminated soils, with 84% w/w of benzo[a]pyrene partitioned to the residual oil phase. Woolgar and Jones (1999) estimated oil–water partition coefficients (termed log K_{mw}) for a series of PAH to be between 4.5 and 6.5, dependent on the source term. The argument is made that, under such conditions, highly partitioned constituents may be biologically inaccessible to microbial communities and resistant to biotransformation. This very inaccessibility may, but not necessarily, also restrict the exposure dose available to receptors. It follows from such studies that free and residual petroleum, as the principal source term for most risk-critical contaminants, must be considered as the primary focus of analytical and remediation efforts (Environment Agency 2002).

ANALYSIS

The analysis of petroleum hydrocarbons during site assessment and the verification of *ex situ* technologies such as biopiling, continues to be expressed in terms of total petroleum hydrocarbon (TPH) load, or 'losses' from the soil being treated, rather than by reference to the reductions in risk. In a typical study, Al Awadhi *et al.* (1996) report an 80% w/w reduction in oil from heavy oil-laden land-farming plots in Kuwait over a

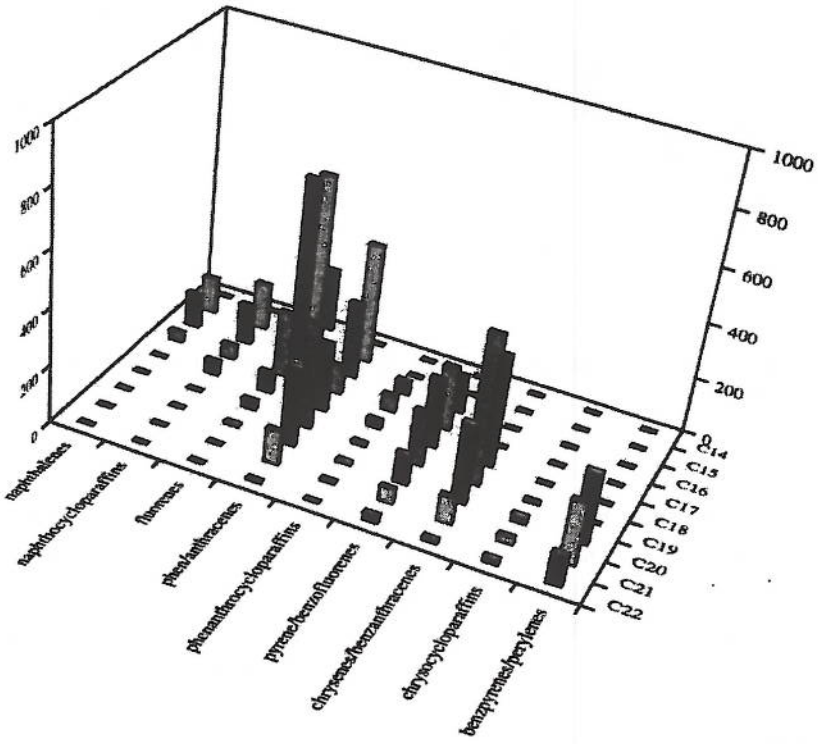


FIGURE 1. RELATIVE ABUNDANCE OF POLYAROMATIC HYDROCARBON COMPONENTS IN SOLVENT-EXTRACTED, WEATHERED HEAVY OIL WASTES (AFTER POLLARD *ET AL.* 1994)

15-month research period, and Milne *et al.* (1998) between 30–50% w/w reductions in total petroleum hydrocarbons from heavy refinery sludge treated in amended composting plots over the treatment period. Guerin (2000) reports a five-year performance study of a land treatment facility for oily wastes from heavy vehicle maintenance. Most of these studies, and many since (e.g. Tien *et al.* 1999; Ressinger *et al.* 2002; Owens and Bourgouin 2003) follow a pattern of reporting reductions in TPH load as surrogates for risk reduction in the absence of a formalised risk management framework. However, the absence of risk from the vocabulary of many operators and remediation projects reduces stakeholder (regulatory, investor, landowner and public) confidence in technology performance, and, in doing so, may limit the market potential of these technologies.

In many countries, the development of regulatory requirements for the assessment and remediation of petroleum-contaminated soils has been the stimulus for improved analytical practice. Analytical strategies, that generate the data upon which risk assessments rely, are now responding to the needs of risk-based approaches, but an intensely competitive marketplace for analytical work and sustained pressure on site investigation costs mean that the adoption of more sophisticated techniques is still the exception rather than the rule. Developments that have occurred include: (i) in the USA, where the Texas Natural Resource Conservation Commission (TNRCC) direct method (AEHS 2000) is gaining acceptance for the evaluation of the total petroleum hydrocarbons criteria working group (TPHCWG) fractions; and (ii) in Canada, where the Canadian Council of Ministers of the Environment (CCME) reference method (CCME 2001*a*) for the Canada-wide standard

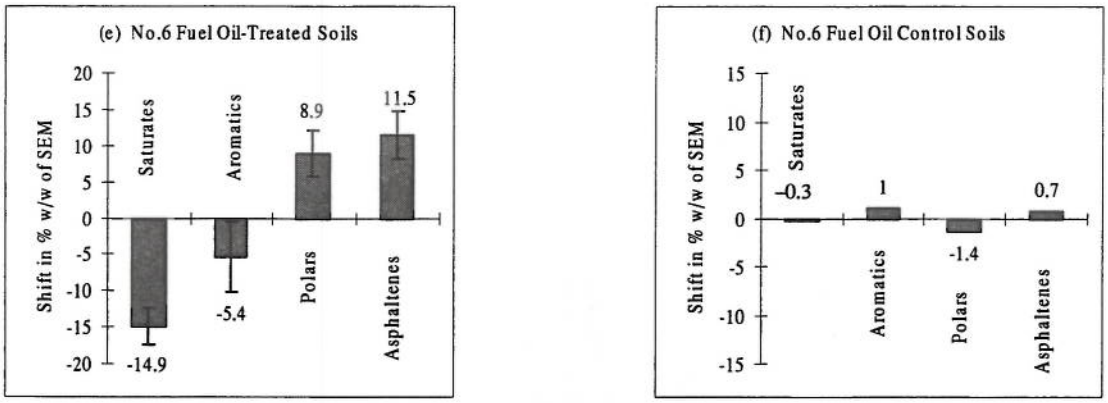


FIGURE 2. CHANGES IN CHEMICAL COMPOSITION DURING BIOTRANSFORMATION OF NO. 6 FUEL OIL (AFTER POLLARD *ET AL.* 1999)

(Tier 1 method; CCME 2001*b*) has been adopted. UK laboratories using accredited methods for the analysis of petroleum hydrocarbons increasingly apply a range of GC and MS methods, including those for the analysis of:

- petrol- (C_5–C_{10}), diesel- (C_{10}–C_{30}) and 'total' petroleum (C_{10}–C_{40}) organics (using US EPA Modified Method 8015M);
- total petroleum hydrocarbon using US EPA or modified US EPA Method 1664, the replacement for 418.1; and
- petroleum hydrocarbons in environmental samples (TNRCC methods 1005 and 1006).

Meanwhile, the research literature continues to provide many examples of developments in diagnostic techniques for petroleum hydrocarbons in soils. Recent initiatives include the application of biomarker analysis (*n*-alkane: substituted *n*-hopane indices), bioremediation verification (Moldowan *et al.* 1995) and the validation of microbial bioassays for petroleum hydrocarbons in soil (Dorn and Salanitro 2000). Pollard *et al.* (1999), building on the work of Prince *et al.* (1994) have demonstrated a ratio of total alkanes (Σn-alkanes) to 17α(H)21β(H)-hopane to be the most sensitive of a series of biomarker ratios in reflecting oily waste depletion in a 256-day soil microcosm study, and illustrated the use of such indices for both source term identification and for tracking the kinetics of petroleum biotransformation. Without a more formal context for the application of these advances, however, such techniques are unlikely to become commonplace, and the valuable insights that they provide risk being overlooked by practitioners motivated by cost-driven site investigations.

RISK ASSESSMENT AND MANAGEMENT

Risk-based land management (RBLM) provides a basis for integrating the science base on petroleum-contaminated soils. Whereas the effectiveness of environmental technologies in treating pollution was historically expressed as a percentage reduction in the pollutant concentration released to, or found in, a medium of concern, regulators are increasingly concerned with mass, toxicity and risk reductions within the multimedia, multiphase environment. For petroleum hydrocarbons in soil, international regulatory guidance on the management of risks from contaminated sites is emerging (e.g. CCME 2001*b*; MADEP 2002; NSWEPA 2002; Environment Agency 2003). Much of this guidance promotes the use of risk management frameworks to guide decision-making, the application of reference analytical methodologies and the derivation and use of acute, sub-chronic, and chronic toxicological criteria for petroleum wastes. The frameworks adopt a variety of approaches to the evaluation of risk-critical components within the oil–soil matrix (Table 2) and, during their development, decisions are required regarding the number of petroleum fractions, their carbon number

Table 2. Some characteristics of regulatory approaches to evaluating the risks to human health from petroleum hydrocarbons in soil (after Environment Agency 2003)

Basis of approach	TPHCWG / RIVM	MADEP
Staged approach	Total petroleum hydrocarbon criteria working group (TPHCWG) and Dutch Institute for Public Health and Environmental Protection (RIVM) approaches assess indicator compounds first and, if necessary, progress to consideration of the (non-carcinogenic) effects of TPH fractions	Requires assessors to look at both indicator compounds (target analytes) and (non-threshold) effects of petroleum fractions
Defining fractions	RIVM and TPHCWG base fractions on equivalent carbon numbers (EC_n)	MADEP base fractions on carbon numbers
Combining fractions	TPHCWG and RIVM combine risk-based screening levels (RBSLs) for all fractions to give an overall petroleum RBSL	Under the MADEP scheme, the RSBL for each fraction is regarded as independent
Indicator compounds	RIVM and TPHCWG consider all compounds (including indicator compounds) in the EC range when assessing the (non-threshold) effects of petroleum fractions	MADEP specifically excludes the indicator compounds from the consideration of the non-threshold effects of TPH fractions

range and the availability and relevance of toxicological information that will be used to generate soil assessment guideline values.

Implementation of these frameworks presupposes an ability to integrate insights from the science base that supports risk-based decision-making. In the USA, a substantial research effort has focused on integrating hydrocarbon fate and transport, petroleum microbiology and environmental diagnostics to inform regulatory processes for site management under the Superfund Program. ThermoRetec Consulting Corporation (2000), reporting for the Petroleum Environmental Research Forum (PERF), provide an authoritative account of the central importance of partitioning within soil-bound hydrocarbons in developing environmentally acceptable endpoints (remedial objectives). Drawing on a detailed understanding of NAPL and the fate and behaviour of residual oil, this work is influencing the development of remediation criteria for petroleum hydrocarbons in soils in the USA for human health, groundwater and ecological receptors. This work has also led to a reappraisal of the level of residual petroleum hydrocarbons that can remain at remediated sites without posing an unacceptable risk.

The science available to support risk management is generally well collated for fresh hydrocarbon products and refinery distillates. In contrast, weathered, mid-distillate and heavier oil sources are generally given a narrow treatment. One of the few environmental exposure assessments explicitly to address heavy oils has been discussed in a recent article relating to worker and visitor exposure following the wrecking of the oil tanker 'Erika' in 1999, 65 km south of the Brittany coast (Baars 2002). Inhalation, dermal and oral PAH exposures from beached No. 6 fuel oil were estimated and found to be negligible for beach cleaners and tourists coming into contact with heavy oil, demonstrating the feasibility of this level of risk analysis for these problematical wastes. The Environment Agency has recognised the lack of emphasis given over to weathered oils in its recent consultation on principles for evaluating the human health risks from petroleum hydrocarbons in soils, and called for views. The outcome of its consultation will be a risk assessment framework, setting out the approach and the representative substances or petroleum fractions to be considered in the health risk assessment of petroleum hydrocarbons in soils. Following this, detailed toxicological and fate and behav-

iour reviews for those substances or fractions selected as representative of petroleum contamination will be prepared (as outlined in CLR9, Defra and Environment Agency 2002*a*). The framework and the review information will be combined to derive soil guideline values (SGVs) for petroleum hydrocarbons in soils that support the contaminated land regime implemented by Part IIA of the Environmental Protection Act, 1990 (for further details see CLR10, Defra and Environment Agency 2002*b*).

FUTURE DIRECTIONS

The move towards risk-based corrective action (RBCA) has been slow in the UK and, whilst some progress has been made in integrating the aspects of analysis, exposure assessment and technology verification, there are gaps in the current knowledge base. There is an urgent need to synthesise our understanding of the toxicology, analytical science, environmental fate and behaviour, risk and technology performance of petroleum hydrocarbons, in order to ensure that risk-based decisions, as they relate to petroleum-contaminated sites, make the best use of the existing knowledge base. To have an impact, research must make use of demonstration sites and facilities that allow the practicalities of integrating the science base to be tested in the context of decisions in real environments. Risk-informed decisions must be optimised by reference to the cost of gathering improved site data, leading to greater confidence in the resulting outcomes.

For petroleum-contaminated soils we need to characterise the risks associated with residuals, and demonstrate that soil treatment can be optimised by reference to risk reduction within a UK risk management framework. This will require the selection and validation of analytical methods, the collation of environmental fate data, and the selection of toxicity data in line with the UK approach to the derivation of soil guideline values.

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Assessing significant harm to terrestrial ecosystems from contaminated land

R. Smith[1,*], S.J.T. Pollard[1], J.M. Weeks[2] & C.P. Nathanail[3]

Abstract. Terrestrial ecosystem risk assessment remains in its infancy by comparison with the aquatic discipline, yet it is advancing quickly in response to increasing concerns surrounding soil quality and the sustainable use of soil. Several international frameworks have been developed during the last decade to aid decision-makers as the need for scientifically derived tools for determining ecological risk from land contamination has been recognized. From the regulatory viewpoint, the priority is establishing what to protect in order to prevent ecological harm. This is a complex issue requiring clear objectives in a risk assessment context. The most important factor in assessing ecological harm is whether or not ecosystem function is altered as a result of land contamination and, if it is, judging the significance. A consensus is developing that ecological risk assessment should aim to protect populations rather than individuals. This paper critically reviews recent developments in risk assessment for terrestrial ecosystems and land contamination in the UK, with emphasis on deriving a measure of ecological harm to assess ecosystem function. We seek to further justify the use of earthworms as a favoured indicator species for protecting ecological function. Guidance on how to measure harm in relation to ecological function is, however, still lacking.

Keywords: Ecological harm, ecosystem function, land contamination, risk assessment, environmental protection, earthworm

INTRODUCTION

Ecosystem management has been described as a magnet for controversy (Lackey 1998), conflict and debate as exemplified by serious national aquatic ecosystem problems in the 1960s and 1970s (Ferguson *et al.* 1998). An ecosystem is defined as a community of organisms and their physical environment interacting as an ecological unit (Lincoln *et al.* 1998). Ecosystems are dynamic, complex living systems subject to important, continuous and natural processes of change in response to various internal and external stresses. Exposure to soil contamination can be one such stress that can have consequences to terrestrial ecosystems, for example, the reduction of earthworm population size due to mortality or as more sensitive parameters, reduced growth and reproduction.

The type and severity of ecological impacts and effects governs the likelihood and rate of ecological recovery. Ecological change or harm caused by stressors such as contamination within an ecosystem will result in slower recovery than adaptation and evolutionary change might otherwise allow, possibly with maintenance of a degraded state (Whitford *et al.* 1999). There are various ways of describing land, the degree of contamination within it, and the consequences for specified ecological receptors.

While primitive civilizations have demonstrated respect for natural systems, the post-industrial society has become separated from the nature and value of Earth's life support systems until their disruption or loss highlighted their importance (Slobodkin 2000). Even as late as the early 1990s, authors (Spellerberg & Minshull 1992) were bemoaning the poor quality of ecological inputs into environmental impact assessments. Though all ecosystems have been at some risk from human impacts for millennia, the use of chemicals has increased over time. It was only two decades ago that ecological risk analysis was promoted as a new concept (O'Neill *et al.* 1982) when laboratory toxicity data were extrapolated to field-scale aquatic ecosystems. Ecological risk assessment is inherently more complex (i.e. multispecies) than human health risk assessment and ecologically relevant data are often based on aquatic systems (Scott-Fordsmand *et al.* 1996). The terrestrial ecosystem risk assessment discipline is advancing but is still in its infancy.

Risks are often characterized on the basis of individuals, so extrapolation is also required from individual to population level. There are many reasons, other than scale, why extrapolation techniques are limited and these are reviewed elsewhere (Douben & Siepel 1993; Forbes & Forbes 1993; Suter 1993; Løkke 1994; Shore 1995; Spurgeon & Hopkin

[1]Integrated Waste Management Centre, Cranfield University, School of Industrial and Manufacturing Science, Building 61, Cranfield, Bedfordshire MK43 0AL, UK. [2]The Centre for Environment, Fisheries & Aquaculture Sciences, Pakefield Road, Lowestoft, Suffolk NR33 0HT, UK. [3]School of Geography, The University of Nottingham, Nottingham NG7 2RD, UK.
*Corresponding author. Tel: +44 (0)1234 754963.
Fax: +44 (0)1234 751671. E-mail: r.smith1@cranfield.ac.uk

1995; Spurgeon 1997; Suter 1998; Forbes *et al.* 2001; Van Beelen *et al.* 2001).

The monitoring of a species within an ecosystem can provide an indication of ecological harm. Some ecosystems are maintained for their importance and scientific interest, for example, in order to protect rare species or habitats. Designated sites are the basis of the Part IIA contaminated land legislative regime in the UK, as detailed further below (Department of Environment Transport and the Regions 2000a, b). Other ecosystems are considered to be more general; for example, farmland and contaminated sites that fall outside of Part IIA and may require management and remediation. Ecosystems evolve naturally due to the presence of niches that allow new species to thrive and others to decline. Thus through niche differentiation certain species may have advantages over others. Human intervention in the form of management is usually to the advantage of rare species. This implies that all species have a value, whether artificial or real, and the value of rare species is often perceived to be higher than 'common' species, even though the ecological value of the latter expressed as ecological function can be of equal or greater importance.

Ecological effects may not be significant if ecological function is maintained. Early case studies of observed ecological effects were not necessarily related to harm or ecological function. For example, probable effects were noted on the evidence of metal contaminants found in organs of avian and mammalian species, and densities of invertebrate species in soil litter were greatly reduced as a result of metal contamination from two zinc smelters in Pennsylvania, USA (Beyer *et al.* 1985). Another study demonstrated effects on two small mammals and two soil invertebrate species caused by fluoride contamination from an aluminium plant at Anglesey, North Wales (Walton 1986, 1987). Ecological effects finally became related to ecosystem function in the 1990s typified by published case studies on earthworm growth, reproduction, sexual development and early cocoon production affected by heavy metal contamination from zinc smelters in the Netherlands (Posthuma *et al.* 1994) and the UK (Spurgeon & Hopkin 1996a, b; Spurgeon & Hopkin 1999a).

The assessment of harm to terrestrial ecosystems from contaminated land is a main facet of the UK contaminated land regime. If ecological harm is to be prevented, understanding the behaviour and effects of contaminants in the environment is important and is a central aim in ecotoxicology (Forbes & Kure 1997). The ability to predict this quantitatively is required to avoid harm. In the absence of an objective definition for terrestrial ecological quality (CLARINET 2001), the assessment of ecological effects and harm is difficult to establish. There is a scarcity of published case-study information for terrestrial ecosystems against which to assess the ecological meaning of 'safe' concentrations (Posthuma 1997) and causal relationships between soil quality and their ecosystem functions still need to be demonstrated (Herrick 2000). Contemporary risk assessment methods do not suggest or identify consequences to a particular ecosystem if exposure exceeds defined 'safe' contaminant thresholds, other than that population responses are observed in the field (Posthuma 1997).

The extent of land contamination worldwide is considerable. In 1998, the European Environment Agency reported that over 300 000 potentially contaminated sites had been identified in Western Europe alone (Andersen 2000). This provides an indication of the scale of the problem, though national estimates vary considerably (e.g. Royal Commission on Environmental Pollution 1996; Environment Agency 2000b). In the UK, the historiassessment of land contamination (1970s to 1990s) has been based on defined 'trigger values' or reference values for individual contaminant concentrations in soil, for example the ICRCL values (Inter-Departmental Committee on the Redevelopment of Contaminated Land 1987). Other countries, including Germany, the Netherlands, Canada, Japan, Estonia and Bulgaria, have developed guideline values for assessing the extent or significance of soil contamination. There has been much concern that soil guideline values, as surrogates for assessing harm, are frequently misused through lack of understanding (Ferguson & Denner 1994). The use of reference values does not account for important ecological characteristics such as the severity of effect, irreversibility and spatial or temporal extent. This restrictive approach is evolving into a combination of chemical, ecotoxicological and ecological approaches as scientific understanding develops. Part IIA of the Environmental Protection Act 1990 was the first UK legislation specifically to cover historic land contamination. While Part IIA seeks to protect a wide range of receptors, the only ecological receptors protected are designated habitats and species, for example, particular species that are the basis of Sites of Special Scientific Interest (SSSIs). In restricting the legislation to designated receptors, the most sensitive, valuable or rare ecosystems should be protected. Other UK legislation, for example, the Wildlife and Countryside Act 1981, also exists to protect such wildlife. However, in some cases the long-term maintenance of a population or a species at any location may depend upon the sympathetic management of areas beyond the boundaries of a protected location (English Nature 2001).

LEGISLATIVE REGIME

Natural soil is one of the key elements enabling life on Earth (Achazi 2002) and justifiably soil is now protected in its own right. In 2002, in response to soil degradation concerns, the European Commission outlined a strategy for soil protection throughout the European Union, putting soil protection on a par with water and air (European Commission 2002). In the UK, there are many laws containing soil protection aspects, including the Town and Country Planning Act 1990. The primary legislation for contaminated land in England and Wales is set out in Part IIA (S78A–S78YC of the Environmental Protection Act 1990, as inserted by Section 57 of the Environment Act 1995; Statutory Guidance contained in DETR Circular 02/2000 (Department of Environment Transport and the Regions 2000a); and the Contaminated Land (England) Regulations 2000 (Department of Environment Transport and the Regions 2000b). This new regime came into force in

Table 1. Selected international approaches to ecological risk assessment for land contamination.

Country / basis	Limitations, benefits and features	Reference
Australia Derivation of ecological risk-based clean-up goals to protect terrestrial receptors	Background concentrations used as default for clean-up criteria if site-specific data are unavailable. Ecological receptors selected to include different trophic levels. Lack of national policy to require criteria to be applied	Benker *et al.* 2000
Canada Recommended Canadian soil quality guidelines; interim environmental quality criteria for contaminated sites. Guidelines for ecological risk assessment. Protocol for the derivation of soil quality criteria	Includes site-specific data and predictive modelling to derive quantitative information on complex ecosystem responses, including chronic effects and interactions between chemicals and ecosystem level studies	Canadian Council of Ministers of the Environment 1998
Denmark Use of no observed effect concentration (NOEC), lowest observed effect concentration and effective concentration, extrapolation of laboratory and field data with use of application factors as a safety margin. Aim to protect function and structure of soil	Soil protection strongly linked to groundwater protection. Funding is remediation driven. Assumes log-normal distribution. Only a fraction of species present in the ecosystem are usually covered by toxicity data. This therefore assumes that protection of those species will be sufficient to protect ecosystem function and structure	Guideline documents on soil quality criteria. *Oliebranchens Miljopulje* (petroleum tax for petroleum contamination remediation). Technology development fund for soil and groundwater innovative remediation techniques.
Germany Federal Soil Protection Act 1999 and accompanying Soil Protection Ordinance designed to protect and restore soil functions.	Soil protection has to be considered in relation to the anthropogenic use of the soil. Establishes what constitutes soil contamination. Soil organisms have not yet been considered	Wilke 2000; CLARINET 2001
Italy Maximum admissible concentrations (MACs) derived. If MAC values are exceeded, then the land is classed as contaminated and clean-up liability is initiated	Ecological criteria not yet used in the development of MAC values	Tunesi & D'Amico 2000
Netherlands Soil Protection Act 1994, as amended. Suitable for use approach, HC_{50} applied to land-use types. Maximum permissible soil concentrations defined. A log distribution of NOEC data provides species sensitivity distributions (SSDs). The serious risk concentration is derived by the 50th percentile of the SSD. Circular on-target values and intervention values for soil remediation 2000. In March 2004, the Dutch government announced proposals to amend the Soil Protection Act as a result of a change in policy. If adopted, the change would result in soil remediation being carried out by combined public and private investment (present system uses public finance) to reduce the time-scales involved to around one generation	The Soil Protection Act aims to prevent, restrict or remedy changes of soil properties, which entail a reduction of or a threat to the functional properties the soil has for man, flora and fauna. Assumes it is acceptable for 50% of the organisms involved to be exposed to contamination levels higher than their NOEC. Toxicity of pollutants for land use specific ecological parameters are mostly unavailable and are highly arbitrary. Remediation is geared to the desired end use. Intervention values, indicative levels for serious contamination and target values equally apply to aquatic sediment	Breure & Peijnenburg 2003; Crommentuijn *et al.* 1997, 2000; Faber 1998; Netherlands Ministry of Housing Spatial Planning and the Environment 1994, 2000; Van Wensem *et al.* 2000

Table 1. *Continued*

Country / basis	Limitations, benefits and features	Reference
Sweden Contaminated land assessment is related to hazard and levels of pollutants, taking into account their migration potential, site sensitivity and protective value. General framework and guideline values which do not pose unacceptable risks to the environment, to indicate the degree of contamination on a site, to develop clean-up goals and to evaluate clean-up results	Policy driven by increasing acidification in SW Sweden and nutrient deficiency in forests	Swedish Environment Code 1998
Switzerland Swiss Ordinance Relating to Pollutants in Soil (1986) and the Ordinance Relating to Impacts on the Soil (1998)	Adopts intervention values for guide, trigger and clean-up. Evidence of widespread contamination; precautionary guide values for inorganic soil contaminants (Appendix 1 of the Ordinance relating to Contaminants in Soil of 1 July 1998) have been exceeded in 42% of the National Soil Monitoring Network's study sites, primarily in topsoil. Main contaminants are Pb, Cu, Cd	Swiss Agency for the Environment Forests and Landscape 2000.
United Kingdom Tiered approach for assessing soil contaminants only on the basis of the legal definition of harm as contained in Part IIA. Uses a weight-of-evidence approach. Soil screening values used for assessment of effects	Consultation framework. Existing soil screening values are limited though they are being developed	Environment Agency 2003
United States of America Tiered approach to ecological risks associated with contaminated soil. Developing a programme to develop ecological (risk) soil screening levels as toxic reference values (Oak Ridge Toxicological Benchmarks)	Standardization is minimized. Based mainly on characteristics and need of decision-makers. Comparable to human health risk-based screening concentration (RBC) values	Sample & Suter 1994; Sample *et al.* 1996, 1997, 1998a, b c; United States Environmental Protection Agency 1998

England on 1 April 2000 and is the first UK legislation to deal exclusively with land contamination. Part IIA is based on the 'polluter pays' and risk management principles; it only applies to existing (historic) contaminated land not being dealt with under different legislative regimes such as Integrated Pollution Prevention and Control.

Definition of contaminated land in the UK

The legal definition of contaminated land is provided in statutory guidance contained in Section 78A(2) (Department of Environment Transport and the Regions 2000a) as '*any land which appears to the local authority in whose area it is situated to be in such a condition, by reason of substances in, on or under the land, that (a) significant harm is being caused or there is a significant possibility of such harm being caused; or (b) pollution of controlled waters is being, or is likely to be caused...*'. The new regime is profoundly restricted by the definition and is subject to interpretation. The regulatory regime set out in Part IIA involves a tiered approach that involves (a) problem identification, (b) risk assessment, (c) determination of appropriate remediation requirements, (d) consideration of costs, (e) establishment of who should pay and (f) implementation and remediation (Environment Agency 2000a). The Contaminated Land (England) Regulations 2000 (Department of Environment Transport and the Regions 2000b) set out further requirements, particularly in respect of the content of remediation notices.

Designated areas

Sites of national, and sometimes international, importance for nature conservation are notified as SSSIs by the government's statutory conservation agencies (English Nature, Scottish Natural Heritage and the Countryside Council for Wales). SSSIs presently cover more than 7% of land in England and Wales and the protection of such sites for their wildlife value is a priority. Many SSSIs are showing damage or neglect; an assessment of SSSIs in England, Scotland and Wales indicated that in England, 58% of SSSI land by area was in favourable or recovering condition, leaving 42% in unfavourable condition (English Nature 2003). Having established the principles of the ecological risk assessment in the context of the legislative regime, the basis of ecological risk assessment is highlighted below.

The identification and assessment of the likelihood of ecological harm for a particular site is not straightforward. There is the possibility that the remediation of a site defined as being contaminated under the Part IIA regime may compromise the survival of species that have adapted to the conditions at that site, for example, arsenic tolerance in earthworms at mine spoil sites in the UK (Langdon *et al.* 1999). In this scenario, the remediation activity itself may result in more harm than might have otherwise occurred by not carrying it out, thus compromising ecosystem function. The adaptation of species is valuable in contributing to biodiversity, and equally biodiversity may diminish if that species is removed by remediation. Such issues must be considered when assessing the need for ecological protection.

APPROACHES TO ECOLOGICAL RISK ASSESSMENT

Definitions

A UK definition of ecological risk assessment is 'an evaluation of the likelihood of adverse effects on organisms, populations, and communities from chemicals present in the environment' (Environment Agency 2003). This definition recognizes that ecological effects can occur at different levels, but it lacks specific reference to the need to maintain ecological function. The USEPA (United States Environmental Protection Agency 1998) similarly defines ecological risk assessment as 'a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors'.

International approaches

A review of international approaches to ecological risk assessment demonstrates that similar approaches are taken, usually on a tiered basis, and that different levels of protection or tolerable effects may be derived. Generally, most countries use generic guidelines for a first screening of ecological risk (Ferguson *et al.* 1998). The basis, limitations and benefits of the approaches in selected countries are presented in Table 1. Many countries, including the UK, are only at the stage of developing or agreeing suitable frameworks. The need for a common European framework in the form of a conceptual model has been identified and formulated (CLARINET 2001; Crommentuijn *et al.* 2001). The approach adopted in the Environment Agency's consultation document on a framework for ecological risk assessment (Environment Agency 2003) follows the conventional approach to environmental risk assessment and management in the UK, as contained in revised departmental guidelines. This provides a tiered framework for characterizing the source–pathway–receptor relationship (Department of Environment Transport and the Regions *et al.* 2000). All three components of a linkage must be present for a risk to exist.

Ecological risk assessment requirements

An ecological risk assessment has two fundamental requirements on a site-specific basis: information on exposure and information on an effect(s). Exposure data typically consist of pore water, soil quality and tissue concentrations in the receptor, and must include ambient reference or control areas to allow for the presence of naturally elevated 'contaminants'; for example, arsenic in parts of the southwest of the UK. Earthworms take up organic chemicals through the skin (Jager *et al.* 2003), and such dermal uptake has been separated from exposure arising from ingestion in the gut. The ingestion route becomes preferential for hydrophobic contaminants (Jager *et al.* 2003) such as benzene, toluene, ethylene, Xylene (BTEX) compounds, chlorinated solvents and nitrotoluene contaminants. A fundamental concept of ecological risk assessment is that increased exposure time increases toxicity or decreases the lethal concentration (usually LC_{50}, defined as the lethal concentration to 50% of the organisms over a given time period in an acute toxicity study).

Triad approach

Ecological risk assessment requires an integrated approach based on a number of measures and criteria (Rutgers *et al.* 2000). The 'triad' approach has often been adopted as a basis for interfacing chemical, toxicological and ecological information (Chapman 1986; Chapman 1992; Breure & Peijnenburg 2003). In this approach, toxicology is assessed by the use of bioassays as experiments in which organisms are exposed to site-specific field samples and ecological responses are observed under standard conditions (Van Straalen 2002) and normalized to reference data. This approach is likely to be adopted in England and Wales (Environment Agency 2003).

No observed effect concentrations

Ecological risk assessment is often based on the standardized no observed effect concentration (NOEC) as the toxicity input parameter (Posthuma 1997). NOEC is a reference level derived as the concentration at which there is no toxicological effect (acute or chronic, though usually chronic) on an ecologically relevant characteristic (typically reproduction) for a chosen receptor after different doses (usually of individual chemicals) have been applied, usually in the laboratory. Organisms are more sensitive to lower NOECs in a given soil. Legislation in the Netherlands is the most advanced in Europe with regard to ecological risk assessment for contaminated land, and the approach of the Dutch Soil Protection Act (Netherlands Ministry of Housing Spatial Planning and the Environment 1994) is to maintain and restore the multifunctionality of soil. The role of ecology is defined by use of the HC_{50}, whereby the hazardous concentration for 50% of the geometrical mean for all available NOECs (assuming log normal distribution) is applied. A procedure for performing population-level ecological risk assessments was required at the Federal level in Oregon, USA (Hope & Peterson 2000). There, the acceptable risk was defined legislatively as 10% or less chance that 20% or more of the total local population would receive an exposure greater than the toxicity reference value for a given substance. As with the Netherlands approach, the toxicity reference value for populations of ecological receptors is defined as the LC_{50}. The use of NOEC is a good starting point but it is limited, as NOECs are based on individual substances rather than chemical mixtures; also actively growing organisms are most sensitive to contaminants, thereby making the age of organism an important factor. Even protection of 95% of the species is unlikely to protect rare or indicator species (Forbes & Forbes 1993; Hopkin *et al.* 1993). The determination of unacceptable and acceptable risk for land contamination in the UK has not been tested, and case law is likely to be important in setting a precedent.

HARM TO TERRESTRIAL ECOSYSTEM RECEPTORS

Table A of the DETR Circular 02/2000 (Department of Environment Transport and the Regions 2000a) specifies the receptors to be protected under Part IIA. The terrestrial ecological receptors of that table are presented in Table 2. Designated areas are defined in the DETR Circular, which also defines significant harm to terrestrial ecosystem receptors among others. Significant harm is described as '*that which results in an irreversible or other substantial adverse change in the functioning of the ecological system... or that which affects any species of special interest... and which endangers the long-term maintenance of the population of that species at that location.*'

Ecological harm and its assessment is a general underpinning concept of the Part IIA legislation and this section therefore focuses on Part IIA receptors. This concept

Table 2. Part IIA the Environmental Protection Act 1990: significant harm to terrestrial ecosystem receptors (Department of Environment Transport and the Regions 2000a).

Type of receptor	Description of harm to the type of receptor that is to be regarded as *significant harm*
Any ecological system, or living organism forming part of such a system, within a location that is: • an area notified as a site of special scientific interest (SSSI) under Section 28 of the Wildlife and Countryside Act 1981; • any land declared a National Nature Reserve under Section 35 of that Act; • any area of special protection for birds, established under Section 3 of that Act; • any European Site within the meaning of regulation 10 of the Conservation (Natural Habitats etc.) Regulations 1994 (i.e. Special Areas of Conservation and Special Protection Areas); • any candidate Special Areas of Conservation or potential Special Protection Areas given equivalent protection; • any habitat or site afforded policy protection under paragraph 13 of Planning Policy Guidance Note 9 (PPG9) on nature conservation (i.e. candidate Special Areas of Conservation, potential Special Protection Areas and listed Ramsar sites); or • any nature reserve established under Section 21 of the National Parks and Access to the Countryside Act 1949	For *any* protected location: • harm which results in an irreversible adverse change, or in some other substantial adverse change, in the functioning of the ecological system within any substantial part of that location; or • harm which affects any species of special interest within that location and which endangers the long-term maintenance of the population of that species at that location. In addition, in the case of a protected location that is a European Site (or a candidate Special Area of Conservation or a potential Special Protection Area), harm which is incompatible with the favourable conservation status of natural habitats at that location or species typically found there In determining what constitutes such harm, the local authority should have regard to the advice of English Nature and to the requirements of the Conservation (Natural Habitats etc.) Regulations 1994. The description of significant harm in this section is referred to as an *ecological system effect*

Table 3. Definition of harm: information required for a site-specific risk assessment

Issue descriptor	Information required
Site designation	How complex is the basis of designation: individual or several species or type of habitat? What is/was background contamination?
Land contamination	Proximity; is the land causing an effect to the designated area? What are the stressors (contaminants)?
Soil quality	Does protection of soil quality protect ecosystem function? Are additive, cumulative and synergistic effects considered or are chemicals assessed in isolation?
Exposure assessment	• Is there predictive capability? • Is exposure occurring? • What is exposed and over what duration? • What are the relevant exposure and uptake routes? • Where and how much exposure occurs? • What is the variance and uncertainty? • What is the probability of harm measured by exposure (dose response or bioavailability)? • Is the harm/effect likely to be irreversible?
Ecological receptors	Which species? Is the use of indicator species appropriate?
Ecological function	Which functional process(es) is/are being affected?
Uncertainty and decision-making	• What is the desired level of protection? • What assumptions have been made? • What is the relative risk versus the scientific basis/judgement? • What are the consequences of harm, that is, the effect(s)? • Is there a scientific and regulatory consensus of opinion? • What are the policy implications? • Is the contaminated land a Part IIA* site? • What are the implications for remediation?

*As defined in the Environmental Protection Act 1990 (Department of Environment Transport and the Regions 2000a).

equires development in order to define how to measure arm in relation to ecological function. Information likely be required for a site-specific risk assessment to deter-ine harm is presented in Table 3. The *de minimus* ecologi-l risk can be a lack of evidence for an impact on selected pecies or ecosystem function. Other authors suggest a 0% level as the threshold for a *de minimus* level of signifi-nt ecological effect (Suter *et al.* 2000) beyond which res-ration is required.

Harm to terrestrial ecosystems can be assessed by con-dering soil quality. Biological indicators of soil quality clude nitrogen and carbon availability, leaf litter composition and soil fauna populations, including arthro-ods and invertebrates. While the measurement of these dicators is readily achievable, their contribution towards e definition of contaminated land and ecological harm is ncertain. In calculating organism exposure, the critical ctor is likely to be the amount of soil ingestion. Soil qual-y indicators are important to ensure maintenance of soil nction for current and future land uses. Historically, liance has been placed on assessing soil quality based on dividual chemical data without considering synergistic or ditive effects.

Assessment of soil quality within a protected area of eco-gical value can indicate the nature and spatial distribution contamination present. Soil quality is defined as the pacity of soil to function as a vital living system to sus-in biological productivity, promote environmental quality d maintain plant and animal health within natural or anaged ecosystem boundaries, and including the support of human health and habitation (Karlen *et al.* 1997). In the absence of a European standard for soil quality, many countries have developed their own standards and guidance based around that of the USEPA (United States Environmental Protection Agency 1998). A common approach is to start with the endpoint; for example, develop guideline values based on land use, which is the basis of the Netherlands approach (van de Leemkule *et al.* 1999; van Hesteren *et al.* 1999; Van Wensem *et al.* 2000; Van Wensem & Vegter 1998). The use of such values is questionable when remediation is initiated (Crommentuijn *et al.* 2000): if soil quality shows marginal exceedance, remediation cannot be justified on the basis that costs outweigh the benefits.

Ecological protection and conservation: individuals or populations?

Selection among different ecological risk assessment endpoints depends on the level(s) of biological organization in question, whether individual, population, community, or entire ecosystem. There is increasing scientific and policy consensus in the UK (Department of Environment Transport and the Regions 2000a) that ecological risk assessment should aim to protect populations rather than individuals, for example, against loss of species diversity (Posthuma 1997). Ecosystems do not exist in the same way that organisms (as individuals) exist (Calow 2000). Population effects are typically assessed by quantifying abundance, mortality and reproduction. With the exception of endangered species, which are protected as individuals, most species decisions are based on population level effects (Suter *et al.* 2000).

Reviews of terrestrial population models for ecological risk assessment have been carried out (Emlen 1989; Hope 1995), including the role of such models (Barnthouse 1992). These reviews concluded that the most easily accessible and appropriate endpoints for population assessment are pseudoextinction (the probability of a population falling below a predetermined fraction of its undisturbed level) and temporal mean population density. Effective conservation measures require knowledge of factors affecting population persistence and the magnitude of their effects (Fahrig 2001). Case studies have demonstrated population level effects along pollution gradients. These effects can be significant; for example, reduced cocoon production rates and reduced growth rates evident in earthworms around the Avonmouth smelter in the UK (Spurgeon 1997). Though no earthworm mortality was evident, zinc was probably affecting earthworm reproduction, a more sensitive indicator, and therefore population viability close to the smelter.

Modelled simulations of habitat loss and species extinction (Akçakaya 2001) suggest that habitat preservation and restoration is the highest priority for ecosystem protection. The prediction of extinction thresholds requires organism movement rates. Conservation strategies should consider the whole landscape quality, not just the protected habitat, since most ecosystem functions are spatially and temporally dependent (Herrick 2000; Fahrig 2001). Critical ecosystems are those with high ecological diversity, potential for long-term sustainability and presence of relic or native communities (Noss 2000).

Significant harm and significant possibility thereof

Assessing the significance of risk is the final stage of the risk assessment process, following hazard identification and identification, magnitude and probability of the consequences (Department of Environment Transport and the Regions *et al.* 2000). For ecosystems, this is defined as being when growth, reproduction or mortality is adversely affected, such that the survival of the population / community / species is threatened (Environment Agency 2003). Species composition may change naturally while ecological function remains unaffected. The importance of maintaining a high level of ecological biodiversity is uncertain, though an ecosystem does not need to be highly diverse in order to maintain ecological function.

Exposure assessment

Exposure represents the probability of harm that can be measured by a dose–response relationship, or by bioavailability. Determining the choice of receptor is crucial and requires careful consideration. Designated areas may require the consideration of harm that affects any species of special interest. A primary assumption is that the habitat determines which and how many receptors are exposed. Assuming that the main objective is to protect, evaluate or measure habitat function, species with a high sensitivity to suspected contaminants are required.

The USEPA uses six criteria for exposure assessment (United States Environmental Protection Agency 1998): (1) how exposure occurs, that is, pathway analysis; (2) what is exposed, that is, receptor analysis; (3) quantifying the amount of exposure spatially and temporally; (4) variability of exposure; (5) uncertainty of exposure estimates; and (6) probability of exposure, that is, risk assessment.

The duration of exposure can be important, and shorter term exposure may be more significant to species of low ecological relevance. If the relevance becomes higher, then the exposure needs to be longer term. This relationship also helps to understand where the ecological response lies.

Effects assessment

The effect represents the consequences of harm: contaminant availability does not equal harm. The possibility of significant harm is crucial but is subject to interpretation and definition. Definitions of harm must be quantified in order to determine whether a given contaminated land site is contaminated land under Part IIA. Ecological effects data typically takes into account organism, species or population parameters such as fecundity, adult survival, reproduction and population growth.

There are four conventional biological measures that can be used to demonstrate whether a source–pathway–receptor relationship constitutes significant harm, all of which have the ability to describe biological organisms or ecosystem components chemically. Biomarkers and toxicity tests are indirect measures, whereas critical body residues and bioaccumulation are direct measures.

Ecosystem effect indicators are a promising way of portraying human influence on ecosystems, if sufficient information is provided for decisions to be made (Merkle & Kaupenjohann 2000). While ecosystem effects indicators can be developed (Figure 1) there is always a need to use indigenous communities.

Assessment of ecological harm must have predictive capability if irreversible effects are to be prevented. However, response to contamination is not entirely predictable (Noss 1990) and ecosystem sensitivity undoubtedly varies. This reiterates the need for an approach combining predictive modelling and monitoring.

USE OF EARTHWORMS FOR ASSESSING ECOLOGICAL FUNCTION AND HARM

Ecological relevance of soil invertebrates

The value of soil invertebrates other than earthworms, such as nematodes, mites and springtails, is high and related to their ecological role; for example, litter decomposers regulate energy flow and nutrient cycles. Many soil invertebrates can be used for monitoring the status of soil ecology and the selection of species for a particular study should be given careful thought. Earthworms are a preferred indicator because key ecological functions are adversely affected by their absence. Nematodes are the most abundant ecologically relevant species, followed by mites and then springtails. Composition of nematode communities in soil may indicate levels of soil contamination (Lau *et al.* 1997). Critical factors in selecting species as indicators of harm to an ecosystem are their ecological relevance, ecological importance and sensitivity. Other less important factors include abundance, ubiquity, ability to

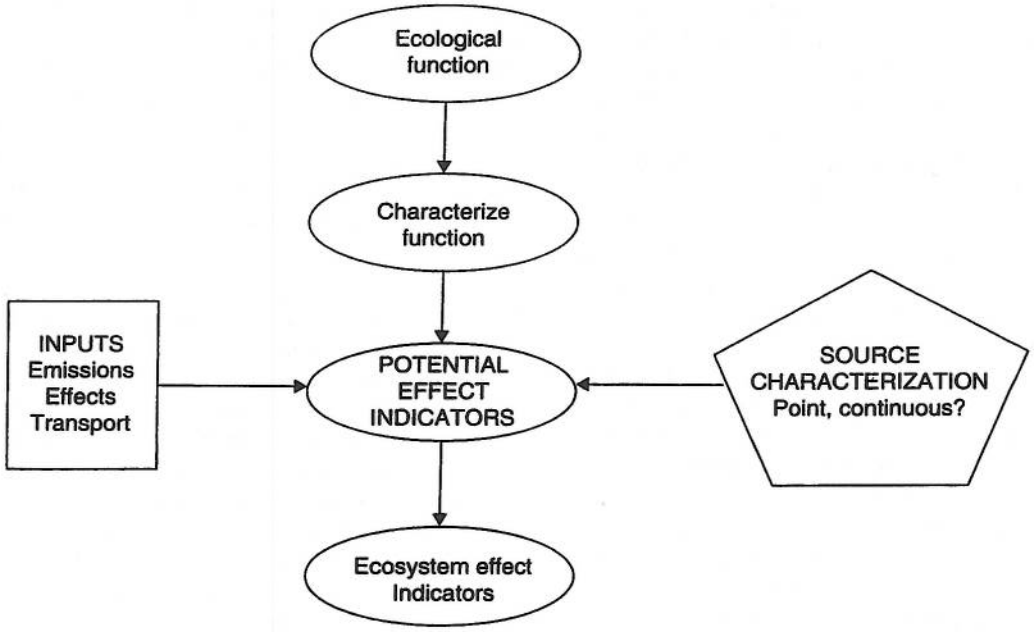


Figure 1. Development of ecosystem effect indicators (after Merkle & Kaupenjohann 2000).

survive in different soil conditions and ability to be exposed to multiple pathways.

Contaminants can be resistant to decomposition processes, for example polyaromatic hydrocarbons (PAHs), and therefore they accumulate in soil (Van Brummelen *et al.* 1996). Soil invertebrates easily become exposed to such contaminants, potentially affecting their ecological functioning. Indicator species may change temporally, so it is important to identify the species that are responsible for maintaining function. Earthworms and woodlice are ecologically relevant soil invertebrate fauna and as such are good indicator species. However, the use of soil invertebrate bioindicators and the measurement of toxicity endpoints such as mortality and biomass loss require careful validation by field studies and should not simply be reliant on extrapolation from laboratory data.

Why earthworms?

Earthworms have been used increasingly for ecological risk assessment since the introduction of international standards including the acute earthworm toxicity test of the Organisation for Economic Co-operation and Development (OECD) in 1984 (Spurgeon *et al.* 2003). There are many reasons why earthworms are widely used and are now regarded as a model organism. Earthworm communities offer many advantages for assessing soil quality (Urzelai *et al.* 2000) and are the favoured indicator species in the Netherlands.

Earthworms are engineers (Lawton 1994) and, as Darwin intimated, they are like an unacknowledged elemental force (Phillips 1999). Earthworms are arguably the most important soil biota in maintaining soil structure, function and fertility (Edwards 2004) and they have an important role in contaminant transfer through the food chain, with potential for predatory secondary poisoning via bioaccumulation and food chain transfer (Spurgeon & Hopkin 1996c). The contribution of earthworms to soil fertility can be considerable (Killham 1994) and earthworms are intimately involved in organic matter decomposition (for example, of surface leaf litter and the remineralization and humification of organic matter). They also contribute to soil aeration and have large direct effects on nitrogen cycling (Killham 1994; Forbes & Kure 1997). Furthermore, earthworms are likely to have long exposure periods to contaminants within land, due to their low mobility, which increases the likelihood of being able to establish effects in the field. Earthworms are also a preferred species for ecological risk assessment because they are more highly exposed to soil contaminants through ingestion and dermal contact than other soil and leaf litter invertebrates (Ma 1994).

Earthworms are intrinsically linked and are therefore vital to ecosystem function. As a receptor, earthworms can be regarded as a surrogate ecosystem, an approach advocated for the conservation of aquatic target taxa and communities (Hitt & Frissell 2004). Various sensitive endpoints, such as biomass change and reproduction, have been identified in earthworm toxicology (Schaefer 2003). The main exposure route for earthworms and most other soil invertebrates is pore water uptake through the dermis, and pore water concentrations are a good measure of bioavailability (Naidu *et al.* 2000). Field contaminant exposure resulting in harm to earthworms has been demonstrated, for example four metals released from the Avonmouth smelter (Cd, Cu, Pb, Zn), of which zinc is the limiting factor for earthworm distribution (Spurgeon & Hopkin 1996b).

Earthworm classification and ecology

Different classification schemes exist for categorizing earthworm communities into functional groupings according to soil properties such as litter-dwellers (epigeic), mineral soil feeders and dwellers (endogeic) or permanent / semi-permanent soil burrowers feeding on surface litter (anecic) (Neilson *et al.* 2000; Edwards 2004). The ecology of earthworm species needs to be accounted for when undertaking

a risk assessment, as species sensitivity to contamination varies, particularly with regard to metal accumulation, for example (Morgan & Morgan 1999). Cadmium in particular is strongly accumulated by earthworms (Mariño & Morgan 1999). The risk of bioaccumulation can be twofold: risk to earthworms and risk to species higher up the food chain. Thus, it may be appropriate when undertaking a risk assessment to select the most vulnerable species in order to derive a conservative risk estimate.

Contaminant exposure studies

In exposure studies most organisms, including soil biota, are ordinarily exposed to different types and concentrations of contaminants. During the last decade earthworms have been used extensively both in the laboratory and increasingly in the field to assess sub-lethal toxicity of different soil contaminants. Earthworm growth, reproduction and mortality have been recorded in response to different exposure levels and contaminants, most commonly for metals, pesticides, PAHs and explosives (see Table 4 for references to selected field exposure data).

Several studies of earthworm exposure to different soil contaminants in the field and the laboratory have been published that demonstrate differing degrees of harm, either as a result of direct contact with the soil, or exposure to free metal concentration in the soil pore water. International test methods like that of the OECD recommend the use of the earthworm species *Eisenia fetida* and *E. andrei*, though *Lumbricus* species are also widely used by researchers. Consequently, *Eisenia fetida* and *Lumbricus terrestris* have been researched more comprehensively than other earthworm species (Scott-Fordsmand *et al.* 2000).

Enzymic inhibition in earthworms is a sensitive parameter that is used increasingly. From the literature we can see, for example, that lead has been shown to inhibit certain enzymes in *Eisenia fetida* and *E. andrei* and this inhibition generally depends on the dose or duration of exposure; significant changes were detected at exposure to $30\,mg\,kg^{-1}$ (Saint-Denis *et al.* 2001). This concentration is considerably less than the maximum permissible concentrations for soil in selected countries identified in Table 1. Body concentrations of metals, which are strongly accumulated in earthworms, may be more representative of bioavailability and toxicity than the conventional total chemical or extractable soil concentrations (Mariño & Morgan 1999). Factors including soil texture and structure are responsible for contaminant migration through the soil matrix. There is some evidence for the distribution of soil contamination also being affected by earthworm activity and behaviour. Farenhorst *et al.* (2000) studied atrazine in laboratory microcosms in which earthworms were shown to influence the distribution of atrazine in the soil matrix. In soil matrices where earthworms were absent, 65% of the atrazine applied remained within the top 4-cm surface layer. In soil profiles where earthworms were added after atrazine application, 60% of the atrazine applied was translocated below 4 cm by feeding activity. Toxicities of the explosive 2,4,6-trinitrotoluene (TNT) and of octahydro-1,3,5,7-tetrazocine (HMX) to the earthworm *Eisenia andrei* have been determined in soil (Robidoux *et al.* 1999; Robidoux *et al.* 2001). Even though HMX has limited water solubility, a number of sublethal effects were identified including growth inhibition and reproductive effects, suggesting the cause was direct contact. These effects were present even at the lowest concentration tested ($\sim 280\,mg\,kg^{-1}$). Lethality was not demonstrated, even at the highest concentration tested ($\sim 2500\,mg\,kg^{-1}$). Soil guideline values for explosive substances do not exist, so a direct comparison is not possible.

Soil is the major sink for PAHs in the environment (Van Brummelen *et al.* 1996). PAH concentrations in the earthworm species *Lumbricus rebellus* and the isopods *Porcellio scaber*, *Oniscus asellus* and *Philoscia muscorum* were measured along a pollution gradient from a blast furnace plant (Van Brummelen *et al.* 1996). Species-specific profiles for PAH contamination have been identified in a soil contamination gradient near a blast furnace plant in the Netherlands; species profiles were found to be dependent on feeding behaviour, whether fragmentation or leaf litter.

DISCUSSION

Preservation of function is of most significance to ecosystem protection. The hypothesis that loss of indicator

Table 4. Selected earthworm exposure data[a] for specific soil metal contaminants and site case studies (after Suter 1990, p 131).

Available contaminant uptake factors (soil or soil pore water concentration)	Case study location	References
Cd, Cu, Pb, Ni, Zn	[Various]	Neuhauser *et al.* 1995
As, Cd, Cr, Cu, Hg, Pb, Mn, Ni, Se, Zn	[Various]	Sample *et al.* 1999
Cd, Pb, Zn	Germany	Emmerling *et al.* 1997
Cd, Cu, Mn, Ni, Pb, Zn	Netherlands	Hendricks *et al.* 1995
Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn	Netherlands	Ma 1982
Cd, Cu, Pb, Zn	Netherlands	Ma *et al.* 1983
Cd, Cu, Pb, Zn	UK, Avonmouth	Spurgeon & Hopkin 1996a, b; 1999b; Weeks *et al.* 2004
Cu	UK, Cumbria & Devon	Langdon *et al.* 2001
Cu, Cd, Pb, Zn	UK, Thames region	Environment Agency 1999
	USA, Maryland	Beyer *et al.* 1987
As, Cd, Cu, Zn	USA, Montana	Pascoe *et al.* 1996
Cd, Cu, Pb, Ni, Zn	USA, Pennsylvania	Beyer *et al.* 1982
Pb	Wales	Corp & Morgan 1991

[a] Laboratory data have been specifically excluded. See Spurgeon *et al.* (2003) for a discussion on the use of laboratory and field tests.

species does not impact on soil ecosystem function requires testing in order to define significant harm for Part IIA that may also derive action levels for remediation, according to future land use. This approach must serve as an ecological indicator by having predictive capability and the modelled prediction must be measurable while being sensitive to change. Although several species are used as indicators for ecosystem protection, the scientific rationale for their selection is not always apparent. Current guideline values for assessing soil quality are frequently misused and should be used cautiously and sparingly. For example, guideline values for lead in selected European countries were up to one order of magnitude in excess of the level at which 'significant changes' occurred in *Eisenia fetida* and *E. andrei* at the biochemical level (Saint-Denis *et al.* 2001).

Priorities for terrestrial ecosystem risk assessment and land contamination include detecting ecological harm, developing modelling capability to assess terrestrial ecosystem function and accepting uncertainty. Long-term studies that include control sites are required. Collaboration and sharing of knowledge are needed if consensus and credibility are to be achieved. In the absence of a full model of generic risk assessment, careful detailed quantitative risk assessments ensure that a precautionary approach is taken. The cumulative effect of the uncertainty surrounding these assessments should not be underestimated. Links between specific ecological harm and the monitoring of individual species have yet to be made. Studies that demonstrate ecological harm resulting from the presence of contamination where there is a lack of earthworms would further justify the use of earthworms as indicator species.

Available evidence to date suggests that most contaminated land in the UK, as determined using the legal definition, will be identified mainly on the basis of risks or harm to receptors other than terrestrial ecosystems. A survey carried out for the year 2001 identified categories of risk and remediation required at 68 contaminated land sites in the UK that had been remediated. Of these, the protection of ecologically sensitive receptors was a factor at only 7% of sites, and protection of human health at 91% of sites (Nathanail *et al.* 2003). This trend is likely to continue (Quint 2001).

CONCLUSIONS

Internationally, because of a scarcity of empirical studies that show an elevated risk to terrestrial ecosystems from land contamination, countries have relied on generic standards that are not necessarily risk-based or scientifically derived. The literature demonstrates that there is a paradigm shift taking place towards developing risk assessment procedures for terrestrial ecosystems and the pace of change is rapid.

The use of earthworms as surrogate species for terrestrial ecosystem risk assessment requires validation and a comprehensive understanding of the relationship between the functional groups is needed. Future research must also critically investigate the extent to which current risk assessment tools, techniques, frameworks and ecotoxicological tests can inform decisions about the significant possibility of significant harm with respect to ecological harm and land contamination under Part IIA (Department of Environment Transport and the Regions 2000a). Ecological risk assessment must focus on the determination of ecological harm measured by ecological effects from contaminant mixtures. Ecosystem function is largely dependent on soil processes, and therefore function – for which earthworms are surrogate model organisms – represents a viable measure of ecological harm. This concept has not been widely applied to ecological risk assessment and requires further development.

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Editorial

Guest editorial

Environmental risk management is a mainstream activity. It is enshrined within industry, consulting practice, regulation and academia, and it is proving dividends in terms of better decision-making, better use of resources and reduced risks to public health and the environment. Distinct practices such as radiological performance and flood damage assessments, contaminated land and production of chemicals risk assessments and water safety plans have developed as expressions of risk management within individual decision contexts and practitioner communities and each have specific risk vocabularies.

Practitioners are increasingly becoming concerned with multi-media exposures to multiple hazards, often at a single site. Coincident with an expansion in the application of formalized environmental risk management has been a growth in the broader suite of decision-making tools, including strategic environmental assessment (SEA), health impact assessment (HIA), multi-criteria analysis (MCA) and stakeholder participation. This raises questions regarding the roles that these tools have within the risk management and decision-making processes and whether there are interfaces between risk assessment and these techniques.

With this in mind, this special issue of Environment International on 'Environmental Risk Management—the State of the Art' has been prepared. A selection of papers presents background information about current risk assessment and management practices on a range of disciplines covering a broad perspective and considering different media. Where relevant, papers challenge the status quo and draw out similarities and differences between a range of contexts in which environmental risk management is applied. Papers cover different aspects of the environmental risk management paradigm where the context best illustrates activities within one or more of the component stages of risk management (e.g. hazard identification, risk estimation, risk communication). Table 1 lists the areas covered by individual papers in this issue and highlights the stages of the risk assessment and management process were the paper has focused on.

We hope that this special issue will act as a reference document for environmental risk analysts and stimulate opportunities for read-across between sub-disciplines. Papers explore the roles that these tools have within risk management and decision-making and the interfaces with other decision-making techniques.

Some disciplines have evolved with time and have more established risk assessment and management processes (e.g. nuclear waste disposal), whilst others are at early stages of development either because they are new disciplines involving novel technologies or because there is a lack of knowledge and/or paucity in the data available. For example, less is known about the fate and behaviour or toxicological properties of nanoparticles relative to chemicals such as benzene and some processes might be better understood in terms of their likely impacts on the environment (e.g. chemical releases from incinerators relative to microbial emissions from composting facilities). Current knowledge within each discipline will determine where efforts need to focus on within the different stages of the risk assessment and management framework. For example, the paper by Moore explores the potential risks posed by nanomaterials and the harmful effects that these may have on the aquatic environment. As current knowledge is this area is very limited, it is important to get information on their toxicity, and to undertake research to test the possible association of manufactured nanoparticles with naturally occurring colloids and particles as this may have an impact on their bioavailability and uptake into cells and organisms. Precautionary approaches often have to be followed, where little is known of the risks posed by these novel technologies.

As knowledge is gained within the technical aspects of the risk assessment process, there is a natural move to improve the understanding of the options appraisal and risk management stages, as well as to better understand ways of managing and communicating the risks, involving stakeholder engagement and participation and ensuring there is public dialogue on proposed risk management solutions. This can be done with more confidence when there is greater confidence on the risk estimates. The paper by Kemp et al. explores risk communication processes within the context of radioactive waste management and highlights the fact that formal procedures are now in place to identify, clarify and integrate stakeholders' issues and concerns within the decision-making process.

A number of papers concentrate on the risk management processes followed for assessing the risks of chemical and biological agents in specific media. The paper by Longhurst et al., for example, examines and evaluates the process of Local Air Quality Management aimed at identifying and remediating areas of poor air quality at a national and local level in a consistent and reproducible manner. This process involves regular reviews by technically competent individuals to ensure that a level playing field is obtained across spatial and temporal scales. Air quality is managed via an effects-based risk management process designed to provide a dynamic solution to public health issues associated with elevated concentrations of specified air pollutants. It follows

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Table 1

Risk assessment/management area	Hazard identification	Exposure assessment	Risk estimation	Risk evaluation/ characterisation	Options appraisal	Risk management	Risk communication
Air quality management	✓	✓	✓				
Drinking water/risk management						✓	
Drinking water/water safety plans	✓	✓					
Aquatic environment/nanoparticles	✓	✓					
Food chain and the environment		✓					✓
Ecological			✓	✓			
Human health/exposure assessment		✓	✓				
Waste management		✓	✓				
Radioactive waste							✓
Production of chemicals/REACH						✓	
Climate change/water framework directive	✓				✓		✓
Risk-based regulation					✓	✓	
Bridging risk science and policy			✓	✓		✓	
Comparative risk assessment/multi-criteria decision analysis					✓	✓	✓
Implementation of capability models						✓	✓

a risk-based approach whereby an initial screening assessment is undertaken and, if this identifies an exceedance of the Air Quality Objective, then a more detailed assessment should follow.

Hrudey et al. have looked at risk management within the context of providing safe drinking water. They explore how a better understanding of the causes of drinking water disease outbreak can lead to the adoption of more effective preventive measures to improve the risk management for the provision of safe drinking water. They conclude that risk management approaches offer a means to benefit from the experience of past failures and that the best drinking water providers have shown an ability to respond to a wide range of challenges with effective prevention programmes by ensuring that they follow a rigorous and comprehensive risk management approach. The development of water safety plans aimed at managing risks from catchment to consumer taps have been increasingly adopted by water suppliers to ensure that preventative strategies are in place to proactively identify, assess and manage risks from microbial and chemical contamination incidents. Hamilton et al. examine water safety plans by looking at a variety of monitoring, optimization and risk management initiatives that can be taken to improve drinking water safety. Their paper also looks at how risk management practices are being integrated across water companies and how this is likely to affect the future development of water safety plans.

The paper by Ould-Dada presents an overview of the approach used to assess radiation dose and risk to members of the public from radioactivity in food and the environment. This paper focuses on the human exposure assessment, describes the uncertainties inherent in the process, and suggests ways of dealing with these uncertainties and communicating them effectively to non-expert audiences.

The development of ecological risk assessment and management practices are reviewed by Hope, who highlights the move in emphasis from evaluating adverse health impacts on particular, often small scale, environments, to undertaking more complex ecological assessments of whole populations and communities. This paper examines current issues that need to be considered in taking forward the scientific development of ecological risk assessment to make it a useful environmental management tool in assessing larger and more complex ecological scales.

As with ecological risk assessment and management, there has also been a change of emphasis within waste management which has presented operators and regulators with new challenges to ensure safe and environmentally responsible operations. This has involved moving from the management of the more established sectors of landfill and hazardous wastes towards including a broader range of waste technologies aimed at pre-treating the wastes prior to the disposal of residues (e.g. in-vessel composting, thermal treatment of clinical waste). Pollard et al. discuss the recent developments in risk assessment within the waste management sector and the future needs of risk assessment required to respond to the new waste and resource management agenda.

Nieuwenhuijsen et al. provide a summary of established techniques of exposure measurement and assessment and highlight new techniques and approaches and their advantages for epidemiology and health risk assessment. This paper explores the importance of having good exposure assessment data as this is often the limiting factor in interpreting the results from epidemiology and risk assessment studies.

A number of papers within this issue look at various aspects of risk assessment and management within different regulatory systems. Warhurst provides a brief overview of the way in which chemical regulation has developed in Europe and examines the changes proposed in the European Union's Registration, Evaluation and Authorisation of Chemical (REACH) proposal. In doing so, he highlights the key innovations in REACH with respect to hazard and risk assessment and risk management. The risks posed by climate change to the delivery of the European Union Water Framework Directive (EU WFD) objectives in the UK are discussed in the paper by Wilby et al. This directive is novel in that it integrates water quality, water resources, physical habitat and, to some extent, flooding for all surface waters and groundwater, and takes forward river basin management. However, it does not explicitly mention the risks posed by climate change to the achievement of its environmental objectives. This issue is explored and future policy opportunities, research initiatives and research gaps are identified which should

help determine new guidance and screening tools required to identify which water bodies may be most vulnerable to the effects of climate change.

Rothstein et al. look at the benefits and challenges of operating within a risk-based regulatory framework from an environmental policy perspective by focusing specifically on the regulation of contaminated land and radioactive waste. They argue that whilst risk-based approaches can offer important benefits, they also face a range of challenges that can play an important role in shaping the way that organizations manage both risks to society and to their own institutional risks.

Risk-based regulation assumes that risk assessment can evaluate risks against policy objectives. Using the contaminated land regime as an example, Evans et al. argue that policy goals are often ambiguous due to problems with normative or unscientific language and to society's uncertain expectations for the environment. This creates a risk assessment—policy gap that requires risk assessors to interpret policy for use in risk assessment. They go on to argue that until this uncertainty is resolved, the democratic and regulatory effectiveness of risk regulation will be undermined by *ad hoc* policy decisions abdicated to risk assessors.

The paper by Linkov et al. brings together a multidisciplinary review of existing decision-making approaches and synthesizes the state of the art research in comparative risk assessment, multi-criteria decision analysis (MCDA) and adaptive management methods applicable to environmental remediation and restoration projects. The authors propose a basic decision analytical framework that uses MCDA together with adaptive management and public participation and stakeholder value elicitation methods and they demonstrate the application of this framework to a case study based on contaminated sediment management issues. They argue that the framework should allow managers to learn about the system they are managing and should help them understand the trade-offs involved between different management alternatives and to make justified and informed decisions.

The success of any regulatory regime is dependent on the capability of the risk generating organizations to manage their risks. In the UK, for example, regulatory controls aim at ensuring that companies place appropriate emphasis on the management of health and safety, environmental and financial risks. Existing approaches to safety assurance based on risk assessment and formal safety assessments are increasingly considered unlikely to create the step change improvement in safety to which the off-shore industry aspires. In their paper, Strutt et al. present a tool used to assess the capability of an organization to perform key processes required to deliver their product or service, the capability maturity model (CMM) and its application to the offshore industry. The paper discusses how this model is related to regulatory mechanisms and risk-based decision-making together with the potential of the CMM to environmental risk management.

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Guest editor
Raquel Duarte-Davidson
Health Protection Agency,
Chemical Hazards and Poisons Division (CHaPD),
Oxon, UK
E-mail address: raquel.duarte-davidson@hpa.org.uk.
Corresponding author.

S.J.T. Pollard
School of Industrial and Manufacturing Science,
Cranfield University, Cranfield, Bedfordshire, UK
E-mail address: s.pollard@cranfield.ac.uk.

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Risk management for assuring safe drinking water

Steve E. Hrudey [a,*], Elizabeth J. Hrudey [a], Simon J.T. Pollard [b]

[a] School of Public Health, 10-102 Clinical Sciences Building, University of Alberta, Edmonton, Alberta, Canada T6G 2G3
[b] Sustainable Systems Department, Building 61, School of Industrial and Manufacturing Science, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK

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Abstract

Millions of people die every year around the world from diarrheal diseases much of which is caused by contaminated drinking water. By contrast, drinking water safety is largely taken for granted by many citizens of affluent nations. The ability to drink water that is delivered into households without fear of becoming ill may be one of the key defining characteristics of developed nations in relation to the majority of the world. Yet there is well-documented evidence that disease outbreaks remain a risk that could be better managed and prevented even in affluent nations. A detailed retrospective analysis of more than 70 case studies of disease outbreaks in 15 affluent nations over the past 30 years provides the basis for much of our discussion [Hrudey, S.E. and Hrudey, E.J. Safe Drinking Water—Lessons from Recent Outbreaks in Affluent Nations. London, UK: IWA Publishing; 2004.]. The insights provided can assist in developing a better understanding within the water industry of the causes of drinking water disease outbreaks, so that more effective preventive measures can be adopted by water systems that are vulnerable. This preventive feature lies at the core of risk management for the provision of safe drinking water.
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1. Introduction

1.1. Risk management in the modern water utility business

Managing risk is an essential business requirement across the process and utility sectors. From embedding good corporate governance within organizations through to the management of individual projects and assets, the ability to understand and assess risk and to implement preventive measures to improve control of risk is a mainstream activity (Pollard et al., 2004). Many of the larger water utilities have connected their responsibilities for financial control with the risk management programmes that are implemented throughout their businesses, including the operational risk analysis and management activities at the process plant level. In the water industry, there is a need for a continued shift in the approach to risk management from one historically implicit to treatment plant design and operation to one increasingly explicit and better integrated within the core business of providing safe and wholesome drinking water that deserves the trust of consumers.

The benefits of good corporate risk management should achieve the preventive management of risks throughout a business. One potential danger may be that the principal goal of assuring public health protection through safe drinking water may be viewed as only equivalent to many other priorities in the organization. With the focus increasingly on income, expenditure and whole-life costing under new institutional arrangements for the provision of drinking water, new facilities are being designed to refined and better-characterized margins of safety. Water utilities must seek not only to meet their legislative requirements but also maximize the availability, serviceability and life of their assets and minimize expenditure on energy, chemicals and processes. But whilst new arrangements undoubtedly offer greater management control and flexibility in decision-making, the drive for shareholder dividend or stakeholder value must be second to maintaining a secure and safe water supply system. We contend that an over-emphasis on the administration of risk management in isolation of practical knowledge on *what can go wrong* in practice, can itself be a hazard. Further, we note caution in an inappropriate use of risk

* Corresponding author. Tel.: +1 780 492 6807; fax: +1 780 492 7800.
E-mail address: steve.hrudey@ualberta.ca (S.E. Hrudey).

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management as the rationale for 'optimizing' infrastructure and process systems below what may inadvertently become inadequate margins of safety. In this paper, we discuss current advances in water quality risk management in the light of six case studies that aptly describe what can go wrong when risk management and specifically, public health risk management fails to be the primary focus.

On a continuing basis around the world an estimated 1.8 million people die every year from diarrheal diseases (including cholera). The majority of these deaths is among children in developing countries and up to 39% of diarrheal disease could be prevented by household water treatment by chlorination (WHO, 2004a). By contrast, drinking water safety is largely taken for granted by many citizens of affluent nations. The ability to drink water that is delivered into households without fear of becoming ill may be one of the key defining characteristics of developed nations in relation to the majority of the world. Valuing that enormous benefit appropriately must be a core value guiding risk management in the drinking water business.

1.1.1. A concept of safe drinking water

If the goal of risk management in the water utility sector is to assure safe drinking water, we need to consider what is *safe*. The concept of safety, while largely intuitive to the public, has confounded debates about risk management for decades. Perhaps these debates can be resolved by first considering what safe is not. Safe does not mean zero risk. To demand an absolute standard would guarantee that nothing could be considered safe, making safety a meaningless concept. There is no sharp line between safe and unsafe because safety has meaning on a relative basis. Finally, each person has an individual notion of safety that may vary from one risk to another. We propose a pragmatic notion of safety as "a level of risk so negligible that a reasonable, well-informed individual need not be concerned about it, nor find any rational basis to change his/her behaviour to avoid such a small, but non-zero risk". This notion was first articulated in the context of addressing whether there could be a safe dose for exposure to a carcinogen, an example that squarely confronts the distinction between safety and zero risk (Hrudey and Krewski, 1995). More recently, the issue of what constitutes safe drinking water was addressed for Part 2 of the Walkerton Inquiry (Canada) that was charged with recommending how a disaster like the Walkerton drinking water disease outbreak, which killed seven and made 2300 ill, could be prevented from re-occurring in Ontario (O'Connor, 2002b). A similar notion of drinking water safety was adopted.

In the context of drinking water, and given our current capability for reducing risk, this notion of safe drinking water should mean that we do not expect to die or become seriously ill from drinking or using it. Assuring that drinking water is essentially free (to negligible levels) from the risk of infectious disease can be, and largely has been, achieved for most public water supplies in affluent nations. The challenge for drinking water risk management is to maintain and extend that remarkable achievement as widely as possible.

1.2. Characteristics of risk management for safe drinking water

The Walkerton Inquiry described some essential characteristics of risk management as:

- "being preventive rather than reactive;
- distinguishing greater risks from lesser ones and dealing first with the former;
- taking time to learn from experience; and
- investing resources in risk management that are proportional to the danger posed" (O'Connor, 2002b).

Managing risk effectively requires making sensible decisions within the constraints of knowledge and resources. Risk management is an exercise of decision-making under uncertainty. Even if negligible scientific uncertainty could be achieved, the wide range of competing views for social priorities would still challenge decision-making, but at least the evidentiary basis for any decision would be clear. For drinking water disease outbreaks, cases with such clarity of scientific evidence are the exception rather than the rule. Because there is always some uncertainty in the evidence, errors in decisions can be of two main types (Hrudey and Leiss, 2003; Hrudey and Rizak, 2004):

(i) a decision could be made to act when there is truly no need—a false positive error;
(ii) a decision could be made not to act, when there *is* truly a need—a false negative error.

These types of errors can be illustrated by reference to some of the cases reviewed below. The 1998 Sydney water crisis has been described as a case of issuing a boil water alert for Sydney residents on the basis of erroneous monitoring results (Clancy, 2000), making that decision a false positive error. Walkerton was perhaps the most severe example of a false negative error. Warnings at Walkerton about drinking water quality had been ignored for over 20 years. Ultimately, tragedy ensued. Given these examples, a commitment to precaution for public health decisions demands a preference for false positive over false negative errors, because the consequences of the latter are usually more direct and potentially more severe. However, there are inevitably policy implications to false positive errors as well. In the Sydney case, tens of millions of dollars of public funds were spent on circumstances where investigation revealed that public health was not harmed. The merits of the decisions involved have remained a source of debate. However, given their access to and understanding of the evidence provided at the outset of this incident, the public inquiry found that health authorities chose correctly in deciding to issue a system-wide boil water alert in the first instance (McClellan, 1998). Although the merits of each case will differ, the general reality remains that frequent false positive errors eventually create a "cry wolf" response with the public such that important measures like boil water advisories may be ignored when they are truly needed to protect public health. Although the decision-making challenge for boil water advisories can be characterized in relatively stark terms after the fact, when outcomes are known (with the benefit

of hindsight), the reality for any outbreak situation is that the evidence is usually not clear as the events are unfolding.

2. Learning from experience

2.1. The analysis of failure

The multiple barrier approach to assuring safe drinking water is founded on the maintenance of multiple unit processes and procedures to ensure that pathogens and undesirable chemicals do not reach the consumer's tap. Maintaining these barriers to exposure is critical because, by and large, each barrier in series can offer orders of magnitude (log) levels of protection to the drinking water supply. The level of barriers required must be a function of the level of challenge posed by the source water (Fig. 1). Barriers are often thought of in terms of treatment technology but additional critical barriers involve source water protection, distribution security and monitoring/response capabilities. The failure, or bypass, of any single barrier must be a major concern for operators. The potential technical failures that might occur provide only part of the story because risks usually manifest themselves through a combination of technical, management and human errors (Fig. 2). Undertaking a 'forensic analysis' of historic incidents can highlight the aspects of risk management that are often ignored.

We performed an analysis of the major factors contributing to drinking water disease outbreaks by searching electronically and through bibliographic cross-referencing the published English language literature over the past 30 years. We screened papers for those that discussed specific disease outbreaks in affluent nations and which described some of the failure modes contributing to the outbreak. We did not attempt to review all outbreaks. There was substantial variation in the quality and detail of the description of failure mechanisms among the papers that we retrieved. In all, over 70 case studies were prepared from this database and are analyzed in detail elsewhere (Hrudey and Hrudey, 2004). The case studies included six outbreaks where fatalities arose, causing a total of 22 deaths during or shortly after the outbreak and an estimated 50–70 deaths over the 2 years following the Milwaukee outbreak (Hrudey and Hrudey, 2004). These fatal outbreaks are summarized in Table 1. The risk management lessons are reviewed in the next section.

2.2. Recurring themes

The factors contributing to outbreak failures summarized in Table 1 included: sewage contamination of raw water, inadequate knowledge of source water hazards, inadequate disinfection, extreme weather (heavy precipitation, runoff), cross-connections and distribution failures, filtration failures, livestock or wildlife fecal contamination and process changes. More than one mechanism was involved in contributing to each outbreak and often vulnerable conditions had been in place for years, if not decades. In hindsight, all of these outbreaks were preventable. Although only fatal outbreaks from Hrudey and Hrudey (2004) are summarized below, these are reasonably representative of the features contributing to failure among the 70 case studies reviewed there.

The 1983 Drumheller outbreak was caused by a spill of raw sewage upstream of the drinking water intake. Sewage overflows were common at this location during heavy storm flow conditions but this spill occurred because of a pump failure. The contamination source was certainly foreseeable. Even though the sewage pump station was operated by the same municipality as the drinking water utility, no notice of the incident was provided. The lack of notice precluded implementation of any precautionary measures, such as additional treatment by the water utility. Likewise, water quality monitoring might have provided earlier warning to initiate a boil water advisory. In this case, the boil water advisory was issued almost 5 days after the first signs of illness.

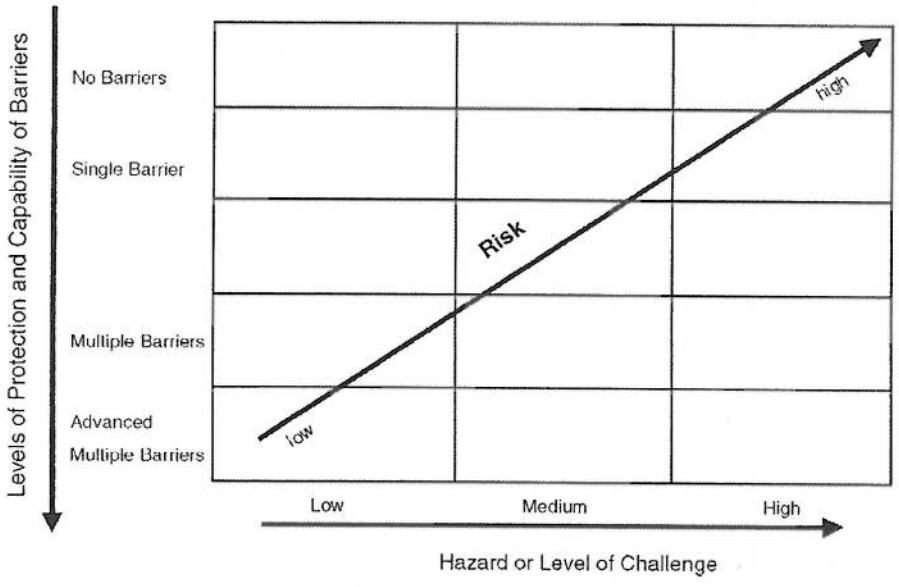


Fig. 1. Drinking water risk management and the multiple barrier approach (Hrudey, 2001).

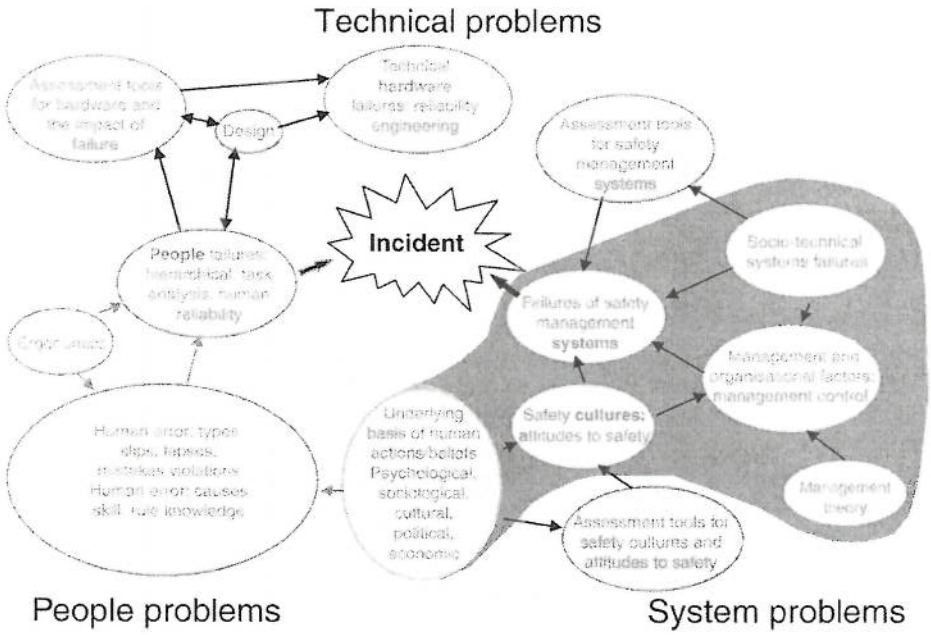


Fig. 2. Reasons for system failures (after Hurst, 1998).

The 1989 Cabool outbreak was caused by sewage contamination of drinking water in the distribution system during water main break repairs following unseasonably cold weather. The distribution system in this community was in poor repair and vulnerable to sewage contamination, while the sewer system was in worse condition experiencing regular sewer back-ups and overflows. The groundwater drinking water source for this community was of excellent quality and this water was distributed with no treatment and or real time warning system (e.g. chlorine residual monitoring). The combination of poorly maintained infrastructure, lack of any treatment or monitoring capacity and unusual weather events triggering upset conditions led to this fatal outbreak.

In 1993, Milwaukee experienced an enormous outbreak of cryptosporidiosis in a drinking water system that practiced full conventional water treatment and was meeting their treated water quality standards at the time of the outbreak. This outbreak has been the subject of numerous publications, but the early speculation that the source of contamination was from upstream agricultural runoff has later been discounted. The most likely source of contamination was sanitary sewage discharge from Milwaukee that impacted the drinking water intake for one of their treatment plants. This circumstance mirrored previous winter outbreaks in Milwaukee in 1916, 1936 and 1938. Despite having what appeared to be adequate water treatment to cope with raw water contamination, the demands for optimum filtration performance, as measured by maximum turbidity removal, and disinfection capable of handling the chlorine-resistant pathogen, *Cryptosporidium parvum*, left Milwaukee vulnerable.

In hindsight, Milwaukee had not learned from the experience of the 1989 Swindon-Oxfordshire outbreak in England which led to the Badenoch expert panel report documenting the measures needed to prevent *Cryptosporidium* outbreaks (Badenoch et al., 1990). Likewise, there was an inadequate response to both the turbidity spike in filtered water and a sharp rise in consumer phone complaints that corresponded with the contamination episode.

The 1993 Gideon fatal outbreak was caused by poor maintenance of water storage facilities that allowed bird fecal contamination that was flushed into the distribution system during an effort to flush the system because of water quality complaints. Like Cabool, this community had a high quality groundwater supply feeding into a poorly maintained distribution system without any treatment barrier.

The 1999 Washington County Fair fatal outbreak was caused by inadequate awareness of the risk of shallow well contamination from a nearby septic seepage field. The well in question was allowed to supply unchlorinated water during the Fair and this source was improperly used for food and beverage production with tragic consequences. The well in question had never produced adverse microbiological monitoring results in the intermittent, seasonal monitoring program, but a severe drought over the previous summer may have made this well more vulnerable to near-surface contamination.

The Walkerton outbreak in May 2000 involved a litany of failures from the operators, through management, the provincial regulator and the Government of Ontario (O'Connor, 2002a). The shallow well that became contaminated by cattle manure following heavy spring rainfall that caused widespread flooding had been identified as vulnerable to agricultural contamination by the hydrogeologist who installed the well in 1978. His warnings were not fully heeded and over the years, adverse microbiological monitoring results were common without any remedial action. The operators were inadequately trained to recognize the risks or the need for requiring adequate chlorination. In particular, they were oblivious to the need for monitoring chlorine residual as a real time measure of disinfection performance for susceptible pathogens (Hrudey and Walker, 2005). The 2-year $9 million public inquiry into this outbreak revealed the numerous failure at

Table 1
Summary of fatal drinking water outbreaks in affluent countries over the past 20 years (Hrudey and Hrudey, 2004)

Date	Location	Source Water	Treatment	Major Failure Factors	Pathogens	Health Consequences	Risk Management Comments
1983 Feb	Drumheller Alberta Canada	Red Deer River	granular filtration chlorination	sewage spill upstream of water intake not reported, likely leading to pathogen contamination of drinking water supply that was vulnerable because of treatment by filtration without coagulation	not identified but likely viral	1326 confirmed cases of gastroenteritis, 3000 estimated cases **2 deaths**	• vulnerable situation of sewage pump station upstream not recognized • failure of internal reporting of sewage spill to water operations • operating winter treatment without coagulation made system vulnerable
1989–1990 Dec–Jan	Cabool Missouri USA	deep ground water	none	likely contamination of distribution system by unseasonably cold weather causing water main breaks leading to sewage cross contamination	*Escherichia coli* O157:H7	243 confirmed cases of *E. coli* O157:H7 32 hospital admissions **4 deaths**	• risks associated with water main break repair during extreme weather not recognized • poor sewerage systems maintenance exposing water distribution to risk • no treatment barrier in place
1993 Mar–Apr	Milwaukee Wisconsin USA	Lake Michigan	chlorination, $KMnO_4$, coagulation, granular filtration, chloramination	sanitary sewage contaminated drinking water intake either directly or via combined storm sewer outfalls during winter storms filtration was not being operated at optimum performance and measures recognized in the UK for reducing *Cryptosporidium* risk were not in use.	*Cryptosporidium parvum* (genotype I, human strain).	285 confirmed cases, 400,000 estimated cases ~4400 hospital admissions **50 deaths** among immune-compromised over the following 2 years	• risks associated with sewage contamination of water intake not recognized • apparently not aware of Cryptosporidium risk • failure to maintain optimum filtration performance • failure to recognize signal from consumer complaints
1993 Nov–Dec	Gideon Missouri USA	deep ground water	none	bird faeces likely contaminated water storage tanks and flushing of system drew contaminated tank water into service	*Salmonella typhimirium*	31 cases confirmed 650 cases estimated 15 hospital admissions **7 deaths**	• poor maintenance of water storage allowed fecal contamination • water quality management not based on good knowledge of system • no treatment barrier in place
1999 Sept	Washington County Fair New York USA	shallow ground water	none	some food and drink vendors used unchlorinated well water for beverages and ice; shallow well was located ~11 m from a septic tank seepage pit with a rapid hydraulic connection to this well	*E. coli* O157:H7 Campylobacter jejuni	161 confirmed cases 2800 – 5000 estimated 71 hospital admissions 14 cases of haemolytic uremic syndrome (HUS) **2 deaths**	• not aware of risk to well from septic seepage field • allowed use of unchlorinated water from a shallow well • failure to consider that extreme drought of previous summer might affect water supply safety
2000 May	Walkerton Ontario Canada	shallow ground water	chlorination only	inadequate chlorination or other barriers to cope with influx of manure contaminated water following heavy rains	*E. coli* O157:H7 *Campylobacter jejuni*	163 cases of *E. coli* confirmed 105 cases of *Campylobacter* 12 cases with both 2300 cases total estimated 65 hospital admissions 27 cases of HUS **7 deaths**	• ignored warnings about vulnerability of shallow well when first installed in 1978 • failed to adopt source protection recommendations at installation • regulator failed to implement policy requiring continuous chlorine residual monitors on vulnerable shallow wells • operators inadequately trained with no knowledge that contaminated water could kill consumers • failure to recognize that extreme weather and flooding could cause water contamination • failure to maintain chlorine residuals • failure to monitor chlorine residuals as required

many levels (O'Connor, 2002a) and made over 100 recommendations for how drinking water safety might be assured in Ontario in the future (O'Connor, 2002a,b).

In every case above, the numerous failures are obvious in hindsight. Yet the case studies presented span almost 20 years and the total collection of cases these are drawn from spans 30 years (Hrudey and Hrudey, 2004). Risk management seeks to achieve a preventive approach and therefore effective risk management needs to demonstrate the ability to translate the enormous collection of hindsight available into effective foresight.

3. Drinking water risk management

3.1. Overall risk management for drinking water utilities

Over the past 25 years, the drinking water industry has faced rising consumer expectations and substantially more stringent regulatory requirements while experiencing dramatic changes from privatization, sector globalization, increased competition, emerging technologies and trends towards financial self-sufficiency. These changes create both opportunities and risks across a variety of categories, including (Pollard et al., 2004):

(i) *Financial risk.* These are risks arising principally from the financial operations and management of drinking water as a business enterprise, whether or not the operating agency is a private entity.
(ii) *Commercial risk.* In many jurisdictions, drinking water utilities are no longer protected as a public monopoly so they are no longer insulated from competition or financial instability.
(iii) *Environmental risk.* Equipment failure or human error canv lead to adverse environmental impacts including waste discharges to the atmosphere, ground or water environment.
(iv) *Public health risk.* The most vital duty of care that a drinking water utility holds is to assure the safety of the water provided to avoid adverse impacts on public health.
(v) *Reputation risk.* Even in the absence of dangers to public health, a water utility can experience harm if water quality characteristics of importance to consumers (taste, odour, appearance) are impaired or customer trust is damaged.
(vi) *Compliance/legal risk.* Legislation, regulations and common law liability set out minimum standards for water quality, the handling and storage of treatment chemicals, the discharge of wastes, and the health and safety of the operational staff and the people living nearby.

The foregoing analysis of failures and the discussions to follow on assuring safe drinking water are focussed primarily on public health risk combined with some obvious elements of reputation and compliance risk.

3.2. A comprehensive risk management approach for drinking water safety (NHMRC)

A comprehensive framework has been developed in Australia to outline a Total Quality Management (TQM) approach for drinking water quality and safety (Rizak et al., 2003; Hrudey, 2004; Sinclair and Rizak, 2004). It is a broad approach to the entire scope of providing drinking water and can readily incorporate the excellent details that have been developed by other initiatives and it has now been adopted as the introductory framework for the Australian Drinking Water Guidelines (NHMRC, 2004). Fig. 3 captures the 12 elements that make up the framework, starting with a policy commitment at the highest levels of responsibility in the organization to achieving drinking water quality. Commitment means more than just meeting regulatory requirements by minimal margins, but a fundamental commitment to continuous improvement, serving as a cornerstone for employee responsibility and motivation. From this commitment flows the series of elements related to system analysis and management with which we are perhaps more familiar as risk management tools.

Assessment of a drinking water system includes: water-supply systems analysis, the review of water quality data, hazard identification, and risk assessment. Preventive measures include the emplacement of multiple barriers and the analysis and maintenance of critical control points. Operational procedures and process control include operating protocols, equipment capability, materials and chemicals, operational monitoring and, ultimately, preventive and corrective actions. Verification of drinking water quality includes conventional water quality monitoring, consumer satisfaction, short-term evaluation of results and corrective actions as required. Incident and emergency response include communication planning and response protocols.

The supporting requirements for this Framework are elements often overlooked in the short term, but which are vitally important to long-term performance. Employee issues include awareness, involvement and training, with particular consideration given to the role of contractors. Community issues include consultation and communication to ensure that the drinking water provider is meeting the needs of the consumer. Research and development has also been neglected in some perspectives when addressing assurance of safety. A commitment to research is vital to assure that emerging risks are managed as thoroughly as possible, based on some predictive capability. Applied research studies can include investigations and research monitoring, validation of process performance and design of equipment. Documentation and reporting are necessary to prove that systems have been working as planned.

Finally, to assure everyone concerned that the systems are functioning as they should be, there must be review processes. These include periodic evaluation of long-term performance and an external audit of drinking water quality management performance. All must be subject to review by senior management for evaluation in view of the goal of continual improvement. This framework has been used to restructure the Australian Drinking Water Guidelines into a TQM risk management approach that will provide consumers with the means for judging whether their water provider is functioning as safely and effectively as circumstances reasonably allow. The elements of this approach are flexible enough to allow implementation by each state in Australia, according to its own regulatory regime. The TQM approach is intended to facilitate and support an effective regulatory process

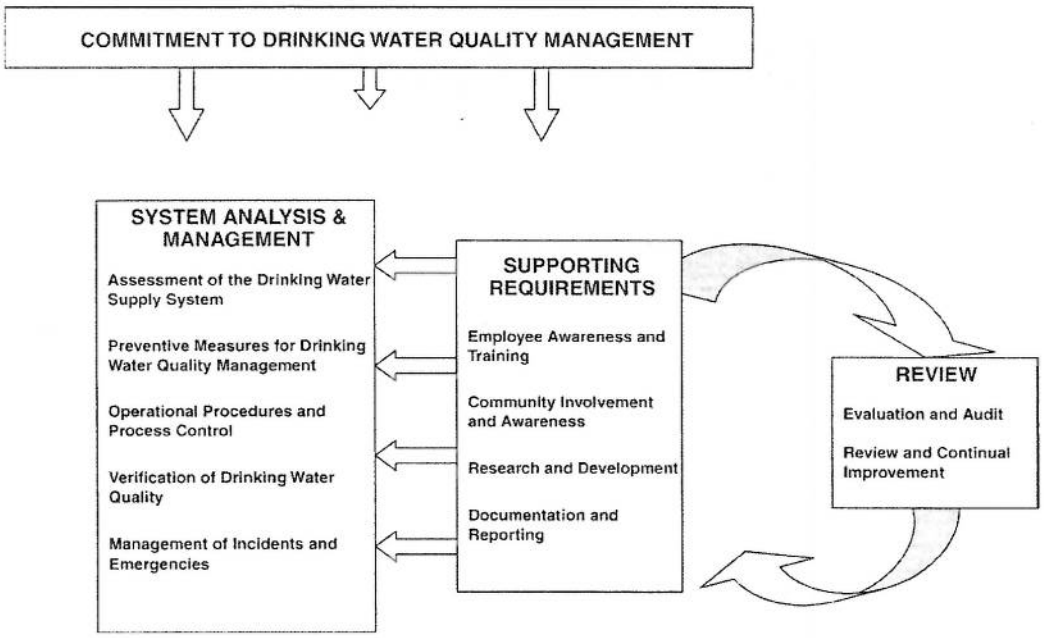


Fig. 3. Framework for Management of Drinking Water Quality (reprinted by permission of the National Health and Medical Research Council, Canberra, Australia).

by helping to define the details of best practice in every jurisdiction and by providing consistent approaches for demonstrating best practice to the regulatory authority. The TQM approach is not intended to replace an effective regulatory process that must be accountable to the public, only to improve the manner in which constructive improvements are achieved.

Now that the framework is being adopted in Australia, more detailed supporting documents are being developed to guide its implementation for individual water utilities. The core capacity of this approach to deliver risk management for the purposes of assuring drinking water safety is found in the second and third elements of the Framework: (2) Assessment of the Drinking Water System and (3) Preventive Measures for Drinking Water Quality Management. These are based on the key concepts of hazard, hazardous event and risk, terms which are too often subject to confusion in applications of risk management. Accordingly, they are defined in the Framework and more recently were adopted within the concept of Water Safety Plans of the Third Edition of World Health Organization Guidelines for Drinking Water Quality (WHO, 2004b):

- A *hazard* is a biological, chemical, physical or radiological agent that has the potential to cause harm.
- A *hazardous event* is an incident or situation that can lead to the presence of a hazard (what can happen and how).
- *Risk* is the likelihood of identified hazards causing harm in exposed populations in a specified time frame, including the magnitude of that harm and the consequences.

These concepts can be illustrated with a pathogen. *Cryptosporidium* is a hazard for any surface water system because it is always potentially present given its occurrence in human sewage and/or livestock wastes. A challenge to a water system by a waste source containing *Cryptosporidium* such as a sewage spill is a hazardous event. The risk associated with *Cryptosporidium* is the likelihood that this pathogen will pass through the treatment system to reach consumers in an infectious state and in numbers sufficient to cause illness.

An important contribution for implementing this element of a risk management approach is a report by Nadebaum et al. (2004) that provides comprehensive guidance on performing the hazard identification and risk assessment of the drinking water supply. The assessment methodology is organized into six steps: (1) understand your system; (2) identify hazards, hazardous events and sources; (3) estimate risk for each identified hazard/event; (4) plan preventive measures for each identified hazard/event; (5) implement and monitor preventive measures; and (6) document a risk management plan. The hazard identification and risk assessment methodology provided by Nadebaum et al. (2004) is supported by individual hazard fact sheets, case studies and summaries of hazards for microbial and chemical contaminants. These are extremely valuable to any water utility committed to implementing a risk management plan because the details of implementation must be based on local experience and the overall approach should be comprehensive, taking full advantage of valuable experience from others. The extent of experience captured in this reference is illustrated by the range of 36 hazard fact sheets and seven case studies that are provided (Table 2).

3.3. Risk management for small treatment system

The New Zealand Ministry of Health (NZMOH) recognized that the vast majority of the country's drinking water systems were small, yet faced important challenges in providing safe drinking water (NZMOH, 2001). The NZMOH also recognized

Table 2
Hazard fact sheets and case studies (Nadebaum et al., 2004)

Catchment and Groundwater Systems	Pipelines and Distribution Systems
Agriculture within catchments	Pipeline repairs and maintenance
Environmental hazards within catchments	Cleaning of mains
Human access to catchments	Pipe materials, private mains and plumbing
Industrial development within catchments	High flow in pipelines
Forestry within catchments	Backflow and cross connections
Waste / wastewater management facilities	Reverse flow in pipelines
Land use within catchments	Stagnant water in pipelines
Roads within catchments	Aqueducts
Urban development within catchments	**Case Studies (from the literature)**
	Backflow in pipelines
Reservoirs and Basins	Inadequate disinfection of source water
Algal blooms within reservoirs	Contamination and disinfection failure
Key hydraulic factors for reservoirs	Distribution system contamination
Contaminated inflows into reservoirs	Contamination and treatment failure
Excessive draw or fill of reservoirs	Groundwater arsenic contamination
	Shallow groundwater contamination
Water Treatment Plants (WTPs)	Reservoir and catchment contamination
WTP reliability	Reservoir contamination and disinfection failure
WTP design capability—toxins	Groundwater contamination not located
WTP design capability—alkalinity	Suspected breaching of mains
WTP design capability—colour	Distribution system contamination
WTP design capability—iron and manganese	Unidentified contamination
WTP design capability—industrial chemicals	Overdose of fluoride
WTP design capability—pathogens	Lead leaching from domestic plumbing
WTP design capability—taste and odour	Sabotage of mains
WTP design capability—turbidity	Cyanobacterial bloom in source water
Disinfection Systems	
Disinfection system—reliability	
Disinfection system—capability	
Service Reservoirs and Tanks	
Floating Cover system contamination	
Timber system contamination	
Internal contamination	
External contamination	

that the traditional approach of relying primarily on water quality monitoring in relation to drinking water quality standards is inherently a reactive approach. Monitoring results are typically available only long after drinking water has left a treatment plant and been consumed. Thus, the NZMOH has developed a pragmatic, down-to-earth program for encouraging Public Health Risk Management Plans (PHRMP). This approach focuses on "*events*," defined as incidents or situations that may lead to hazards being introduced into or not being removed from water (Nokes and Taylor, 2003). In developing this approach, four barriers were identified that, if maintained effectively, will adequately control hazards:

- prevention of contaminants entering the raw water of the supply;
- removal of particles from the water;
- inactivation of microorganisms in the water; and
- maintenance of the quality of the water during distribution.

This approach is meant to ensure that these barriers are present and functional to minimize the chance of failure that would give rise to "*events*." It was adopted on the premise that small water operators could relate better to the tangible concept of an event rather than a hazard, which some operators find to be more hypothetical. Currently, the NZMOH has produced 40 specific, practical guides for various elements of typical water supply and treatment systems, all available at the NZMOH web site (www.moh.govt.nz/water). Their sensible, pragmatic approach for developing a PHRMP is implemented in 11 steps:

1. Produce an overview of the supply and decide which of the PHRMP guides are needed.
2. Identify the barriers to contamination.
3. Use the guides to identify events that may introduce hazards into the water.
4. Use the guides to identify causes, preventive measures, checks and corrective actions.
5. Decide where improvements should be made in the supply to better protect public health.
6. Decide on the order in which improvements need to be made.
7. Draw up a timetable for making the improvements.
8. Identify links to other quality systems.
9. Prepare contingency plans.
10. Prepare instructions for performance assessment of the plans.
11. Decide on communication policy and needs.

The New Zealand system of Public Health Risk Management Plans are an excellent contribution towards greater drinking water safety and deserve wider application.

4. Discussion

A clear message that emerges from the case studies is that the painful experience at locations that have had drinking water outbreaks has not been readily recognized by other vulnerable utilities (Hrudey and Hrudey, 2004). In a few cases, outbreaks recurred in the same community indicating a failure to determine and correct the flaws in the system. In other cases, cogent warnings have been missed, such as the Washington County Fair outbreaks which had a highly relevant warning for Walkerton, but which failed to change the course of events in Walkerton. The New York State Department of Health investigation was made public in March of 2000, less than two months before the Walkerton outbreak happened 600 km to the west.

In another case, Orangeville, a community only one hour away from Walkerton, experienced a spring outbreak caused by agricultural runoff contaminating the town's shallow wells in April 1985. The analysis of this outbreak published in the *Canadian Journal of Public Health* in 1991 noted that chlorination required close monitoring because manure contaminated runoff

could overwhelm a fixed dose of chlorine, which is exactly what happened in Walkerton in May 2000.

There are several key aspects of waterborne pathogens that characterize the challenge they pose to drinking water safety. Some of these are readily evident from the outbreak case studies:

- Fecal (human or animal) contamination can be found wherever humans, their domestic animals or wildlife reside; although exposure is reduced as sanitation and waste management are improved, complete elimination of potential exposure to fecal contamination is not possible.
- Loading of pathogens into a drinking water system sufficient to cause outbreaks of disease will not be consistent, rather it will be intermittent and infrequent when higher levels of sanitation are achieved. As a result, extended periods without apparent problems do not guarantee future safety.
- Pathogens are likely to be heterogeneously distributed in water because of their origin in fecal particles that will not be totally dispersed in receiving waters and because of clumping promoted in treatment processes.
- Some pathogens have high infectivity, which, combined with a likelihood of pathogens clumping into fine particles, makes inconsistent and non-uniform consumer exposure to infective doses a likely mode of infection.
- Some pathogens (e.g. *Cryptosporidium*) are resistant to chemical disinfection, making fine particle removal and alternative disinfection processes, such as UV, critical elements of a multiple-barrier approach.
- Conditions that create a pathogen challenge to the treatment process are often event-driven (e.g. extreme weather, unusual operating conditions), meaning that such events should be recognized as potential triggers of trouble.
- Multiple failures in a system must usually combine for disaster to occur, particularly as more barriers are made effective in seeking higher degrees of safety. This reality also means that one or more barriers can be failing and ineffective without an outbreak occurring. This makes the independent evaluation of treatment performance by measures such as turbidity or chlorine residual monitoring a necessary activity to assure that all of the multiple barriers are effective.

Many of these challenges are intuitive for experienced drinking water professionals, but they are not necessarily established in the corporate memory of a water utility, particularly where substantial staff turnover is a reality. The intuitive experience within a successful organization needs to become accessible to struggling organizations. This implies the need for some form of networking to share experience and good practice.

Responses to these challenges are compounded by a number of basic limitations in relation to the public health significance of available monitoring capabilities:

- Monitoring methods for pathogens and useful indicators are generally neither sufficiently sensitive nor sufficiently specific to capture the full range of pathogen threats facing a water system.
- Monitoring for pathogens and useful indicators cannot be achieved in real time.
- Monitoring methods cannot be directly interpreted for public health significance because the viability and infectivity for most pathogens is usually not determined by routine methods.
- Interpretation of monitoring results will be challenged by a preponderance of false positives because of the low frequency of pathogen hazards (Hrudey and Leiss, 2003).
- Population health surveillance is insensitive and is likely blind to low-level endemic disease and all but the largest outbreaks.
- Adaptation and tolerance (immunity) in resident populations may hide local, chronic problems while leaving visitors vulnerable to infection that may be difficult to trace back to the source, particularly in resort communities.

Despite the challenges and limitations, the best drinking water providers have shown an ability to respond to a wide range of challenges with effective prevention programs. The processes in these organizations may bend under stress, but they do not break, so failures are not allowed to accumulate to the point where they can impact the health of a consumer. An optimal preventive approach will be creative and forward-looking:

- Informed vigilance is actively promoted and rewarded.
- Understanding of the entire system, its challenges and limitations is promoted and actively maintained.
- Effective, real-time treatment process control, based on understanding critical capabilities and limitations of the technology, is the basic operating approach.
- Fail-safe multi-barriers are actively identified and maintained at a level appropriate to the challenges facing the system.
- Close calls are documented and used to train staff about how the system responded under stress and to identify what measures are needed to make such close calls less likely in future.
- Operators, supervisors, lab personnel and management all understand that they are entrusted with protecting the public's health and are committed to honouring that responsibility above all else.
- Operational personnel are afforded the status, training and remuneration commensurate with their responsibilities as guardians of the public's health.
- Response capability and communication are improved, particularly as post 9–11 bioterrorism concerns are being addressed.
- An overall continuous improvement, total quality management (TQM) mentality will pervade the organization.

5. Conclusions

Risk management approaches offer a means to benefit from the experience of past failures. A rigorous and comprehensive approach such as reflected in the 2004 Australian Drinking

Water Guidelines makes it possible for water utilities to improve their operations to the level of the best water utilities, making it extremely unlikely that consumers ever need face a drinking water outbreak. Safe drinking water is a remarkable bargain for consumers and should be valued much more highly than commonly occurs in our affluent societies.

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Risk Analysis Strategies in the Water Utility Sector: An Inventory of Applications for Better and More Credible Decision Making

B. H. MacGILLIVRAY, P. D. HAMILTON, J. E. STRUTT, and S. J. T. POLLARD
School of Water Sciences, Cranfield University, Cranfield, Bedfordshire, United Kingdom

Financial pressures, regulatory reform, and sectoral restructuring are requiring water utilities to move from technically inclined, risk-averse management approaches toward more commercial, business-oriented practices. Risk analysis strategies and techniques traditionally applied to public health protection are now seeing broader application for asset management, assessing competition risks, and potential threats to the security of supplies. Water utility managers have to consider these risks alongside one another, employ a range of techniques, and devise business plans that prioritize resources on the basis of risk. We present a comprehensive review of risk analysis and management strategies for application in the water utility sector at the strategic, program, and operational levels of decision making.

KEY WORDS: decision making, risk analysis, utilities, water safety plans

I. INTRODUCTION

A. Background

Providing wholesome, affordable, and safe drinking water that has the trust of customers is the overarching goal of the water utility sector. The sector

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Address correspondence to S. J. T. Pollard, School of Water Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 OAL, United Kingdom. E-mail: s.pollard@cranfield.ac

has publicly stated[8] that achieving this requires, at a minimum, that water is safe in microbiological and chemical terms; that it is acceptable to consumers in terms of taste, odor, and appearance; and that the supply is reliable in terms of quality and quantity. Delivering these objectives in the context of an increasingly demanding consumer and regulatory environment, under constraints imposed by aging infrastructure and the trend toward financial self-sufficiency, is challenging. Many within the industry, spurred on by developments in international regulation and guidance, are now promoting a business-wide approach to risk management as a means to ease and exploit this transition (e.g., Lifton and Smeaton[82]). In practice, water quality managers and internal audit functions within the sector are working more closely to address issues of business risk, and many of the larger international water companies now have "group risk managers" in place to manage business and consumer risks within a single portfolio. Implementation of this business-wide approach to risk management is not straightforward, however, it requires:[121]

1) Integrated frameworks for the management of internal risks (e.g., from aging infrastructure) and external risks (e.g., from "competitor" actions) to the utility.
2) The support of board level, executive management, and operational staff, as well as that of external stakeholders.
3) The effective communication of risk and engagement within decision-making processes both within companies and with external stakeholders.

Furthermore, as illustrated in this review, there are potential tensions between managing the risks of a commercial water business and the overarching public health goal of the water industry, stated earlier. Critically in this regard, the transition to an explicit risk management philosophy within the water utility sector is now reflected in recent revisions to the World Health Organization (WHO) *Guidelines for Drinking Water Quality*.[45,167,168] This is placing an emphasis on the development and implementation of "water safety plans" for water quality management and, within these, the application of risk frameworks and risk tools such as the hazard analysis and critical control points (HACCP)[34,64] approach as a basis for prioritizing risk management measures within the water supply chain from catchment to tap. The risk management approach is becoming increasingly embedded within utilities and with it a maturing view of risk analysis, shifting from that of a one-off technique to "placate" regulators toward that of a practical methodology to facilitate process control, optimization, and corporate decision making within a cost-effective framework. Despite a growing consensus, there remain significant barriers to the implementation of risk management within utilities. These can be categorized as business-related, the challenge of integrating risk

management within organizational cultures and decision-making processes (e.g., Pollard et al.[121]); and technical, relating to the selection and application of risk analysis tools. One of the key difficulties all organizations face in implementing risk management is managing the interfaces between high-level corporate objectives, business plans, and operational reality. Here, then, we critically review the risk analysis strategies and tools and techniques available for risk analysis within the sector, with particular emphasis on decision making at the corporate (strategic), business (program level), and operational levels in water utilities. Necessarily, the discussion requires excursions into the management and technical environmental literature. However, we view the juxtaposition of these aspects of risk management as central to providing a well-rounded examination of the prior art in the current context of its application within the sector.

B. Risk Analysis and Decision Making

Before entering a discussion on risk analysis, we must be clear in our terminology. In simple terms, risk is widely accepted to consist of a combination of probabilities and consequences. However, further clarity is required. Adapting Hrudey's[68] elaboration, we consider the notion of risk to be a prediction or expectation that involves:

- An agent with the potential to cause either harm and/or benefit (e.g., a chemical contaminant, or an investment opportunity).
- Uncertainty of occurrence and outcomes (expressed by the probability or likelihood of occurrence).
- Consequences (the possible outcomes).
- A specified time frame.

The exploration of these facets provides us with an analysis of risk (note that the authors consider the terms *risk assessment* and *risk analysis* to be interchangeable). Risk is inextricably linked to uncertainty. Thus, uncertainty analysis plays a prominent role in many risk analysis strategies. Finally, and in a distinct business context, we consider risk management as the sum of the constituent sets of sociotechnical decisions and actions taken by staff members to optimize their organization's exposure to risk.

Risk analysis plays a role alongside other decision tools for risk management.[121] Detailed risk analysis is not a prerequisite for effective risk management. In many industries there are accepted standards of performance and codes of practice (e.g., engineering standards; accepted best practice; Figure 1) that, if adhered to, provide high degrees of control. These are applied in familiar and well-characterized situations where uncertainties and system vulnerabilities are well understood. However, complex, uncertain,

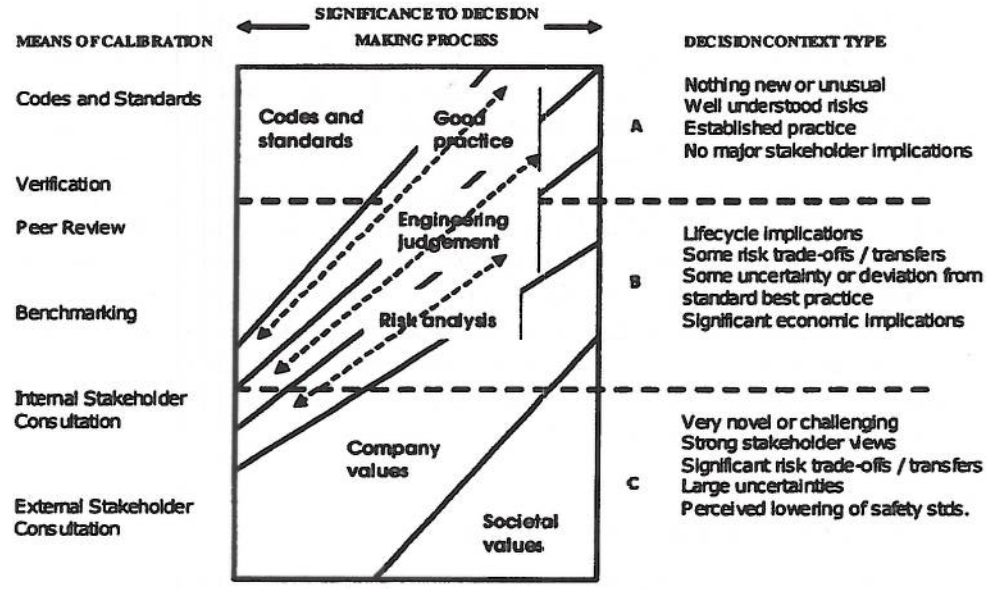


FIGURE 1. Decision framework for the offshore oil industry (UK Oil Operators Association,[159] with permission).

and novel systems that deviate from routine operation may require risk analysis so as to better understand what drives the risk from or to the plant, process, or operation, thereby allowing management measures for the reduction of unacceptable risks to be targeted for greatest effect.[121] This principle extends beyond the operation of technical systems to embrace all aspects of managing a business. This said, risk analysis is, in many respects, a practitioner-driven discipline. Its application within water utilities has its roots firmly in the protection of public health from pathogens afforded by the multiple barrier approach to raw water treatment. While the extension of risk analysis to asset management, water supply security, and catchment (watershed) management is clearly evident, these applications and the use of risk-based techniques for optimizing treatment plant performance, on-site energy use, maintenance programs, and compliance monitoring regimes can inadvertently but easily detract from and confuse the principal purpose of the water supply industry—to provide wholesome, affordable, and safe drinking water that has the trust of customers. In all these applications this goal must remain paramount.

C. The Risk Hierarchy

The organizational hierarchy that exists even within "flat" organizations requires that risks are actively managed at the strategic, program, and operational levels (Figure 2). Typically, there are split accountabilities for these

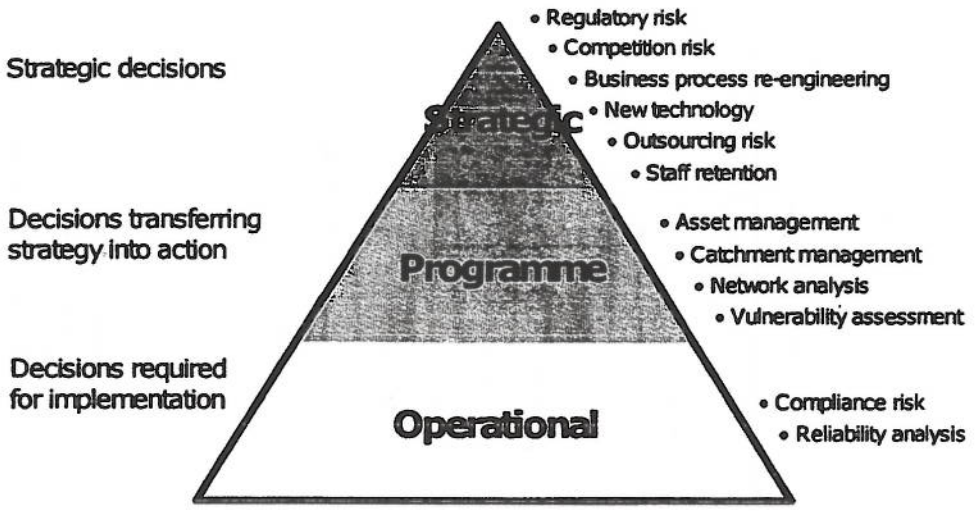


FIGURE 2. The risk hierarchy (adapted from Prime Minister's Strategy Unit[124]).

risks such that the chief financial officer/financial director and board have overall responsibility, supported by an internal audit or control function for the management of strategic risks; executive and senior management address program level risks (e.g., asset management, maintenance planning); and operational (e.g., site) managers bear responsibility for operational risks (e.g., treatment plant performance).[121] A range of strategies exists for assessing and managing these risks in a business context. The focus in this review is sector specific, addressing "process" risk analysis (i.e., risks at the operational and program level), but in establishing a business-wide context for this activity we also draw on the experiences of organizations assessing risk at the strategic level.

II. STRATEGIC RISK ANALYSIS

Within an overarching context of public health protection and the maintenance of process reliability, utility managers are increasingly concerned with managing the risks inherent to corporate-level decision making. Critical issues include decisions on outsourcing asset maintenance, billing and monitoring, the management of change, staff retention, the long-term viability of investment decisions, and the management of external interfaces with regulators and "competing" utilities. Risk analysis tools are available to inform decisions on these issues (Table 1).

A. Regulatory Risk

Throughout the 20th century, the central role of water quality in the protection and preservation of public health encouraged governments to manage

TABLE 1. Strategic Level Risk Portfolio

Context	Tool/Technique	Application	Reference
Regulatory risk	*Ex-post* modelling	Interpreting/evaluating the relationship between stock risk and regulatory events	Buckland and Fraser,[19] Morana and Sawkins.[98]
	Ex-ante modelling	Modelling evolution of regulatory environment	Larssen and Bunn,[78] Bunn *et al.*[20]
Competition risks			
1) Comparative	Competitor analysis	Reducing price review uncertainty (and conventional benefits)	Drohan and O'Connor,[38] Rothschild.[133]
2) Capital market	Screening	Tracking take-over risk	
	Investment analysis	Evaluating take-over opportunity	Thomas.[157]
3) For the market	Investment analysis	Evaluating joint venture	Ranasinghe,[128] Grimsey and Lewis.[55]
4) Product market	Competitor identification/ analysis	Minimising competitive threats	Rothschild,[133] Drohan and O' Connor.[38]
	Investment analysis	Evaluating *de facto* take-over	
BPR risks	Scenario planning	Exploring potential BPR outcomes	Clemons.[23]
	Quantitative 'risk of failure'	Evaluating success likelihood of BPR efforts	Crowe *et al.*[28]
	Risk matrix	Appraising and comparing risks of BPR strategies	Remeyi and Heafield.[130]
1) New technology	Risk matrix	Appraising and comparing risks of new technology projects	McGaughey *et al.*[92]
	Risk algorithm	Characterising risk of new technology 'problems'	Hartmann and Lakatos.[62]
	Checklist	Minimising risk of new technology introduction	Hartmann and Lakatos.[62]
	Profile	Guiding strategic technology planning	Wildemann.[170]
Outsourcing	Outsourcing decision models	Evaluating core competencies and appraising market opportunities for outsourcing candidates	Quélin and Duhamel,[125] Lonsdale.[86]
	Scenario planning	Exploring 'what-if' scenarios	Zsidisin *et al.*[176]
Employee retention	OCP	Evaluating 'cultural fit' of prospective employees	Sheridan,[141] O'Reilly *et al.*[109]
	Early warning system	Identification of 'at-risk' employee groups	McNally.[94]
	Gap analysis	To assess employee development and benefit schemes	
	Checklist	Informal assessment of retention risk	Anon.[4]
Investment analysis			
1) Assets-in-place	NPV/IRR	Valuation of an ongoing business or some part of one	Barriex *et al.*,[10] Mosca *et al.*,[99] ADB,[6] Burchett and Tummala,[21] Luehrman,[87] Thomas.[157]
	Strategic portfolio planning	Creating a balanced utility investment portfolio	Rothstein and Kiyosaki.[134]
2) Opportunities	Option pricing theory	Valuation of possible future operations	Luehrman,[87] Black and Scholes.[14]
3) Joint Ventures	NPV/IRR	Valuation of prospective partnerships, strategic alliances	Grimsey and Lewis,[55] Ranasinghe,[128] Luehrman.[87]

utilities within the public sector.[138] Regulation was historically self-imposed and limited in scope, and, by extension, posed relatively low risk to municipalities and utilities (in terms of both the likelihood of noncompliance and the associated penalties). In contrast, more recent (since the 1980s) regulatory pressures and drives to impose market discipline on the sector, whether directly (privatization) or by proxy (e.g., corporitization or required self-sufficiency), have externalized and broadened the role of regulatory scrutiny and intervention. Here our discussion is largely restricted to economic regulation.

A concept of regulatory risk is difficult to grasp. Parker[114,115] contends that it arises from the nature of the regulatory rules and practices, with rules determining the extent to which interventions are discretionary, and practices relating to the interpretation the regulators and others (particularly government) place on the rules. Kilpatrick and Lapsey[75] consider regulatory risk as the uncertain impact of regulatory decisions on regulated companies. Regulatory risk may best be considered as a combination of these interpretations, encompassing both the uncertainty of the decision-making process and of its impact on utilities.

The core issues of regulatory risk are regulatory independence, regulatory discretion, and transparency and accountability. Independence is critical to minimizing the risk of political interference in a regulatory regime. For example, in England and Wales, the economic regulator (the Office of Water Services; Ofwat), acting in the public interest, is vested with a high degree of autonomy from central government, ensuring that the regulatory process is not subject to direct political interference. In contrast, in South Australia (SA), the state government directly controls the tariff setting process, and as the dividend from SA Water is a significant contributor to the state budget, there is the danger that political considerations, as well as commercial ones, might be perceived to influence regulatory pricing.[7]

Regulatory discretion refers to the freedom afforded to regulators to interpret the importance of set duties and objectives and to determine how best to accomplish them.[75,114] In the United Kingdom, Ofwat's director general is free to identify and change the importance attached to set objectives within the regulatory system, within broadly defined constraints.[114] Arguably, the greater the discretion afforded to the regulator, the greater is the uncertainty related to future regulatory decisions. Ofwat's regulatory practices are characterized by high levels of transparency and accountability. In practice, utilities are fully engaged in regulatory decision making, with avenues for consultation and appeal established should companies wish to challenge the outcome. Similarly, the New Jersey Board of Public Utilities, which regulates all investor-owned utilities in the state, publishes reports on its activities and is transparent and accountable in its decisions and processes.[7] These arrangements compare to the German system. Water and sewerage in Germany are the responsibility of the municipalities, and the municipalities regulate and

manage the water supply based on European, national, state, and municipal legislation. Though many are satisfied with these relationships, there has been criticism in a recent report,[7] where regulatory decisions were viewed as being taken in a closed fashion with little clear accountability.

The nature of a regulatory system (i.e., its objectives and the systems in place for their achievement) represents a core strategic risk for water utilities. For example, in many developing countries, regulatory scrutiny is largely confined to ensuring a safe, secure water supply,[7] which, while introducing inherent operational risks, does not invoke strategic uncertainty. In contrast, the main goal of Ofwat is to facilitate competition within the sector, an objective that introduces utilities to a range of hitherto unknown risks.

Quantitative treatments of regulatory risk within the literature are restricted to ex post analyses of the relationship between utility share price volatility and the regulatory process. Buckland and Fraser[19] modeled variations in the systemic (market) risk, using a variable β (which measures the variability in returns of a stock relative to the variability of the broader market), of UK water utilities over time, examining the extent to which observed variations were associated with the regulatory process. A key finding was the surge in the market's assessment of the systemic risk to the industry accompanying the "surprise" result of the 1992 general election. The authors' analysis illustrates the influence of politics in even the most independent of regulatory systems. Similarly, Morana and Sawkins[98] modeled the London stock market's response to the 1994 "periodic review" of water price setting in the England and Wales utility sector, finding a significant reduction in share price volatility, which they postulated to be a reflection of shareholder confidence in the credibility and sustainability of the settlement.

Ideally, for the active management of regulatory risk, analyses should extend to ex ante treatments of risk. This is of particular relevance to the modern water utility sector, where widespread structural reforms are requiring utilities to operate under rapidly evolving regulatory systems—creating unprecedented uncertainty. In such a market, there has been no historical evolution and the participants, including the regulatory institutions, have a limited understanding of how it will operate in the short term and evolve in the future.[78] In such situations, analytical models may offer value in alerting utilities to unintended consequences of their actions that may trigger the regulator into reaction.[78] Larsen and Bunn[78] argue that system dynamics, which incorporates systems thinking into simulation modeling, is conducive to the dynamic, uncertain, and subjective nature of assumptions inherent to strategic analysis. To illustrate, Bunn et al.[20] developed a system dynamics model to simulate regulatory problems in the restructured UK gas and electricity markets. Following problem definition and hypothesis formulation, the authors constructed a simulation model describing the main feedbacks involved in the exercise of "latent" market power. Their analysis explored the relationship between corporate strategies designed to exercise this power and the

risk of regulatory scrutiny. The authors concluded that market mechanisms were open to exploitation. Such analysis, and assessments of system sensitivity, could provide utility managers with a priori insights into opportunities for exploiting market "imperfections," thus aiding the development of corporate strategies.

B. Competition Risks

1. COMPARATIVE COMPETITION

On account of the water industry's inherent monopolistic nature, many governments and their regulators have sought to expand the role of sectoral competition—none more prominently perhaps than in the United Kingdom, where the concept of comparative competition underpins the regulatory regime.[135,137] The theory of comparative or "yardstick" competition may be traced to the work of Shleifer,[143] who proposed a regime in which the price (or financial rewards) received by a regulated firm depends not on its costs (as in traditional "cost-of-service" or "rate-of-return" regulation), but rather on the costs of "identical" firms operating within the same sector. Shleifer reasoned that by breaking the dependence between the price a firm received and its own costs, and ensuring that the rewards for a given firm depended on its standing vis-à-vis a "shadow firm" (a weighted average of other firms operating within the sector—an idealized benchmark), each firm would be forced to "compete" with its shadow, providing incentives for cost efficiency (widely perceived as lacking in rate-of-return regulation). In practice, the inherent risks of this "competition by proxy" pale in comparison to those found in fully liberalized markets because market share is not directly threatened.

Techniques for evaluating the "explicit" risks posed by competitors have been well developed in the business and economic literature. A notable example is competitor analysis, with its potential to reduce the uncertainty of the price review process (as price setting is linked to competitor performance). Its application is helped by the tendency for regulatory bodies to disclose company performance data in the interests of transparency. In addition to reducing uncertainty, competitor analysis represents a strategic tool that assists managers in evaluating competitors' strengths and weaknesses; identifying sources of competitive advantage; and assessing the implications of competitors' strategies on both the sector and their own utility.[38,133]

2. CAPITAL MARKET COMPETITION

As Cowan[27] contends, competition in the capital market can be thought of as a private-sector version of yardstick regulation, in that it derives from the ability of investors to make comparisons between different companies in the same sector. Littlechild,[85] in his report to the UK Department of the Environment on the prospects for water privatization, emphasized that this

would be an important incentive mechanism for utilities, as inefficient firms would have this reflected in their share price and be vulnerable to takeover, in addition to facing higher costs of capital. Although Ofwat's restrictions on mergers within the UK water sector, in the interests of maintaining sufficient comparators, act as a constraint on capital market competition,[27] the growing internationalization of the industry increases the risk of "external" mergers, while firms looking to diversify remain a threat to existing utilities.

Furthermore, the quality and quantity of comparative information available under the "yardstick" system assist predators in identifying and assessing potential takeover targets.[136] Singh and Harianto,[145] in reviewing the acquisition literature, surmised that profitability, size, leverage, and dividends were negatively correlated with the risk of being acquired. In contrast, profitability and liquidity were positively correlated with the probability of a firm acquiring, with leverage and dividends negatively so. In light of this information, the dynamic risk of takeover can be tracked both in real time (e.g., with respect to the transfer of, for example, more than 5% of firm stocks to a potential acquirer and, in the United States, the filing of 13D statements indicating investor intent) and proactively (by "screening" the external environment for trends and potential hostile bodies). Of further interest to corporate strategists, recent research by Dickerson et al.[35] suggests that acquisition can be used as a strategy to reduce the risk of takeover. The researchers concluded this strategy allows firms to grow quickly, thus protecting them from subsequent takeover. For utilities considering expansion or diversification strategies, takeover represents not just a threat but also an opportunity.

3. COMPETITION FOR THE MARKET

Another means of fostering competition is to encourage the private sector (perhaps along with the incumbent public utility) to bid competitively for a concession, lease, tender, or management contract.[27] The two key vehicles for doing so are franchising and, more conservatively, contracting out (not involving the transfer of assets). Numerous variants of these processes are adopted internationally, including build, operate, and transfer (BOT) arrangements; finance, operate, and own (concession); and operate and provide working capital (*affermage*). The inherent complexity of many of these arrangements, the generally low equity in the project vehicle,[55] and the often significant investment obligations required of the sponsor create a pressing need for comprehensive risk assessment.

The project and financial risks associated with public–private partnerships have been reviewed by Grimsey and Lewis.[55] Using the financing of Stirling Water, a Scottish design–build–operate contractor, as an illustrative example, they discuss the complexity of the contractual arrangements within such partnerships and use a quantitative analysis of returns on investment to characterize the robustness of cash flows from each of the senior lenders

to this joint public–private venture. From the procurer's perspective, project risks (e.g., delays and claims) are valued and incorporated within the net present value (NPV) calculation, while the impact of financial risks (inflation and interest rate changes) is evaluated through sensitivity analysis. From the sponsor's perspective, risk analysis centers on simulating the effect of the underlying variables (e.g., operating performance) upon the equity return. Ranasinghe[128] uses water supply projects in Sri Lanka to outline a methodology based on financial risk analysis that a government or public utility can use to assess the viability of private sector participation in new infrastructure projects. The author links a commercially available simulation package to the financial model to analyze the uncertainty associated with the underlying variables (e.g., escalation in cost).

4. PRODUCT MARKET COMPETITION

The traditional approach to introducing direct product market competition into utility services has been to separate the monopolistic component of the industry and regulate it, and to encourage competition in all other areas, for example, the UK model of separating the gas, electricity, and railway networks (monopolistic) from the supply of services over the network.[27] This so-called "vertical disaggregation," although promoted by the World Bank,[172] has not been widely adopted in the water sector, with the implicit assumption being that the industry is naturally monopolistic.[27,138] The United Kingdom has led the way in adopting alternative approaches to facilitate product market competition. This can be traced back to the 1991 Water Industry Act, which introduced the concept of "Inset" appointments, whereby a utility can apply for an appointment to provide water to a "large" customer located within the statutory area of an existing company, usually by seeking a bulk supply from the incumbent.[65] Sawkins[136] reports that the first Inset appointment was granted in May 1997, when Anglian replaced Essex and Suffolk Water (ESW) as the supplier to Buxted Chickens Ltd. Company licences were altered and a new pipe was constructed linking the site with an Anglian water main.

In practice, various restrictions, recently eased, have meant that this form of competition has been slow to develop.[136] Similarly, although the 1992 Competition and Service Act allows for cross-border competition, the costs are prohibitive in the majority of cases. Perhaps the most significant recent development has been the introduction of the 1998 Competition Act, which created the possibility for common carriage agreements, or network sharing, in the water industry. Here, the shared use of an incumbent's infrastructure by a third party enables the latter to provide services within the incumbent's area. To aid this, Ofwat now requires that all water utilities publish "Access Codes" that set out their terms and conditions for common carriage, and has published guidance on this procedure.[110] Hern[65] reports that under the act,

utilities risk infringement if they refuse access to any parts of their infrastructure deemed "essential" without objective justification, or if their access terms are considered unreasonable. Although no successful applications for common carriage have resulted to date, the threat alone acts as a catalyst for performance improvements.

The authors were unable to uncover literature quantitatively addressing the risks of product market competition within the water utility sector, a reflection of its nascent development and descriptive nature. It seems appropriate here, however, to introduce an oft-neglected truism: Quantitative risk analysis is not a prerequisite of effective risk management. This is apt in addressing the threats introduced by product-market competition, where competitor identification and analysis, in concert with a critical appraisal of self-performance and room for improvement, often provide an appropriate foundation for minimizing competitive threats. In contrast, harnessing the opportunities presented by product-market competition requires more detailed analysis, and in the absence of a relevant body of literature, the authors suggest treating what are effectively, at least in the UK model, potential acquisitions of company operations in the manner of strategic investment decisions.

C. Business Process Reengineering Risks

Our discussion thus far has focused on the strategic approaches to risk management within the sector. The pressures described are having important impacts on the performance of the water sector. Structural changes to utility markets, an increasingly demanding political and consumer environment, and more stringent regulation are requiring utilities to improve financial and operational efficiencies. As Westerhoff[166] notes, water utilities are responding by rethinking their operations, finding new ways to address problems, and revamping traditional business models—in other words, reengineering. According to Clemons,[23] major business process reengineering (BPR) initiatives—which range from the redesign of existing processes for efficiency improvements, to the development of novel processes in support of a new corporate vision—require the commitment of substantial resources and often constitute a lasting legacy. If we define the risk of a project as the deviation in results from the established goals, then there is substantial empirical evidence marking BPR as a high risk-endeavor. Many, if not most, reengineering efforts ultimately "fail" (see Crowe et al.[28] and Remenyi and Heafield[130]). Of particular relevance is the work of Dean et al.,[31] whose analysis of change programs undertaken in the UK water industry suggests that reengineering efforts, while often effective, produce highly variable outcomes. On account of this, project risk analysis should be an integral part of any reengineering effort.

Clemons[23] considers the core determinants of the risk profiles associated with large-scale BPR efforts to be (a) functionality risk—the risk of making inadequate or incorrect changes to systems or processes—and (b) political risk—the risk that the organization will not complete the project, either because of significant internal resistance to the proposed changes or due to a more gradual loss of will. Clemons promotes scenario planning—a strategic planning tool that embraces uncertainty—as a means for assessing and subsequently managing the risks associated with reengineering efforts. Rather than determining a single "correct" view of the future with its implicit single response, scenario planning acknowledges the key sources of uncertainty and incorporates these in developing a range of future scenarios and strategic responses for exploration. Clemons argues that its use is suited to the context of reengineering efforts, as it encourages the critical examination of potential futures and strategies, reduces functionality risk, and helps ensure the need for change is internally addressed and accepted, thus reducing political risk. Scenario planning has been embraced by the majority of UK water utilities.[120] A 2001 study[120] explicitly linked the tool's use with improved financial performance on the part of utilities, although notably the authors suggest that scenario planning may implicitly encourage firms to focus on financial returns at the expense of customer service levels.

Recent work by Crowe et al.[28] has led to the development of a semi-quantitative tool for estimating the "risk of failure" of companies about to undertake reengineering efforts. The tool, developed through a survey of BRP-experienced organizations, is based on measures of the core success (e.g., egalitarian leadership; collaborative working environment; top management commitment; and change management systems) and failure (middle management fear of losing authority; fear of job loss; skepticism; discomfort of new working environment) factors of implementing change. Raw data is extracted by questionnaire (e.g. "do managers usually share vision and information with their subordinates" is used to mine information on the general leadership style) and refined via fuzzy mathematics. The Crowe et al. model is intended to provide companies with an estimate of the likelihood of success or failure of proposed efforts prior to committing resources and to improve management's a priori insights into the potential outcomes of re-engineering. Similarly, Remenyi and Heafield[130] outline a methodology for evaluating the key risk issues relating to reengineering efforts. The methodology centers on a risk matrix (Table 2) that groups a variety of potential BPR risks under the categories of business risk, financial risk, corporate structure, corporate culture, technology, and human. Organizations identify, weight, and rank what they consider to be the 10 factors most pertinent to their proposed reengineering efforts. The framework represents a succinct method for appraising and comparing the risks associated with BPR strategies. A perceived failure of much of the BPR literature is the limited emphasis placed on the

TABLE 2. BPR Risk Matrix (after Remenyi and Heafield[130])

Indicate the 10 most relevant factors	
Factors	
Business risks	Corporate culture
Change to business scope (e.g., from diversifying)	Staff attitude to technology
Change to market structures	Staff attitude to changes
Change of regulatory relationship	Staff attitude to senior managers
Change of supplier relationship	Managerial style
Impact on (potential) "competitors"	Positive shared vision
Financial risks	Technology
Funded from current cash flow	Size of project
Funded from new equity	Structuredness of project
Funded from long-term debt	Complexity of technology
Funded from short-term debt	Complexity of application
Corporate structure	Novelty of technology
Bureaucratic structure	Novelty of application
Outsourcing utilization	Impact on technical infrastructure
Flexibility of job positions	Human
	Skills base

risks introduced by adopting new technologies, an aspect critical to many reengineering efforts.

1. TECHNOLOGICAL RISK

Clark et al.[22] report that technology adoption is increasingly becoming a concern of strategic planners and policymakers within the water industry. The introduction of novel technology poses risks due to the inherent difficulty of preparing accurate estimates of the costs, performance, and system-wide effects of new components and processes; and the long development cycles required for changes in regulations and consumer demands.[26] This has led many researchers to advocate the incorporation of risk management techniques for the effective implementation of new technologies (e.g., Colmer et al.[26] and Fitzpatrick[47]). This is highly relevant to the water sector, where, as Maxwell[91] notes, the advance of modern technology is illustrated by such trends as the replacement of traditional methods of water treatment with advanced oxidation and other novel physical and mechanical technologies; the broad use of membrane systems to desalinise seawater for human consumption; and the increasingly widespread use of recycling systems and technologies.

McGaughey et al.[92] describe a framework for viewing and comparing the risks inherent in the adoption of new technologies, specifically relating to information technology (IT). Initially, proposed projects are assessed, through value chain analysis, in terms of their potential positive and negative outcomes. These are then mapped onto a "speculative" risk matrix to provide management with an initial screening of alternatives. In later stages of planning, specific threats and opportunities associated with the project are

identified and ranked, by likelihood and consequence, for prioritization purposes. Hartmann and Lakatos[62] drew on case studies monitoring the pace and quality of technology delivery within two product development programs and generated an algorithm characterizing the risk of each technology problem (Figure 3). The authors suggest that its use can aid in the refinement

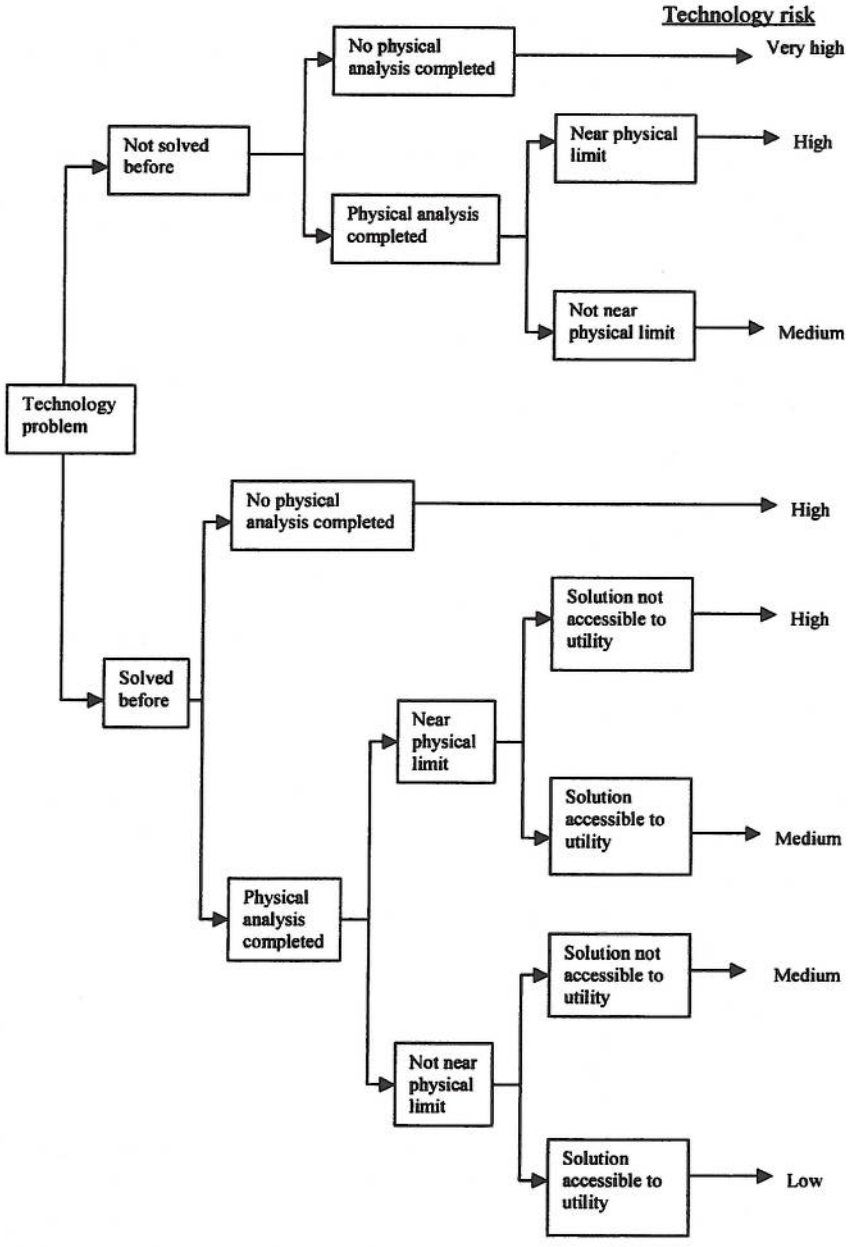


FIGURE 3. Technology risk algorithm (Hartmann and Lakatos[62]).

of technology development and implementation plans following risk identification. Hartmann and Lakatos define technology problems as those arising:

- From the application of a new process, material, or subsystem before fully understanding parameters that control cost, latitudes, and failure modes.
- When a previously commercialized technology is extended outside the known domains of the pertinent design rules.
- From unexpected interactions arising from a new or unique combination of known subsystems of components.

Of further interest, the authors[62] developed a checklist to help technology and product developers audit technology progress, which we have adapted to serve as a tool for minimizing the risk associated with introducing new technologies (i.e., beyond the development stage):

- Implementation goals confirmed:
  - Validate business assumptions and technology specifications for cost, performance, and reliability.
- Technology mastery demonstrated:
  - Critical parameters identified.
  - Failure modes identified.
  - Set risk tolerances relating to the critical parameters so as to avoid failure modes and deliver the required performance.
  - Performance demonstrated using a combination of hardware and mathematical simulation.
  - Manufacturing feasibility established.
- System specifications reestablished:
  - System and subsystem financial and operational performance targets are reestablished and reassessed based on technology specifications.
- Additional assessments completed:
  - Supporting assessments completed, such as safety and environmental impact study.
- Contingency planning
  - Develop contingency plans should critical risks materialize in spite of control procedures in place.

Wildemann[170] describes a framework for guiding technology planning. Risk profiles are constructed displaying the relative importance of identified threats and opportunities, and thus the inherent "attractiveness" of the technology, complemented by a strengths–weaknesses analysis that estimates the ability of the firm to successfully implement the technology. The author's aim

was to provide an analytical basis on which strategies may be developed for the introduction of new technologies.

D. Outsourcing Risks

Our discussion of risk analysis strategies moves to one of the key features of the international water business: outsourcing. A significant feature of water utility management in recent years has been the growth in outsourcing, defined as the transfer of previously in-house activities to a third party. Outsourcing allows utilities to focus on critical functions (core business), access economies of scale, minimize investment, increase quality of service, transfer risk, and reduce administrative burdens, including regulatory compliance.[36,42,116] Common candidates for outsourcing include information technology, maintenance, distribution, manufacturing, and customer care and billing.[116] A widely held view is that the potential for outsourcing is far from exhausted. A holistic approach to risk being promoted in this review requires that in addition to the traditional review of legal and regulatory responsibilities following contractual agreement, the process of outsourcing should fall within the remit of corporate risk management. That is, outsourcing alters the boundaries of the firm, and the scope of risk analysis and risk management programmes should be extended to reflect this.

Risks are inherent in the process of outsourcing, from the decision to outsource, to the management of agreed contracts. Received wisdom has been that companies should focus on "core competencies" and outsource the remaining parts of the business (although the validity of this distinction has been questioned of late, notably by Heikkilä and Cordon[63]). The core risks discussed in the literature relating to decisions over what to outsource and who to outsource to include the loss of key capabilities, developing dependence on the vendor, and risks linked to the service provider's deficient capabilities. Each decision to outsource must be carefully assessed from a risks and benefits perspective.[36] Decision-making frameworks are available for this purpose. Lonsdale's[86] decision tree for outsourcing provides a framework for evaluating what constitutes an organization's core competencies, and analyzing market opportunities for outsourcing the remaining parts of the business. The framework seeks to ensure managers retain those resources responsible for competitive advantage, avoid monopolistic or oligopolistic supply markets, and effectively manage the risk of postcontractual dependency. A similar model, although focused at the policy level, is provided by Quélin and Duhamel.[125] Of course, successful outsourcing further depends on managing supply risks, defined as the transpiration of failures with inbound goods and services.[176] Core categories of supply risk discussed in the literature include the financial stability of the supplier, cost fluctuations; capacity constraints of the market and specific suppliers; variations in quality; the ability of the supplier to adapt to required changes in design or technology; and natural

disasters. Two diametrically opposed approaches to managing supply risk are the active management of risk interfaces with the intention of reducing vendor failures,[176] and the construction of barriers (e.g., safety stock, multiple sources) to buffer the effects of inherent uncertainties.[46,104] Tools in support of the former approach include qualitative assessments of the financial stability of potential suppliers; formal models for the demonstration of supplier capacity performance; "what-if" scenario planning; and statistical process control to detect deviations from desired quality.[176]

E. Employee Retention

Retaining valued employees has long been an implicit component of good utility management. The recent emphasis on people as *the* resource, along with the external realities of an increasingly dynamic and pressurized labor market, have led to the sector embracing employee retention as a critical risk issue—particularly in the technically specialized areas of the water business. This focus is exemplified in recent sectoral research initiatives (e.g., American Water Works Association Research Foundation [AwwaRF] project 2850 "Succession planning for a vital workforce in the information age"), and a recent (2001) policy statement from AWWA calling on utilities to establish formal employee retention plans.

Maintaining employee retention, thus managing the risk of losing organization capacity, begins at the recruitment state (e.g., Barney,[9] McNally,[94] Denton[33]). Empirical evidence suggests that ensuring a "cultural match" between employees and the organization plays a critical role in reducing staff turnover.[141] The tool applied by Sheridan[141] to "measure" culture (beliefs and values) was the Organisational Culture Profile (OCP) instrument developed by O'Reilly et al.[109] The OCP assesses candidates by encouraging them to sort value statements on norms regarding the completion of work tasks, norms regarding interpersonal relationships and norms regarding individual actions. Utilising the OCP as a part of the recruitment process could provide utilities with a proactive tool for minimizing staff turnover, by filtering those most likely to leave the organization early from the selection process. Additionally, it enables the risk-based targeting of retention efforts, for example, by focusing efforts on employees hired regardless of "cultural misfit".

This philosophy is mirrored in the work of McNally,[94] who promotes the use of more traditional tools such as personality assessments at the recruitment stage to ensure "good fits" of personality and work ethic. As Denton[33] notes, while "good recruitment is certainly important, it is what happens to recruits after joining an organisation that determines whether a company will retain them." In relation to this, McNally[94] encourages organizations to develop "early warning systems" to identify employees at risk of leaving. Such a system requires the collection and analysis of retention data by subgroup

(e.g., ethnicity, gender, function, organizational level, etc.) to facilitate identification of "at-risk" groups. Following identification, tools such as employee surveys, employee reviews, mentor or manager feedback, local economic trends, headhunter activity, and, crucially, the exit interview may be used to determine factors driving high rates of defection.[94] Adherence to such a system would provide utilities with comprehensive data on who is leaving and why, providing the foundation for developing effective, tailored retention strategies. A recurrent theme of the retention literature is that incentives (e.g., salaries and benefits) alone are not enough for achieving high levels of retention, the contention being that retention is related more closely to employee development and intrinsic benefits such as working relationships, job satisfaction, and a sense of empowerment (e.g., Hagevik,[60] McNally,[94] Thompson,[158] Denton[33]). Accordingly, utilities may consider undertaking a gap analysis of their employee development schemes (interestingly, Brueck[18] reports that water utilities spend as little as 1% or less of their labor budget on nonmandatory employee training) and benefit programs before remedying deficiencies in order to minimize turnover rates. An alternative approach to identifying the level of retention risk is to undertake an informal risk assessment,[4] which is essentially a checklist addressing the core issues influencing turnover (e.g., employee–manager relationships, communication, job satisfaction, etc.).

The negative consequences of employee turnover are clearly emphasized throughout the literature, leading to the implicit assumption that organizations should "pull out all the stops" to minimize defection rates. However, as Sigler[144] and Mowday[100] contend, the costs of reducing retention may, in some cases, exceed the benefits to be derived. It is thus incumbent on organizations to critically analyze the costs and benefits of implementing retention strategies; the cost-benefit analysis approach offers a promising framework for this purpose.

F. Assessing Investment Risks

Behind each strategic investment an organization considers lies some calculation of the move's worth.[87] Following Rothstein and Kiyosaki,[134] we define strategic investments as those resource allocations that will yield substantial advances toward the achievement of a utility's strategic goals. Whether considering a joint venture, acquisition, or a major extension of an existing facility, how the utility estimates value is a critical determinant of how it allocates its resources, which is in turn a key driver of its overall performance.[87] Valuation methodologies range from the formal (comprising an appraisal model and a supporting theory) to the informal (based on heuristics).[87] However, since the 1970s there has been a trend toward applying valuation methods that are more formal, explicit, and institutionalized.[87] The most widely

adopted framework is the net present value (NPV) model, which estimates value by capitalising (discounting) future streams of cash flow that the investor expects to receive from an asset. The capitalization rate is the minimum expected rate of return needed to induce an investor to acquire. Capitalization is comprised of two components: the risk-free rate of return (accounting for the time value of money) and the risk premium (the additional compensation demanded by investors for assuming risk). Although issues have been raised regarding the applicability of conventional appraisal methodologies to the water industry, specifically relating to the long life spans of many capital projects and the fact that they often do not generate revenues in the traditional sense (e.g., Tebbutt et al.[155]), they remain favored by academics and industrialists. Our subsequent discussion focuses on three distinct investment problems: valuation of assets-in-place; valuation of "opportunities"; and the valuation of joint ventures.

1. ASSETS-IN-PLACE

The most basic valuation problem is valuing assets-in-place, that is, the valuation of an ongoing business or some part of one, for the purposes of informing decisions ranging from a change in suppliers to an acquisition.[87] It is for such situations that discounted cash flow (DCF) techniques (methodologies for determining the capitalisation rate) are suited.[87] In brief, the established DCF methodologies include the weighted-average cost of capital (WACC),[97] the capital asset pricing model (CAPM),[140] and the adjusted present value (APV).[102] The WACC, which establishes the risk premium on the basis of the "cost of capital" financing the investment, remains the most commonly practised approach,[87] though it is increasingly criticized in academic circles (e.g., Luehrman,[87] and Gregory[54]). The fundamental idea behind CAPM is to use β, a measure of systemic (market) risk, to adjust cash flows. In contrast, APV seeks to unbundle the various components of value (i.e., cash flows), analyze them separately, and then add up the present values. For a fuller discussion of these and other DCF techniques see, e.g., Modigliani and Miller,[97] Sharpe,[140] Myers,[102] Berry et al.,[12] Gregory,[54] Luehrman,[87] and Ye and Tiong.[173]

Regardless of the individual strengths and limitations of the models just described, a common deficiency is that there is no indication of the confidence level on the determined capitalisation rates.[173] Following on from Hertz,[66] who highlighted the misleading nature of single-point estimates in investment analysis, most researchers advocate the appraisal of investments within a nondeterministic framework; the principle is that investment forecasts are, by definition, uncertain. Reflecting this uncertainty in model outputs lends some assurance to the decision makers that the available information has been used with maximum efficiency.[66] This is reflected in Guidelines published (1999) by the Asian Development Bank[6] on the application of

financial evaluation methodologies to water supply projects. Risk analysis, in the form of sensitivity analysis and stochastic simulation, is promoted as a means to examine the influence of changes in key underlying variables on forecast cash flows, and the probability that project NPV will fall below zero. Incorporating these principles, Barriex et al.[10] describe the application of the NPV framework to the proposed restructuring, privatization, and optimization of water utility operations in Panama. The focus of their study is on the proposed rehabilitation of systems supplying water to Arraijan, Chorrera, Colon, and Panama City, a "holistic" program entailing the upgrading of commercial, technical and operational aspects. Through stochastic simulation and sensitivity analysis of forecast financial returns, the authors confirmed the project's robustness from a financial standpoint, determining a "zero" probability of negative NPV.

Thomas[157] uses an illustrative example to examine the role of CAPM in adjusting for the risk inherent to acquisition/diversification appraisals (using internal rate of return [IRR], an appraisal framework similar to NPV). Accounting for the unique nature of acquisition/diversification appraisals, the author provides a methodology for integrating expected financial and operational synergies (e.g., derived from financial and operating economies, or the pooling of functional areas) within the analysis. However, through applying a risk premium to projected cash flows (which by definition accounts for the increased returns investors demand for variable cash flows) and undertaking simulation of the variables influencing future cash flows (thus explicitly modeling the variability of returns), Thomas[157] is effectively "double counting" for risk, introducing a bias against investment decisions. This criticism is supported in the work of Burchett and Tummala,[21] who apply Monte Carlo simulation to an NPV-based appraisal of an infrastructure capital investment decision. These researchers argue that applying specific probability distributions to the relevant variables captures all potential risks relating to the investment, thus negating the requirement for incorporating a risk premium as part of the capitalization rate.

Although it is widely accepted that a probabilistic approach to investment risk analysis is desirable, problems exist. As Songer et al.[148] assert, the failure to identify all significant risks (i.e., to apply appropriate probability distributions to all relevant underlying variables) quickly undermines model validity and output. A further pitfall is identified by Mosca et al.,[99] who in applying simulation methodologies to a proposed plant investment, found that the frequency distribution chosen (often arbitrarily) for the independent variables can have a marked effect on the process outcome. These are important observations in that they highlight the biases inherent to all risk models, reminding us of the need to use risk analysis output diagnostically rather than to overinvest belief in quantitative risk estimates.

In financial circles, recent times have seen an increasing adoption of tools that can perform economic evaluation and modelling on the combined

entity of investments (portfolio) as well as for each individual project. This trend extends beyond the financial sphere, as is illustrated in the work of Rothstein and Kiyosaki,[134] who describe the application of portfolio management theory to water utility investment planning. The philosophy of their approach is to create a portfolio representing a balanced array of investments that mitigate uncertainties and that are likely to realize potential returns. Of particular interest is their use of multiattribute analysis, which allows the risk-based prioritisation of monetary and nonmonetary investment decisions within a single analytical framework.

2. OPPORTUNITIES

It is relevant here to further discuss the work of Luerhman,[87] who categorizes a second type of valuation problem—the valuation of opportunities (i.e., possible future operations)—as distinct from the valuation of operations (assets-in-place). The distinction is that with the former, the decision to invest may be deferred. In opportunity valuation, risk matters in two ways: the risk of the investment, and the risk that circumstances will change before a decision has to be made. Such contingencies are not well handled by the traditional DCF approach.[87] Luerhman[87] states that a common approach in the valuation of opportunities is simply not to value them formally until they mature to the point where a decision can no longer be deferred, where they can then be valued, in effect, as assets-in-place. Critics have decried this practice, on the premise that it leads companies to undervalue the future and hence underinvest.[87] In response, Luerhman[87] discusses the potential of "option-pricing theory"[14]—an analytical strategy that allows managers to handle the contingencies created by the time-dependant nature of opportunity valuation—as a supplement, not a replacement, for the valuation method for in place assets.

3. JOINT VENTURES

A further category of investment decisions is found where firms participate in joint ventures, partnerships, or strategic alliances. This takes on particular resonance in the water industry, where recent years have seen a proliferation in public/private partnerships. In such cases, where ownership is shared with other parties, managers need to understand both the value of the venture as a whole *and* the value of their company's interest in it.[87]

The investment risks associated with public-private partnerships have been reviewed by Grimsey and Lewis.[55] Using the financing of Stirling Water, a Scottish design–build–operate contractor as an illustrative example, they apply quantitative analysis of returns on investment from the perspective of the private (sponsor) and public (procurer) sector entities.

A common observation of the risk management literature is an all too obvious gap between theory and practice. Much of the highly theorized investment literature does not reflect standard industry practice, particularly that relating to the application of complex methodologies such as simulation and scenario analysis. The discrepancy is explained, in part, in that such techniques do not fit naturally into most companies' skill sets or capital-budgeting systems.[87] Despite this, there is a dearth of literature focusing on the practicalities of integrating such tools deep within company structures. To address this issue and as part of the research that has informed this review, the authors will be undertaking a benchmarking of risk management capabilities within the international water utility sector.

III. PROGRAM RISK ANALYSIS

We turn to a more familiar discussion of the application of risk analysis to the water utility sector. The revised WHO guidelines[167] are promoting the implementation of water safety plans for water quality management from catchment management, through process control, distribution, and on to the tap.[160] Application of risk analysis to these aspects of the water "supply chain" extends to programs of work as well as individual plant operations. A discussion of the latter, operational risk analysis, follows, but here we are concerned with the analysis of risks associated with programs of activity that are "rolled out" across organizations, such as asset management and maintenance planning. Here, managers are responsible for the implementation of strategies across company functions, multiple sites, and geographic regions. They are concerned with evaluating the risks posed by a similar hazard at a variety of locations (e.g., mains bursts, network intrusion—in asset management, for example); the risk-based appraisal of operational strategies and long-term planning in relation to the water supply-demand equilibrium; and the wide variety of risks existing within a catchment or watershed. Table 3 summarizes the portfolio of analysis techniques available at the program level.

A. Asset Management

In line with Booth and Rogers,[16] we consider asset management as "managing infrastructure capital assets to optimise the total cost of owning and operating them while delivering the service levels customers desire." Managing risk in the face of limited resources has long been an implicit component of asset management. Within the United Kingdom, pressure from the economic regulator has ensured that the explicit incorporation of risk analysis into asset management programs has taken on added momentum. Water utilities are

TABLE 3. Program Level Risk Portfolio

Context	Tool/Technique	Application	Reference
Asset management	Risk ranking	Prioritisation of remedial work on infrastructure assets	Kent *et al.*,[73] Radovanovic and Marlin,[126] Foster *et al.*[50]
	FMECA	'Source to tap' risk identification and prioritisation	Lifton and Smeaton.[82]
	Logic models	Evaluating structural failure modes	Gray and Powell,[53] Parr and Cullen.[117]
	GIS risk tracking	Infrastructure risk-tracking, visualisation and communication	Kaufman and Wurtz.[72]
	GIS spatial analysis	Risk-mapping of infrastructure	Doyle and Grabinski,[37] Ta.[153]
	GIS risk simulation	Evaluating degradation risk	Lindley and Buchberger,[83] Besner *et al.*[13]
Catchment management	Risk ranking	Prioritisation of monitoring strategies	Dabrowski *et al.*,[30] Verro *et al.*,[164] Boak and Packman,[15] Feijtel *et al.*[44]
	GIS risk mapping	Mapping areas of catchment critical to water quality	Lytton *et al.*,[88] Sivertun and Prange,[146] Wickham and Wade,[169] Foster and McDonald,[49] Osowski *et al.*,[111] Fuest *et al.*,[51] Lantzy.[77]
	Contaminant flow/ transport modelling	Projecting degradation patterns/assessing risk of water quality violation	Anderson and Destouni,[2] Gündüz *et al.*,[56] Halfacree,[61] Liou and Yeh,[84] Cole *et al.*[25]
	Kriging	Projecting degradation patterns with limited sample data (*e.g.* groundwater)	Passarella *et al.*,[118] Wingle *et al.*,[171] Rautman and Istok.[129]
	GIS risk simulation	Quantified risk mapping over space *and* time	Dabrowski *et al.*,[30] Verro *et al.*,[164] Feijtel *et al.*[44]
Network analysis	Network reliability modelling	a) Assess susceptibility to supply-demand scenarios; b) aid development of supply strategies and policies; c) assist design of distribution networks; and d) inform the need for capital expenditure.	Stevens and Lloyd,[150] Lifton and Smeaton,[82] Wang *et al.*,[165] Merabtene *et al.*,[96] Ostfeld,[113] Stahl and Elliot,[149] Zongxue *et al.*,[174] Andreu *et al.*,[3] Jinno *et al.*[71]
Vulnerability assessment	RAM-W	To assess system vulnerabilities and develop measures to reduce risks of attack.	SNL news release.[147]
	Questionnaire-based self assessment	As above	NRWA.[107]

expected to: "demonstrate how the flow of services to customers can be maintained at least cost in terms of both capital maintenance and operating expenditure, recognising the trade off between cost and risk, whilst ensuring compliance with statutory duties" (Ofwat letter MD 161, April 2000).

In addition to regulatory pressures, the global trend toward requiring financial self-sufficiency on the part of public and private utilities has created a climate in which management can no longer seek to "overengineer" facilities with the presumption of screening out technical risk. A recent (2004) report[163] to the U.S. Senate cites "mounting evidence suggest[ing] that the integrity of the nation's [water] infrastructure is at risk without a concerted effort to improve the management of key assets ... and a significant investment in maintaining, rehabilitating and replacing these assets." The report goes on to explicitly endorse the role of risk analysis in asset management. More than ever, utilities must now seek to balance spending with risk minimization. A risk-based approach to asset management requires an integrated, systematic process drawing on a broad range of methodologies for the identification, analysis, and prioritization of assets-at-risk, from the process to the component level (e.g. Lifton and Smeaton[82] and Booth and Rogers[16]).

On a national scale, the U.S. Natural Resources Defense Council (NRDC)[106] recently (2003) reported on the risk to drinking-water quality from aging pipes and process plants across the United States, with individual city "rankings" being informed by water quality data, U.S. EPA compliance records, and water utility annual reports. Many water companies have in place risk-ranking procedures to evaluate and rank potential risks across a variety of categories, and thus help inform and prioritize risk management procedures.[121] For example, Radovanovic and Marlin[126] describe the risk-based approach to water mains asset management in place at Sydney Water (Australia). Budgetary requirements are estimated through the application of KANEW, a statistically based survival model that aids the calculation of pipe rehabilitation and replacement needs for distribution networks. The identification of specific pipes requiring work is external to the model, with separate approaches for trunk and reticulation mains (the latter generally being run to failure). Critical trunk mains are identified by means of a checklist-aided screening approach, wherein preliminary assessments of failure likelihood and consequence are combined to create an overall risk score. This combined risk score is used to identify critical water mains deemed to require more detailed analysis (e.g., condition-based assessments). This methodology allows Sydney Water to identify and prioritize water mains in need of rehabilitation/renewal, and to proactively assess budgetary requirements.

Louisville Water Company (Kentucky) applies its Pipe Evaluation Model, which integrates data such as pipe age and maintenance history, as a tool for prioritising pipe and water mains for rehabilitation and replacement.[163] Utility managers report that this model, in combination with wider asset management practices, has helped reduce the frequency of water mains breaks

from 26 to 22.7 per hundred miles and the frequency of joint leaks from 8.2 to 5.6 per hundred miles.[163] Seattle Public Utilities adopt a risk-based approach to asset management, considering likelihood and impact of pipe rupture with reference to such factors as age, material, location, and historical cost of repair.[163] Drawing on this analysis, utility officials were able to delineate their pipe network into areas of critical and noncritical risk, and allocate maintenance and rehabilitation resources accordingly. Through adopting this approach, officials believe that they are using staff resources more efficiently and that, over time, the program will lead to a reduction in maintenance costs.[163]

Kent et al.[73] describe how risk analysis informs the prioritisation of investment strategies for trunk main maintenance at *Dwr Cymru* Welsh Water. The methodology is based on the available records of asset performance, condition, and serviceability, which are stored on the company's WAM (Water Asset Management) database. STRUMAP, a software-based mapping system, allows clustered failures to be considered separately from "random" bursts, a task performed as the former are considered likely to be representative of underlying susceptibilities. For each location where a cluster is identified, specific failure rates are derived. For random bursts, failure data is separated according to pipe material and diameter, with failure likelihood determined by group. STRUMAP further enables consideration of failure consequences, in terms of the number of properties potentially affected by an event, taking into account service reservoir storage. Failure likelihood and consequence are then combined to derive an overall severity score, which in turn informs the derivation of investment requirements. The National Research Council of Canada is currently developing a prototype Water Mains Renewal Planner (WARP),[127] which is aimed at integrating the most promising breakage analysis models into one discrete decision support tool. At present, WARP consists of three modules: (a) analysis of water main breakage patterns; (b) short-term operational forecasting; and (c) long-term renewal planning. A fourth module is to be added to enable prioritization of individual water mains for renewal.

Foster et al.[50] detail a risk-ranking approach for estimating the relative likelihood of failure of embankment dams by piping. Failure likelihood is assessed by weighting the historical frequency of piping failure with respect to dam zoning, filters, dam age, core soil types, compaction, foundation geology, dam performance, and monitoring and surveillance. The methodology allows the prioritization of dams-at-risk for more detailed analysis, and is further offered as a check on traditional event-tree methods (see also Seker et al.[139])

Failure modes and effects analysis (FMEA), developed by the U.S. military, is an engineering technique that tabulates failure modes of equipment and their effects on a system[1] (Table 4). The failure mode describes how equipment fails (open, closed, on, off, leaks, etc.). The failure effect is determined by the system's response to the equipment failure. When FMEA is

TABLE 4. Component FMEA for Chlorine Cylinder and Outlet Valve (Egerton,[39] with Permission)

Failure mode	Failure effect on process	Failure effect on system	Methods of detection	Comments
Fail to open/Reduced output/No output	Loss of adequate chlorination	Non-potable water will leave plant	Changeover should detect loss of supply	System failure would require combination of loss of flow and failure of changeover
Fail to close	None–changeover should transfer to standby cylinders	None	None	
Excess output	Excess chlorination	Possible taste and odour complaints. No serious consequences	Changeover should detect excess chlorine flow	
Outside specification (wrong or contaminated gas)	Outside specification (wrong or contaminated gas)	Non-potable water will leave plant. POTENTIAL FOR MAJOR SAFETY HAZARD	QA checks on delivery. Low chlorine residual readings and alarm	

extended by a criticality analysis, it is known as failure modes, effects, and criticality analysis (FMECA).

Lifton and Smeaton[82] detail how Scottish Water applies source-to-tap FMECA studies across its water supply systems as part of its "asset management toolkit." This allows priority risks to be identified and subsequently compared across the utility portfolio (e.g., various mains, raw and treated reservoirs, treatment works, etc.) in order to focus attention on the most serious threats to system performance. Infrastructure investment strategies are further informed by the HYSIM-AQUATOR supply–demand model. Of particular interest is the description of the asset risk and criticality scoring system implemented at Scottish Water. The system is designed to assess the relative "total business impact" of asset failures across the company by reference to a "common currency of risk" (one point equates to £1000 of business impact), facilitating a consistent approach to risk scoring across Scottish Water. Additionally, this scoring system guides the prioritization of reliability studies at the operational level, which further informs asset management strategy.

Given the complexity inherent in describing modes of structural failure and assessing their likelihoods,[53] logic models (visual risk schematics, e.g., reliability block diagrams, fault tree analysis [FTA] and event tree analysis [ETA]; see Figures 4 and 5) have found application in support of asset management. Parr and Cullen,[117] through examining the applicability of logic modeling techniques to dam failure analysis, illustrate how such an approach can inform the prioritization of expenditure on monitoring, maintenance, and

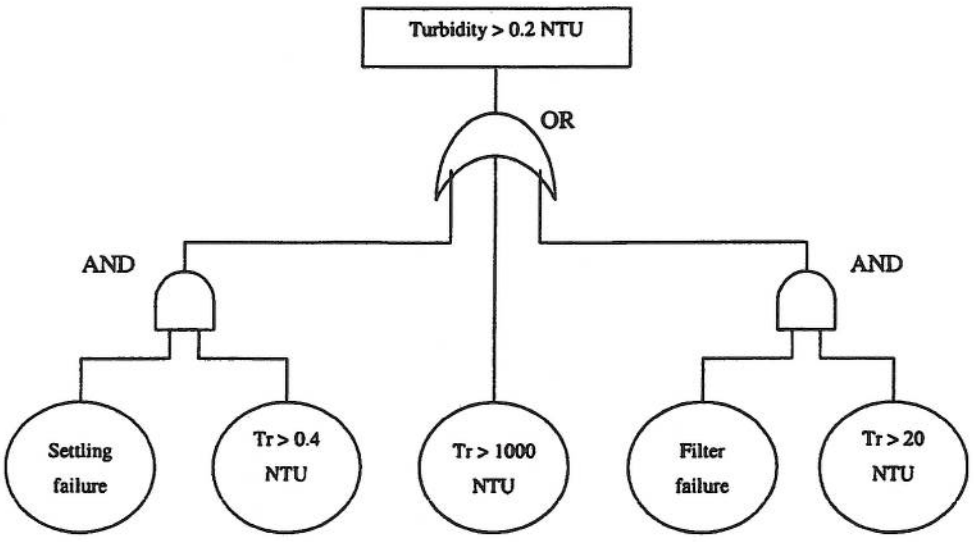
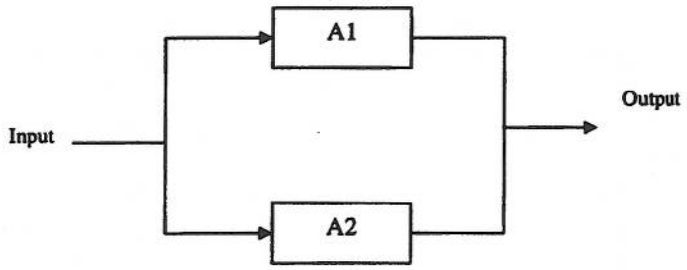


FIGURE 4. Illustrative fault tree for turbidity noncompliance (Demotier et al.[31]). Tr, resource turbidity. The probability of the top event may be calculated if the probabilities of the subevents are known or estimable.

a) Series diagram – here, the system / process is working if A1 and A2 are working



b) Parallel diagram – here, the system / process is working if A1 or A2 are working



c) Redundancy diagram – here, the system / process is working if at least r elements among n are working

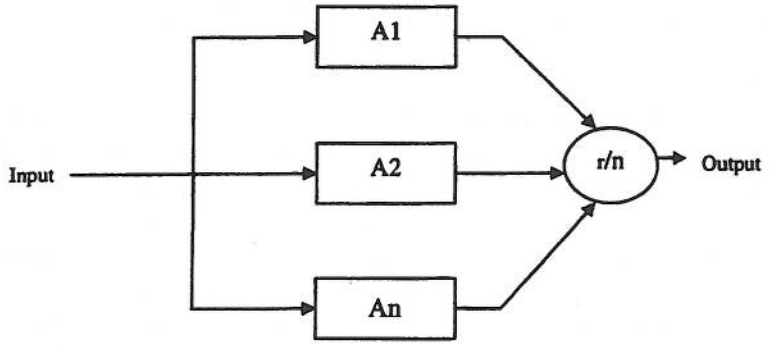


FIGURE 5. Reliability block diagrams (Cyna[29]).

remedial works. Similarly, Gray and Powell[53] promote the use of logic diagrams in aiding the development of risk-based strategies for maintaining asset security. The authors model the interactions leading to failure for each class of aqueduct structure. To this, historic data or, where data are deficient, engineering judgement is applied in order to derive failure probabilities. A cautionary note is sounded by Latiffe,[79] who contends that risk analysis, specifically logic modeling, is not yet effective in modeling dam failure. The

author cites insufficient statistical data on the deficiencies of structural components as the core drawback.

1. SPATIAL CONTEXT OF RISK

Geographic information systems (GIS) technologies now play a critical role in asset management. At its most basic level, GIS allow utilities to convert data ordinarily displayed on paper maps into one single, easily accessible digital format, representing an excellent method for storing and collating data for future use.[49] The level of detail (i.e., the layers of spatial data) contained within such systems varies widely. Kaufman and Wurtz[72] describe the evolution of a GIS for a small utility (Beecher Water District, Michigan). An extensive inventory of asset condition records and failure and maintenance data is collated within the system, supporting the risk-based planning of capital improvement and maintenance works. Pertinently, the system took only 3 months and less than $3000 to develop. Similarly, Booth and Rogers[16] illustrate how the implementation of GIS technologies within an asset management decision support system can allow for the visual tracking of infrastructure assets and their associated risk factors.

Although applications of GIS technologies in support of asset management have proven to be powerful risk-tracking, visualization, and communication tools,[16] they rarely utilize the capabilities of GIS to spatially analyze data in the classical sense.[49] Doyle and Grabinski[37] illustrate these capabilities through quantitatively relating Toronto's infrastructure deterioration to spatially variable corrosion risk factors, providing a basis for the identification of network areas most at risk from external corrosion. Such an approach may allow utility managers to better focus rehabilitation efforts through having a more complete understanding of the causative factors behind water main deterioration. Of further interest is the work of Ta,[153] who describes the application of a probability model for burst risk studies of water mains. Contributing factors (e.g., pipe number density, pipe age, material and diameter, soil corrosivity, etc.) are represented as GIS data layers and correlated with past failure data in order to deduce burst probability scores for each water main. The tool, developed for Thames Water Utilities Ltd. (UK), is not intended to predict the likelihood of pipe bursts, but rather to aid utilities in sourcing the origin of an area burst (i.e., following a pipe burst in the area, the value of probability evaluated for a particular pipe section would indicate the likelihood that the burst actually occurred at that section).

While GIS represent powerful tools for spatial data analysis, their inherent capabilities for complex and dynamic analysis are limited.[43,152] In contrast, traditional simulation models are powerful tools for complex and dynamic situations, but often lack the intuitive visualization and spatial-analysis functions that GIS offers.[43,152] Consequently, researchers have sought to couple these systems. Lindley and Buchberger[83] describe the integration

of hydraulic modeling within a GIS for the purpose of assessing intrusion susceptibility in distribution systems. The holistic methodology enables the synthesis of multiple risk factors describing the three key (geographically variable) susceptibility conditions of adverse pressure gradient, intrusion pathway, and contaminant source, thus identifying areas susceptible to intrusion (accidental or intended). Susceptible locations are then prioritized for attention by considering how they are hydraulically connected to local sensitive populations. In addition to informing asset management programs, this framework may also be applied in a reliability context at the design stage. Similarly, Besner et al.[13] illustrate via case study how the coupling of a GIS containing structural, operational, and water quality parameters with simulation model EPANET facilitates the identification of key factors responsible for water quality degradation in the distribution network. Through identifying quality network areas presenting the greatest risk, this technique can inform the prioritisation of risk management strategies.

B. Catchment Management

The concept of catchment (or watershed) management has gained widespread international support, representing a shift from the sole reliance on end-of-pipe treatment technologies for point sources toward the watershed-specific prioritisation of water quality problems and their integrated solution.[48] An outcome of this is that the assessment of hazards to the quality of water resources within a catchment is increasingly subject to formal risk assessment and can be expected as part of routine water safety plans.[160,161,167] In Europe, the DPSIR approach to identifying key hazards within a watershed, by reference to the driving forces (e.g., population growth), pressures (sewer discharge), state (increased nutrient load), impacts (anthropogenic eutrophication), and policy response (discharge control) is being adopted under the European Water Framework Directive.[70] Here, risk assessments of activities posing a an actual or potential threat to the quality of water bodies in "river basin districts" are intended to inform and help prioritize a program of multiagency action plans targeted at raising the overall ecological status of the watershed within statutory timescales. Given the plethora of potential catchment management issues in any improvement program, there is a need to prioritize risk management efforts within the watershed by concentrating on those measures that reduce the significant likelihood of severe impacts being realized. Southern Water (UK) adopt a semiquantitative ranking scheme in screening their groundwater sources for *Cryptosporidium* contamination risk, as described by Boak and Packman.[15] The methodology consists of ranking source waters across 10 risk categories (e.g., land use) using predetermined scoring hierarchies (e.g., occasional livestock grazing: 2), before combining these category rankings into an overall weighted risk

score. Through this approach, the utility identifies those sources deemed to be at significant risk of oocyst contamination and that therefore require continuous monitoring (in line with regulations).

Given the improved capabilities and functionality of modern GIS and their inherent ability to map and analyse data that are spatially variable in nature, many catchment-level ranking methodologies have sought to incorporate their benefits. Various authors[49,51,88,111,146,169] describe the use of map overlay techniques (which essentially combine the attributes of two or more data layers across geographic space) in the identification and mapping of areas critical to catchment water quality. These risk-mapping (essentially spatial risk-ranking) methodologies center on the analysis of those spatial attributes considered to play a significant role in pollutant transport (e.g., geology, rainfall, soil type, agricultural activities, etc.) according to predefined formulas (e.g., a weighted runoff-potential index). Their focus may be generic or targeted toward specific hazards (e.g., animal feeding operations) or pollutants (e.g., through incorporating measures of their leaching potential).

Risk-ranking methods are applied to help target more detailed analysis toward critical risks and to inform the prioritization of catchment management activities, specifically monitoring programs. Of course, the potential exists that as the costs of planned monitoring decrease on the one hand, the risks may increase on the other. When designed well, piloted and implemented with feedback, risk-based resourcing strategies (Figure 6) can

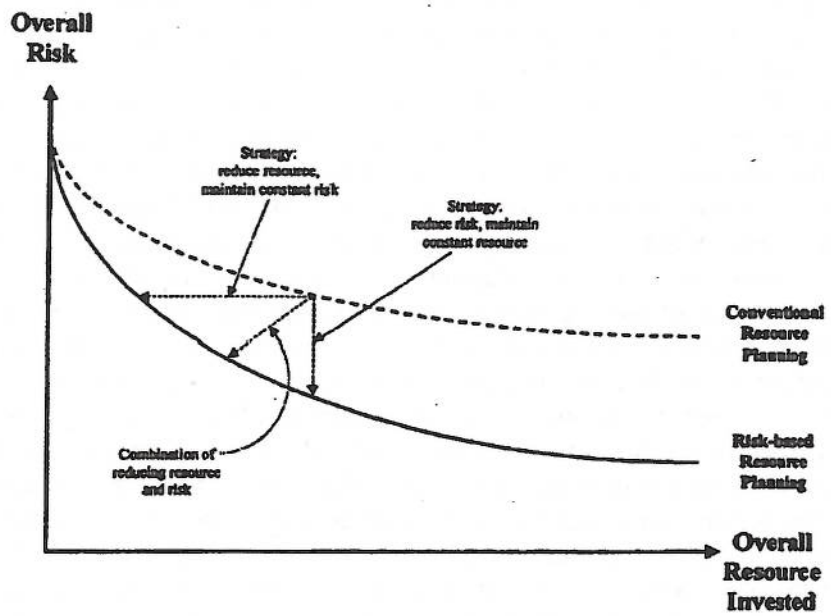


FIGURE 6. Risk-based workforce planning (after Pollard et al.[122]).

provide a sound basis for distinguishing greater risks from lesser ones, and for investing resources in risk management that are proportional to the risks posed.[122]

Most critically, however, these risk-based optimization tools, whether intended to drive monitoring regimes, maintenance schedules, or workforce planning, may themselves incur significant risk unless the consequences of resource trade-offs are themselves assessed. Consider the actions of the Saskatchewan Department of Environment and Resource Management (SERM) prior to the North Battleford cryptosporidiosis outbreak in April 2001.[121] SERM held legislative responsibility for the Saskatchewan drinking water program and, partly in response to budget cuts in the mid 1990s, drastically reduced the already limited field inspection and enforcement of municipal utilities. This culminated in SERM proposing to eliminate its drinking water program altogether, a motion tentatively approved by the Treasury Board in 2000/2001 and justified as being "risk-based." The subsequent North Battleford outbreak, infecting between 5800 and 7100 persons in the immediate community plus a large number of visitors from 3 other provinces, led to a public inquiry into the outbreak and the provincial drinking water regulatory system. Justice Laing[76] concluded in his Inquiry report "that the current risk-based model employed by SERM since 1996 is arrived at on the basis of economics, and has nothing to do with how best to safeguard the health of the population, all of whom consume water." The example aptly illustrates the inappropriate use of risk analysis as a justification for the removal of processes critical to public health protection. Tensions that arise between those seeking economic efficiencies and preservation of the principal goal of providing safe drinking water are often played out in the conflicting expectations and presumed purposes of risk analysis made by different professionals. The real consequences of stripping away levels of safety, precaution, and protection using "risk analysis" as a justification can be to render the system as a whole less safe, more precarious, and more susceptible to catastrophic failure, so optimization programs, maintenance schedules, and risk-based monitoring require special scrutiny as to the balance between risk and the full cost of implementing these programs.

Where more detailed analysis is deemed necessary, a common recourse is model-based approaches. Water quality and flow/transport models represent core tools for this purpose, due to their combined ability to model the dispersal of pollutants and predict the resultant deterioration of water quality. Aside from the inherent value of fostering an increased understanding of catchment water quality issues, the core benefits of model-based analysis stem from their ability to test management scenarios (through, e.g., sensitivity and scenario analysis), thus enabling informed decisions on how best to manage the resource. A range of models is available for catchment risk analysis, from micro to landscape scales, and from deterministic to stochastic approaches (Table 3).

Common practices of hydrological and water quality modeling have been based mostly on deterministic analysis, producing single-point estimates that neglect prediction uncertainty.[2] Determinism has been embraced by many risk analysts; for example, Gündüz et al.[56] describe the use of the combined hydrodynamic and water quality model CE-QUAL-W2 in projecting potential water quality degradation patterns under different pollution loads. The tool is intended to aid management in the development of appropriate strategies for the management of water quality. Similarly deterministic approaches to catchment analysis are described by various other researchers (e.g., Cole et al.[25]). The limitations of determinism in risk analysis, discussed earlier, are particularly relevant in the context of hydrological and water quality modeling, considering the often scarce or incomplete data available.[89] This uncertainty takes on particular importance from the utility standpoint, as the assessments of catchment water quality are performed with regard to set regulatory standards. To illustrate this point, the uncertainties inherent in flow and contaminant transport modeling (from, e.g., spatial variability, data scarcity, model imperfections) imply that there will always be a risk of exceeding a given standard at some point over space or time following a pollution event, regardless of the estimated single-point (mean) contaminant levels.[2]

An argument can thus be forwarded for the explicit consideration of prediction uncertainties in catchment-level risk modeling. There exist two dominant approaches toward this task: stochastic modeling, and deterministic modeling allied with uncertainty analysis of the output. Adopting the former approach, Andersson and Destouni[2] outline the application of stochastic transport modeling to quantify the risk of exceeding regulatory standards for groundwater at any point on the compliance boundary. This quantification is coupled with an analysis of the abatement costs required to attain an "acceptable" risk level. Halfacree,[61] for example, describes the use of PRAIRIE, an aquatic dispersion modeling tool for assessing chemical pollution risks to water bodies. The main elements are an aquatic dispersion model; hydrological, substance, and standards databases; and a tabular/graphical output facility. The model has a deterministic mode used to "screen out" low-risk sites, and a probabilistic mode for more detailed analysis of high-risk sites. The output results (e.g., frequency vs. concentration curves) are compared with predetermined criteria to inform regulatory actions on risk management from hazardous activities within a sensitive catchment. An advantage of the stochastic approach is that uncertainty is interwoven within the model.[175] However, the solution of stochastic equations is often impractical for complex problems.[81] This explains, in part, the preference for deterministic approaches to water quality/hydrological modeling, creating the subsequent need for external consideration of output uncertainty.

In this context, uncertainty analysis is performed to estimate the probability of obtaining a given output value when uncertainties on input variables

and parameters are known.[89] Liou and Yeh[84] outline the use of a groundwater transport model in deriving the risk of contaminant concentration exceeding a maximum acceptable upper limit (e.g., regulatory standard). The analytical uncertainty of the predicted contaminant concentration is derived by first-order mean-centered uncertainty analysis, prior to the application of Monte Carlo simulation in order to compute the mean risk and associated confidence interval of exceeding standards. For detailed discussions of the forms of uncertainty in water quality modeling and the techniques for their analysis, see Mailhot and Villeneuve,[89] Portielje et al.,[123] and Beck.[11]

In the event of pollution leading to a violation of water quality standards, remediation may be required. Researchers have developed methodologies for optimizing remediation strategies (e.g., Rogers et al.[132]). However, as Latinopoulos et al.[80] contend, if the inability to meet the constraints of a groundwater quality program is considered a significant risk, then quantifying the risk of remediation failure in terms of failure to comply with regulatory standards is a primary task. In relation to this, Latinopoulos et al., through coupling stochastic flow and transport simulations with a risk–cost–benefit objective function, have developed a methodology facilitating the risk-based evaluation of remediation strategies (costing the risk of failure in terms of regulatory fines and the need to import/develop alternative supplies).

An alternative approach to characterizing the extent and severity of source contamination is that of geostatistical inference (e.g., Passarella et al.,[118] Wingle et al.,[171] and Rautman and Istok[129]). These kriging methods—essentially a form of least-squares linear regression—focus on providing an estimate of a spatially distributed variable (e.g., contaminant concentration) at unsampled locations as a function of a limited set of sample values taken from surrounding locations.[129] As such, they are ideally suited to groundwater quality issues, where data collection is limited by expense and access. Of particular relevance to risk analysis is the discipline of geostatistical simulation, where multiple, unique estimates of site conditions that mimic the random variability of the parameter(s) of concern are produced.[171] Various authors[118,129,171] have illustrated how such an approach may answer the following questions: What is the probability that contaminant levels exceed regulatory standards? Where are the compliance boundaries (and what is the associated level of confidence)? How much contaminant is present (and hence, how much must be removed)? Although the principles of geostatistical simulation are well established, the technique has yet to be widely applied to problems of groundwater contamination.[129]

Applications of GIS to catchment risk analysis were discussed earlier in the context of risk mapping. Although representing efficient risk screening tools, their ability to quantify risk over space *and* time is limited. To counter this, researchers have sought to integrate these systems with simulation models. Feijtel et al.[44] illustrate that the embedding of chemical fate prediction models within a GIS allows for calculation of the distribution of predicted

environmental concentrations, both in space and time, of "down-the-drain" chemicals in catchment surface waters. Similar approaches are adopted by Dabrowski et al.[30] and Verro et al.[164] to assess surface water pesticide loading.

C. Network Analysis

A water distribution system may be viewed as an interconnected collection of sources, pipes, and hydraulic control elements (e.g., pumps, valves, regulators, tanks) delivering water to consumers in prescribed quantities and at desired pressures.[112] System behavior, which is governed by hydraulics, supply, demand, and system layout, may be described mathematically.[112] This description forms the basis of water supply and distribution modeling (network analysis), a discipline practised in the water industry for many years, particularly to inform the development of operational strategies.[17,154] Water utilities routinely apply network analysis in order to assess their "security of supply," defined as the probability of being able to meet consumer demands (i.e., network reliability). "Best practice" utilities extend their analysis beyond routine operating conditions to examine network performance under various supply–demand scenarios, thus reflecting the inherent uncertainty of the supply–demand balance. The standard Scottish Water methodology of yield assessment uses the software tool HYSIM-AQUATOR.[82] HYSIM, a hydrological rainfall-runoff simulation model, is used to derive historic inflow series, based on historic rainfall, potential evapotranspiration, and if necessary any artificial influences (e.g., abstractions). AQUATOR, a water resource system model, uses the output from HYSIM to simulate reservoir storage based on system demands and compensation flows. The model assists Scottish Water in understanding the level of supply availability risk in the current system and in determining the impact of prospective investment strategies to mitigate this risk.

Stevens and Lloyd[150] describe the application of the resource modeling package WRAPsim, with reference to the Yorkshire Water (UK) Grid. The model contains over 1200 components including all river and reservoir sources, boreholes, water treatment works, pipelines, and demand centers. Through simulation of the conjunctive use of Yorkshire Water's sources over a given time period, model output provides the decision maker with an accurate assessment of the behavior of each source, its ability to meet demand, and the frequency of restrictions that would need to be imposed. Further insights are gleaned through the application of scenario analysis, wherein the supply–demand balance for each zone under variable scenarios (e.g., average year, dry year, peak week, etc.) allows an assessment of security of supply over a range of time scales and operating conditions. The authors report that WRAPsim's ability to predict future supply conditions, to optimize allocation of water resources, and to rebalance stocks has significantly increased the yield and reliability of Yorkshire Water's supply system.[150]

Stahl and Elliott[149] discuss the Essex and Suffolk Water (ESW) use of the risk-based resource planning and operational support model DROP (Drought Reliable Output Programme), an adaptation of WRAPsim designed to accommodate the utility's specific technical requirements. The model has been applied in a variety of areas, particularly in support of investment planning and the determination of operational strategies. The authors state that DROP has enabled ESW to improve their understanding of system performance, identify new schemes or short-term options to improve reliability of supply, and more accurately determine future operating costs associated with new developments. Such methodologies, although able to examine system reliability under a range of operating conditions, do not adequately address whether the system is *sufficiently* reliable, as this requires the definition and quantification of appropriate and meaningful reliability measures, a computationally difficult task.[113] Harnessing developments in computer processing power and operability, Ostfeld[113] has developed a methodology for the explicit reliability analysis of water distribution networks, with reliability defined, quantified, and measured as the probability of zero annual shortfalls. The methodology, whose development was funded with the intention of practical application by the Israeli Water Commission, is comprised of two interconnected stages: (a) analysis of the storage-conveyance properties of the system, and (b) implementation of stochastic simulation through use of RAPTOR (Rapid Availability Prototyping for Testing Operational Readiness) software.

However, researchers in the field of network analysis are increasingly aware of the need to take account of both the frequency and severity of modeled failures, and as a result analyses are often suggested to extend beyond measures of reliability to incorporate resiliency (e.g., the capacity of a system to recover to a satisfactory state from a state of failure) and vulnerability (e.g., a measure of failure significance).[71,165] Adopting this paradigm, Zongxue et al.[174] describe the coupling of a risk model (comprising measures of reliability, resiliency and vulnerability), which incorporates predictions of water demand, with a traditional network simulation model. The approach aids the identification of operational strategies of minimum risk under given supply and demand scenarios, and is illustrated by application to Fukuoka Water Supply System, Japan (see also Jinno et al.[71]). Similar methodologies are described by Wang et al.,[165] Merabtene et al.,[96] and Andreu et al.,[3] although supplemented with formal optimization procedures to assist derivation of the most appropriate operational policies of minimum risk.

To summarize, network analysis can: (a) allow utilities to assess their susceptibility to various supply–demand scenarios (e.g., drought or increases in demand); (b) aid decision makers in determining "optimal" supply strategies and policies; (c) assist in the design phase of distribution networks; and (d) inform the need for capital expenditure.

following both the Walkerton outbreak (settled out of court) and the Sydney Water crisis (largely dismissed, costs still incurred).[121]

Conventionally, the public health impacts of drinking water consumption have been assessed retrospectively using epidemiological studies.[69] Recognition of the need for a preventative approach to managing risk and providing safe drinking water, however, has driven international interest in the application of risk assessment methodologies within the sector, for both chemical and microbiological hazards.[5,59] The generic approach is based on the risk assessment framework developed by the National Academy of Sciences (NAS),[103] which consists of four key steps.[59]

- Problem formulation and hazard identification—to describe the human health effects derived from any particular hazard (e.g., infection, carcinogenicity, etc.).
- Exposure assessment—to determine the size and characteristics of the population exposed and the route, amount, and duration of exposure.
- Dose-response assessment—to characterize the relationship between the dose exposure and the incidence of the health effects.
- Risk characterization—to integrate the information from exposure, dose-response, and health interventions in order to estimate the magnitude of the public health problem and to evaluate variability and uncertainty

Several substantive differences exist between assessment of risk of microbial agents and assessment of risk of chemicals.[58] Accordingly, the NAS approach has been adapted to account for the dynamic and epidemiologic characteristics of infectious disease processes,[45] to form what is known as quantitative microbial risk assessment (QMRA). The application of these models has long been the basis for the derivation of water quality guidelines for drinking water.[168] The substance-specific health risk assessments that have historically informed the guidelines may, however, be somewhat distanced from the immediate operational context of individual utilities.[121] However, recent work has extended the application of these models to the operational (plant-specific) context. For example, Medema et al.,[95] Masago et al.,[90] and Teunis et al.[156] describe the application of QMRA in determining the public health risks posed by the presence of microbial contaminants in treated water. The first step in the process is to define the relationship between measured pathogen source levels and the consumed dose (incorporating analytical detection levels, treatment removal efficiencies, drinking water consumption), followed by the construction of a deterministic model mathematically describing this relationship. Monte Carlo simulation (a method of uncertainty analysis) is then applied to the output of the deterministic model to determine the distribution of the daily consumed dose, to which the relevant dose-response relationship is applied in order to determine the cumulative distribution of the probability of infection. From this, the mean annual individual risk of infection may be determined. Such approaches are of particular relevance

in areas, such as the Netherlands, where water supply legislation expresses acceptable health risks in terms of infections per year.[95] Of course, core microbial standards generally refer to a maximum level of organisms in the treated water, so consideration of consumption levels and the dose-response relationship is superfluous to compliance risk assessment. The approach perhaps has most utility in "what-if" mode to answer questions such as, "What are the public health implications of a failure of part of the treatment process or of a re-designing of the treatment process?"[52]

Tools are available to assess the risk of exceeding water quality standards relating to physical or chemical parameters. For example, Demotier et al.[32] describe an integrated FTA/FMEA approach to determining the risk of producing noncompliant drinking water across a range of parameters, taking into account the quality parameters of raw water and the removal efficiencies and reliability of the full set of treatment processes. Similar methodologies are described by Eisenberg et al.[41] and Haas and Trussell[57] in assessing the reliability of multiple, independent barriers in water treatment. These three pieces of research explicitly consider the performance variability of individual processes along the treatment line, an approach rarely described in operational QMRA. Not only does this offer a more realistic appraisal of compliance risk, it is in line with recent proposals from regulatory bodies (e.g., National Health and Medical Research Council [NHMRC][105] calling on utilities to formally adopt the multiple barrier approach to risk management to ensure multiple levels of protection are afforded against specific contamination threats (see Rizak et al.[131]).

Of course, limitations in resources (human and financial) and in the data to underpin such sophisticated analyses often restrict the practical application of these more advanced methodologies within the sector. A more pragmatic analysis of the risks of process failure is commonly undertaken using a semiquantitative risk ranking of hazards according to their likelihood and consequence. Egerton[40] describes the application of ranking techniques for the prioritization of contamination risks at a water treatment plant. Risks are scored according to the frequency with which they may occur, the ability to take action to contain the event, and the consequence of subsequent contamination. The methodology is intended to aid the targeting and prioritization of remedial actions. Such approaches rely heavily on the experience and judgment of the assessment team and, depending on the level of guidance provided for scoring within these criteria, remain open to bias especially from unforeseen circumstances that often fall beyond the process boundary, such as deliberate or accidental human error.

Finished water can undergo a variety of physical, chemical, and biological changes during transportation through a distribution system.[13] Understanding the nature and likelihood of these risks has become a priority for water producers,[13] in part due to research linking such degradation to the incidence of gastrointestinal illnesses (e.g., Payment et al.[119]). Application of the methodologies developed by Lindley and Buchberger[83] and

These methodologies represent an informed and structured, if time-consuming, framework for pinpointing weaknesses in utility design and operation. Applied effectively using personnel with appropriate skills, experience, and resources, they provide operational management with a basis for improving process reliability and identifying issues early. Ineffectively applied, they become little more than acronyms for complacency. As discussed, reliability analysis may require a quantitative treatment of the effect of identified risks at the system level. The importance and complexity of this task have increased in recent years, due in part to the increased range of available technologies and the tighter operational margins imposed by regulators.[41]

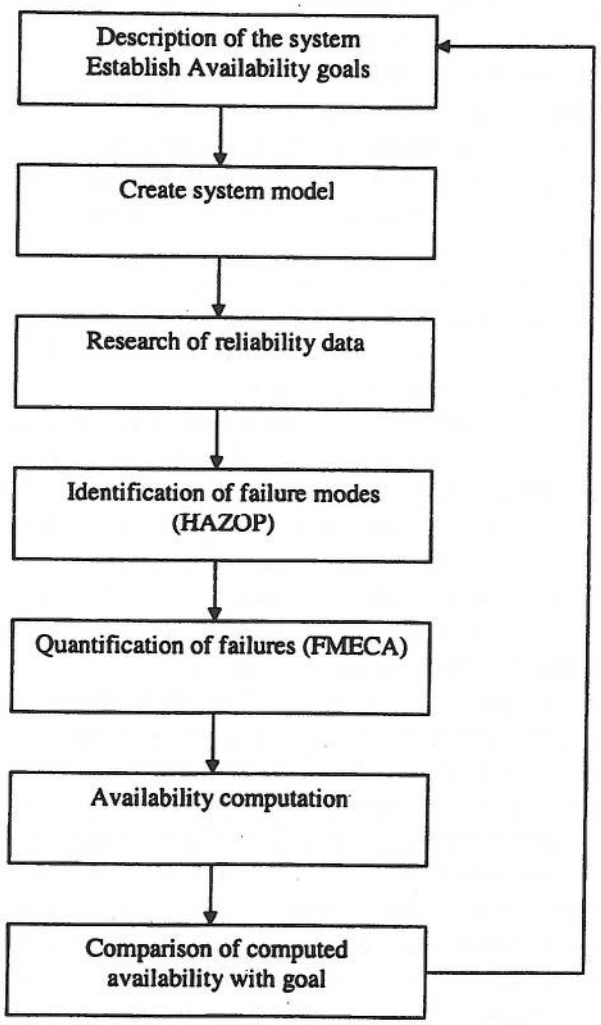


FIGURE 7. Methodology for reliability analysis of a water treatment plant (Cyna[29]).

For unreliable or heavily used equipment, an analysis of historic data may be sufficient for this purpose. In the absence of such data, there is a requirement for the formal modeling of risk consequences. There exists a range of techniques for this task, including logic modeling (e.g., Demotier et al.,[32] and Cyna[29]), "quantitative" FMECA (e.g., Cyna[29]), and multiple barrier approaches to treatment reliability (e.g., Demotier et al.,[32] Eisenberg et al.,[41] and Haas and Trussell[57]). An illustration of an integrated approach to evaluating plant reliability is provided by Cyna, who describes the methodology developed and applied by the Compagnie Generale des Eaux (France) (Figure 7). Following system definition and modeling (via reliability block diagrams), risks are identified and classified using HAZOP. Risk consequences are subsequently quantified via FMECA, allowing the computation of system availability (the probability of the system to be found operative at a given time). Cyna describes how the methodology was applied to a proposed postchlorination system in a Neuilly-sur-Marne plant, arguing that its employment helped conceive a reliable system and verified the adequacy of plant availability. The author concludes that reliability analysis is an essential tool at "conception," which allows the adjustment of project design, and thus cost, to the level of reliability required, and, when associated with maintenance procedures, can provide insurance of design quality.

V. CONCLUSION

Risk management for water utilities is fast becoming an explicitly stated paradigm, recognizing the implicit approach performed over the last 150 years. With increasing globalization, outsourcing, and increased regulation of the industry, tools that allow system vulnerabilities to be identified before failures occur are essential. In many ways, however, the industry is discovering risk analysis afresh, and there is a learning curve to climb in terms of the capabilities and limitations of these tools and techniques. The international water sector has helpfully restated its overarching goal, reminding us that even in the face of rationalization and economic pressure, public health protection[8] is the principal business of the water industry. Risk analysis has a part to play in focusing effort in the right places, but should not be treated as a panacea or substitute for managing risk nor allowed to dictate the outcome of decisions without recourse to the fundamental goal of the business. Flexibility of approach is key to the successful application of these tools, as is their appropriate selection within the organizational context and legal framework. For large multi-utilities, one can expect highly developed business risk capabilities, whereas for smaller and single utilities, an approach based on accepted codes and standards may be more suitable. Our analysis provides a comprehensive inventory of the current state of the art as a reference for developing a risk analysis strategy that is fit for the purpose.

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A commentary on recent water safety initiatives in the context of water utility risk management

Paul D. Hamilton [a,*], Paul Gale [b], Simon J.T. Pollard [a]

[a] *Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK*
[b] *59, Fairway Avenue, Tilehurst, Reading, Berkshire, RG30 4QB, UK*

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Abstract

Over the last decade, suppliers of drinking water have recognised the limitations of relying solely on end-product monitoring to ensure safe water quality and have sought to reinforce their approach by adopting preventative strategies where risks are proactively identified, assessed and managed. This is leading to the development of water safety plans; structured 'route maps' for managing risks to water supply, from catchment to consumer taps. This paper reviews the Hazard Analysis and Critical Control Point (HACCP) procedure on which many water safety plans are based and considers its appropriateness in the context of drinking water risk management. We examine water safety plans in a broad context, looking at a variety of monitoring, optimisation and risk management initiatives that can be taken to improve drinking water safety. These are cross-compared using a simple framework that facilitates an integrated approach to water safety. Finally, we look at how risk management practices are being integrated across water companies and how this is likely to affect the future development of water safety plans.
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1. Introduction and context

Internationally, the last two decades have witnessed a large number of microbial and chemical contamination incidents (Table 1), many of which have led to illness and even fatalities in the community. In developed countries, the most serious of these was the 1993 cryptosporidiosis outbreak in Milwaukee (Lisle and Rose, 1995; Solo-Gabriele and Neumeister, 1996; Deininger, 2004; Hrudey and Hrudey, 2004). *Cryptosporidium parvum* is a human and animal pathogen that has exhibited some resistance to the conventional water disinfection method of chlorination (Smith et al., 1990). Water companies have therefore sought to minimise the risk of contamination by ensuring the organism's physical removal from drinking water supplies. In examining the cause of the Milwaukee outbreak, studies such as Lisle and Rose (1995) highlighted a number of flaws in the design and operation at the treatment plant in question; not least a prolonged period of poor coagulation control and filter performance, evidenced by increases in the measured turbidity of water leaving the works. This and other diagnosed incidents in Australia, Canada, Japan, UK, and the USA (Baudin and Laîné, 1998) have led to an increased global awareness of the potential consequences of waterborne cryptosporidiosis and other microbial diseases and have reinforced the need to maintain high standards of process design and operation at vulnerable water treatment works.

A further defining moment was the 1998 *Cryptosporidium* crisis in Sydney (McClellan, 1998; Cunliffe, 2003; Hrudey and Hrudey, 2004). A 'boil water' notice was issued after a high concentration of *Giardia* cysts and *Cryptosporidium* oocysts were found in raw and treated waters. Fortunately, the pathogens were apparently inactive and no illness in the community resulted, although it did serve as a wake-up call for the industry, both in terms of catchment management and the way risks are communicated to the public. For commentators such as Deere and Davison (1998) and Cunliffe (2003), the Sydney incident highlighted the limitations of management based purely on end-product monitoring, and the lack of a coordinated approach to dealing with water quality.

Soon after, another incident, this time resulting in fatalities, took place in Walkerton (Canada) in 2000. Here, the water

* Corresponding author. Tel.: +44 1234 750 111x2570; fax: +44 1234 751 671.
E-mail address: paul.hamilton1@tiscali.co.uk (P.D. Hamilton).

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Table 1
Some documented water quality incidents

Incident	Location	Year	Cause and impact	Ref
Microbial contamination of drinking water[a]	Milwaukee, USA	1993	Sub-optimum design and operation of a water treatment works was suspected to have been responsible for a massive outbreak of cryptosporidiosis, believed to have affected up to 400,000 people and left 69 dead, although these numbers are disputed. Factors that may have contributed to the outbreak include the recycling of used filter washwater back to the head of the works.	Lisle and Rose (1995), Solo-Gabriele and Neumeister (1996), Deininger (2004), Hrudey and Hrudey (2004)
	Gideon, USA	1993	An outbreak of *Salmonella* is believed to have arisen when droppings from nesting pigeons fell into in an open and disused, private water storage tank. These accumulated droppings are thought to have been washed into the drinking water during a programme of mains flushing. Around 500 people became ill and 7 elderly people died.	Deininger (2004), Hrudey and Hrudey (2004)
	Sydney, Aus	1998	High concentrations of *Cryptosporidium* and *Giardia* (oo)cysts were found in a works' raw and treated water. No incidence of disease was reported, although a boil water notice was issued to residents. The official inquiry into the incident was critical of the poor communication and cooperation between Sydney Water and state health officials.	McClellan (1998), Hrudey and Hrudey (2004)
	Walkerton, Can	2000	Around 2300 residents were ill and 7 died from drinking water contaminated with *E. coli* O157:H7 and *Campylobacter jejuni*. The contamination was traced to the run-off from a local farm which had infiltrated a nearby well. Chlorine residuals were not being maintained with operators failing to carry out simple checks and falsifying records.	O'Connor (2002), Deininger (2004), Hrudey and Hrudey (2004)
Chemical contamination of drinking water	Camelford, UK	1988	A stand-in delivery tanker driver pumped 20 tons of aluminium sulphate directly into the final chlorine contact tank at an unmanned works.	Environmental Data Services (1999), Buckley (2004)
	Worcester, UK	1994	Water supplied from a river abstraction works became tainted with low concentrations of a industrial solvent, which had passed through an upstream sewage treatment works. This led to taste and odour problems, inconveniencing around 110,000 customers over a two-day period. No illnesses or health risks were believed to have resulted from this incident.	Furness (2004)
	Glasgow, UK	1997	Around 200 l of diesel were spilled during an unmanned fuel transfer to a mobile generator at a water treatment works. Unbeknownst to the treatment operator, the drain into which this spillage had entered, fed directly into the works' washwater recovery system. The problem lay unrecognised for 24 h. The water supply to 60,000 customers was affected and the water deemed unfit to drink for 8 days.	Fraser (1997), Fawell (2004)

[a] Summaries of microbial disease outbreaks are also presented in Badenoch (1990), Lisle and Rose (1995), Solo-Gabriele and Neumeister (1996), Hrudey et al. (2002) and Hrudey and Hrudey (2004).

supply became contaminated with microbial pathogens after manure was spread on a farm near a public supply well. More than 2300 people became ill and seven people died. The official inquiry (O'Connor, 2002) reported a litany of bad practice prior to and during the incident including the failure of operational staff to maintain effective chlorination of the water supply and carry out routine chlorine residual checks, the falsification of water quality records by staff and the failure of treatment managers to respond satisfactorily to positive microbial tests, any one of which may have significantly reduced the impact of the incident or prevented it altogether. The official report into the Walkerton incident (O'Connor, 2002) recommended that water suppliers adopt a Total Quality Management system based upon

- the adoption of best practices and continuous improvement;
- 'real time' process control (e.g. continuous monitoring of turbidity, chlorine residual, and disinfectant contact time) wherever feasible;
- the effective operation of robust multiple barriers to protect public health;
- preventative rather than strictly reactive strategies to identify and manage risks to public health; and
- effective leadership.

Providing safe drinking water requires sound risk management. This is recognised in, and forms the central feature of, the recent revision to the WHO's (World Health Organisation's) drinking water guidelines (WHO, 2004). The rationale for this approach is that delivering safe water is not just about achieving a high level of compliance (Walker, 2005). Water supply systems can attain this and yet can still have serious latent flaws in their design or operation that are 'accidents waiting to happen'. These may include uncontrolled contamination hazards in water catchments, flaws in treatment design, leaks in distribution systems, and bad operational practices.

Water safety plans are frameworks or 'route maps' that set out preventative, step by step processes for managing water contamination risks. At an international workshop in Bonn, recommendations were made, with the aim of providing "*good, safe drinking water that has the trust of customers*" (AWWA et al., 2001). Key principles were set out for creating an integrated

approach to water safety across the four stages of water supply: (a) catchment, (b) treatment, (c) distribution and (d) customer plumbing systems. It was also recognised, that close cooperation is required between water suppliers, governments, health agencies, environmental agencies, land users and other stakeholder groups to maintain and promote drinking water safety. After a second workshop in 2004, the Bonn Charter was published (IWA, 2004), setting out high level frameworks describing both the operational and institutional arrangements for managing water supplies.

One country that has driven much of the development of water safety plans is Australia. In 1996, the National Health and Medical Research Council (NHMRC) revised its Australian Drinking Water Guidelines (NHMRC, 1996). This noted that testing does not guarantee the safety of water supplies, as it is quite possible that contamination may occur between sampling events. In 2001, the NHMRC released its 'Framework for Management of Drinking Water Quality' (NHMRC, 2001). The Framework listed a sequence of 12 elements considered to be good practice for the management of drinking water supplies from catchment to consumer. In 2002, the NHMRC provisionally redrafted its guidelines (NHMRC, 2002), incorporating the Framework's 12 elements as its focus. An amended draft was officially endorsed two years later (NHMRC, 2004). This was intended to introduce a standard approach throughout the industry and establish due diligence and credibility. The process is divided up into four main sections:

- a commitment to drinking water quality management;
- system analysis and management;
- supporting requirements e.g. employee training, community involvement, research and development, systems for documenting and reporting etc.; and
- review.

In a field that is largely practitioner-led, the development and implementation of water safety plans have varied widely. The following study considers several different approaches to water safety planning and proposes a conceptualisation that brings water safety plans and other quality management initiatives together under a single umbrella. Finally it looks briefly at wider risk management practices carried out by the industry. Utilities are seeking to adopt a more consistent, integrated approach to managing risks across their organisations, a trend which is likely to further affect the development of water safety plans.

2. Hazard Analysis and Critical Control Point (HACCP) approach

Most water safety plans (e.g. NHMRC, 2004; NZMOH, 2001; UKWIR, 2003; WHO, 2004) published to date have been based on adaptive forms of the HACCP procedure. Its application within the water sector has been widely discussed in the literature (e.g. Havelaar, 1994; Deere and Davison, 1998; Deere et al., 2001; Stevens, 2003; Hrudey and Hrudey, 2004). In brief, HACCP was developed by the US Space Agency in the 1960s to ensure the safe manufacture of foodstuffs to be used in spaceflight. It was quickly implemented across the food industry, and in principle, provides a hazard-based monitoring system for protecting water supplies from different contaminants. In 1997, the Codex Alimentarius Commission released its most recent guidelines for HACCP application within the food industry (CAC, 1997), restating its seven key principles:

1. Conduct a hazard analysis.
2. Determine the critical control points (CCP).
3. Establish critical limit(s).
4. Establish a system to monitor control of the CCP.
5. Establish the corrective action to be taken when monitoring indicates that a particular CCP is not under control.
6. Establish procedures for verification to confirm that the HACCP system is working effectively.
7. Establish documentation concerning all procedures and records appropriate to these principles and their application.

HACCP promotes the proactive management of hazards through the identification of 'critical control points' where they can be monitored and reduced. Its application to drinking water supplies was first described in the Netherlands by Havelaar (1994). Since then it has gained some prominence internationally, but has been championed, in particular, by the Australian water industry. Following the 1998 *Cryptosporidium* crisis in Sydney, Deere and Davison (1998) argued that Sydney Water should adopt a full HACCP system as the most cost-effective means of assuring drinking water safety, pointing out that the UK system of increased end-product monitoring (for *Cryptosporidium*) had been designed primarily for legal reasons and not specifically to protect the public.

In terms of water safety, a limitation of the HACCP methodology, as originally conceived, is that it is largely concerned with hazards, not risks. Hrudey and Hrudey (2004) note that *"a formalized structure has evolved with HACCP in the food industry and the prospect of (water suppliers) being HACCP-certified is appealing. These considerations need not be an impediment to effective application of the useful HACCP principles. The caution is that HACCP must be sensibly and pragmatically adapted to identify hazards and then to assess and manage their associated risks for drinking water systems"*. This perceived weakness was partially addressed by CAC (1997), at least in principle, which recommended that an assessment of hazard severity and likelihood could be conducted as part of the 'hazard analysis' process. Indeed, the most credible advocates of the HACCP procedure for drinking water systems such as Mullenger et al. (2002) and Hellier (2003) have also extended their plans to incorporate elements of risk assessment, typically employing a semi-quantitative method for ranking likelihood and consequence of initiating events.

Progressing from hazard management to effective risk management requires a richer understanding of the technical, managerial and humans systems within which risks may be realised (Pollard et al., 2005). NHMRC (2004) point out that HACCP's scope and application is limited in several important areas such as employee training, emergency response and community involvement. As they concede, however, HACCP was never designed to be a fully comprehensive management system, but

was intended to be added on to existing, good management practices. The NHMRC (2004) Framework therefore draws not only from HACCP, but also from other established systems such as ISO 9001 (ISO, 2000) and AS/NZS 4360 (AS/NZS, 1999) and is itself designed to be flexible and be integrated with other programmes and systems already present in organisations. Thus, although HACCP can be considered to be a blueprint for many water safety plans, it has also been largely superseded by these newer frameworks.

Another contentious issue regarding HACCP is the question of how readily the concept of CCPs can be transferred to the water industry. Codex Alimentarius Commission (1997) defines a CCP as *"a step at which control can be applied and is essential to prevent or eliminate a food safety hazard or reduce it to an acceptable level."* When trying to apply this within the context of water safety, however, it is sometimes difficult to gauge the criticality of the CCP i.e. what determines a control as 'essential'. Nokes and Taylor (2003), for example, have argued that by concentrating on CCPs, water suppliers may perceive that they need to identify only a limited number of control points at the expense of a wide range of other 'preventative measures' that may also be important in reducing risk. Another potential difficulty with using HACCP directly within the water industry is that the concepts of 'control points' and 'critical limits' tend to be viable only when applied to treatment processes (Hellier, 2003; Nokes and Taylor, 2003), which are amenable to, and thus receive a more intense, varied and quantitative level of monitoring than other stages in the water supply chain; catchment management, for example.

Despite this, however, advocates of HACCP's such as Mullenger et al. (2002) and Hellier (2003) maintain that its application can yield several advantages to drinking water safety. In the case of Melbourne Water, Hellier (2003) concludes that their resulting HACCP document became a road-mapping of all the systems that control drinking water quality and due to the introduction of regular auditing became a driving force for improving systems. In particular, Hellier cites five areas of improvement:

- the development of 15 new operational procedures;
- an evaluation of catchdrains around reservoirs;
- an adjustment of treatment plant alarm settings;
- documentation of corrective actions plans; and
- training of operators on response levels to alarms at critical sites.

Similarly, Mullenger et al. (2002) relate positive experiences from South East Water's (Australia) implementation of a HACCP plan across all of its water operations. Although staff were initially 'unenthusiastic' about the initiative, its adoption appeared to lead to an increase in knowledge and understanding of the water supply system at all levels and an improved ability to identify hazards to water quality or supply. This is a frequently cited outcome of many such management systems in that the analysis itself reveals enhanced knowledge of system behaviour and vulnerability. This had led to a number of changes to operating procedures.

Another example is presented in Metge et al. (2003), who describe the application of HACCP on three critical plants on the Morsang sur Seine River in France. Their analysis realised three key hazardous events:

- aluminium contamination due to coagulant overfeeding;
- microbiological contamination due to chlorine underfeeding; and
- microbiological contamination due to chlorine dysfunction.

Critical limits were set for chlorine and residual aluminium concentrations. Although it is possible that this exercise did provide some benefit (e.g. through the tightening of controls), HACCP and water safety plans in general, will only be useful if they lead to a demonstrable and actionable improvements either in understanding or in the design or operation of a water supply system. If the approach is to be truly proactive, water suppliers should try to avoid identifying hazards retrospectively to suit existing controls; otherwise the exercise may become bureaucratic and tend towards tokenism rather than active risk management.

Perhaps the most critical aspect to HACCP and water safety plans is that these may inadvertently become exercises in documenting something that companies already do rather than a step change in the approach to managing risk. A salutary lesson for risk managers can be learned from commentaries on the implementation of the international quality standard ISO 9000 (Seddon, 2000; Hoyle, 2001). Hoyle (2001) argues that although some organisations used the standard wisely, for many, it became a 'badge on the wall' with little to do with improving performance. Some believed the standard was only about documenting what they did. Moreover, the persistence of auditors to require documentation led to situations where documentation only existed in case something went wrong. A similar point is made by Hrudey and Hrudey (2004) regarding HACCP, namely that if it is pursued primarily for public relations, little risk reduction may be achieved.

3. Multiple barrier approach

Although many would contend that the HACCP system does not preclude a 'multiple barrier' approach to water quality management, arguably neither does it really promote this line (Nokes and Taylor, 2003). In developing their water safety plans, many water suppliers/administrators have sought to take a broader perspective, looking at the widest possible range of 'preventative' or 'control measures' from catchment to tap to protect the public. These can include qualitative checks and measures such as the regular inspection of catchment areas as well as continuous on-line monitoring. For example, the WHO recently set out an authoritative ten-step process for developing safety plans for water systems (WHO, 2004). As with the NHMRC (2004) guidelines, this advocates that water suppliers focus on the broadest possible range of 'control measures'. In the UK, a set of frameworks and guidance material has recently been published to help water companies implement water safety plans from catchment to tap (UKWIR, 2003). Again the focus has been placed on 'risk reduction measures' rather than CCPs

for hazards. A practical set of guidelines has also been developed by the New Zealand Ministry of Health (NZMOH, 2001). This promotes the concept of multiple barriers although here, a conscious decision was made to focus on hazard identification by reference to the initiating events or situations that may lead to hazards being introduced in the water. As reviewed by Pollard et al. (2004), the NZMOH approach targets smaller systems and may be particularly valuable for systems with limited technical resources. The rationale behind the NZMOH framework is explained in Nokes and Taylor (2003). They reflect that for smaller water suppliers, whose operational staff may be less familiar with water quality issues, it may be simpler for them to try to prevent certain, well-accepted hazardous events from occurring at the plant level (e.g. the loss of chlorination) rather than trying to direct spare resources to hazards they may know little about and have less control over (e.g. *E. coli*, *Cryptosporidium* in catchments).

3.1. Assessing barrier integrity

Once contamination barriers have been identified within a system, water suppliers need to demonstrate their effectiveness continuously either through direct measurement or a programme of spot checks and/or maintenance. Many treatment barriers can be assessed by on-line monitoring and sample analysis. A common means of assessing treatment barriers for the protozoan pathogen *Cryptosporidium*, for example, is to measure the removal of water turbidity across a treatment process. This is typically cited as a log-removal which conveys the order of magnitude of the removal. For example, '1-log' removal is equivalent to a 90% reduction, '2-log' equivalent to a 99% reduction etc. Studies have shown that there is often a direct correlation between the level of particles removed by a process and the removal of microbial pathogens such as *Cryptosporidium* oocysts (Hamilton et al., 2002). A criticism that could be leveled at some approaches to barrier analysis is that approaches may be driven more by a willingness to comply and less by concern for assessing and managing risk, leading to a progressive overstating of a barrier's effectiveness. Often overlooked is the significance of (a) barrier integrity and (b) barrier independence.

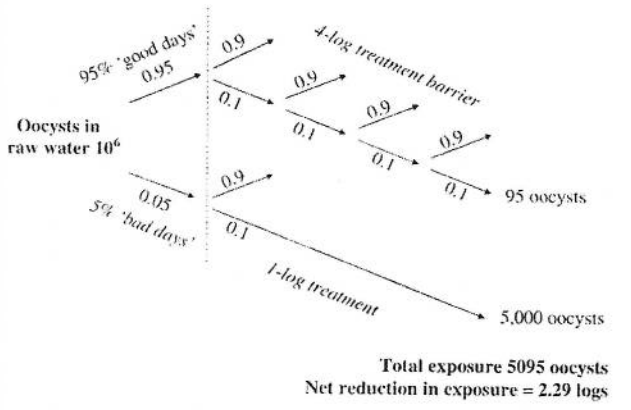


Fig. 1. An example showing impact of 'bad days' on overall effectiveness of a treatment process (after Gale, 2002).

Two concepts that are highly relevant with regard to barrier integrity are 'bad days and bypass' (Gale, 2002). 'Bypass' can be envisaged as 'spatial variation' where certain areas within each batch (i.e. a proportion of water to be treated) are not treated to the full extent or where raw material continuously contaminates each batch of treated material. In contrast, 'bad days' occur when the overall treatment efficiency falters or fails completely for a time giving rise to 'temporal' variation. Using probabilistic event trees, Gale (2002) shows how 'bad days' can have a substantial effect on overall treatment performance. For example, if a process that typically operates at 4-log (99.99%) oocyst removal drops down to 1-log (90%) removal, say for 5% of the time, then the net result is that effectively the overall performance of the process is reduced to 2.3-logs (Fig. 1). The net risk of *Cryptosporidium* oocyst presence in the drinking water supplied to consumers is therefore increased fifty-fold. This can have serious implications in terms of risk management and shows the need to understand and target the weak points in process barriers.

'Bypass' can have a similar deleterious effect on a system. Gale (2002) describes a hypothetical situation where adding extra filtration stages to a treatment process to increase *Cryptosporidium* oocyst removal, yields diminishing returns if a small proportion of raw water bypasses the works in some way e.g. as a result of infiltration within the distribution system. For example, under a scenario where 1% of the total flow bypasses treatment, a 3-log (99.9%) or higher removal system is effectively reduced to a 2-log (99%) system. Examples of bypass within the field of water supply include:

- exposure of populations to microbial pathogens through less tightly regulated private water supplies;
- ingress into water supply distribution systems;
- short-circuiting of raw water storage reservoirs;
- surface water intrusion into groundwater supplies;
- deliberate bypass of a treatment stage;
- reduced filter effectiveness during ripening after backwashing;
- failure by staff to observe correct operational procedures and practices;
- improper application of fertilizers and pesticides to land in drinking water catchments;
- illegal discharge of trade wastes into sewers or water courses upstream of a treatment works; and
- sabotage or deliberately released contamination.

There can be a tendency for treatment scientists to cite their works' performance in terms of percentile statistics. Although this may be a sensible approach when benchmarking plant performance or presenting regulatory compliance, for example, to allow otherwise well-run works some leeway, arguably this is not compatible with a true water safety approach. In terms of risk management, emphasis should be placed on identifying weak spots within the process flowsheet and testing worst-case event scenarios and not merely in achieving a level of compliance. Care must be taken not to be complacent when assessing barriers, despite the obvious requirement to satisfy water quality regulators and the public. In order to engender a proactive and transparent culture of risk management within the water supply industry, a

different mindset may need to be adopted by water suppliers and regulatory bodies alike when dealing with risk as opposed to straightforward compliance issues.

Barriers should also exhibit a high degree of independency of one another, so that failure of one barrier does not reduce the efficacy of subsequent barriers. In terms of water treatment, a potential problem is posed by flooding or river spate conditions that may have a 'domino effect' in reducing the effectiveness of treatment barriers in succession. Rapidly deteriorating raw water quality presents complications for operators trying to maintain optimal coagulant dosing, which in turn can lead to sub-optimal filter performance and increased chlorine demand. This issue is also discussed in LeChevallier and Au (2004). A good example of an independent barrier is the use of ultraviolet (uv) irradiation plants alongside conventional physical barriers (clarification and filtration) to deactivate microbial pathogens in the final water. Although, increased particle numbers in treated water do reduce the effectiveness of uv irradiation, studies by Christensen and Linden (2003) have shown that the effect is negligible in water below 10 NTU turbidity, a level far in excess of most drinking water supplies. In the UK, however, the effectiveness of uv for *Cryptosporidium* deactivation is not officially recognised in water quality legislation: a water supplier can still potentially be prosecuted if the oocyst concentration exceeds 1 per 10 l (on average) of drinking water sampled, irrespective of whether they have been deactivated or not (DETR, 1999). Clearly then, managing risks to water safety requires more than the identification of hazards and their control points. It requires an integrated and complete view of the vulnerabilities to the system from catchment to tap.

4. The US Partnership of Safe Water

Another significant water safety initiative is the US Partnership of Safe Water. This is a voluntary cooperation formed jointly in 1995 by the US Environmental Protection Agency, the American Water Works Association and several other drinking water organisations with over 200 surface water treatment works in the US currently participating in the scheme (AWWA, 2005). The Partnership currently recognises four levels of accreditation. It has evolved separately from HACCP and although it is not intended to be directly analogous, does have some elements in common with a water safety approach, such as the focus on 'performance limiting factors', which has some similarity to the 'preventative measures' of Nokes and Taylor (2003). However, unlike other water safety plans, the Partnership is not 'risk-based' in the sense that it does not adopt risk assessment as a starting point for risk management. WHO (2004) concedes that some elements of a water safety plan will often be implemented as part of drinking water suppliers' usual practice, but that existing systems may not include tailored hazard identification as a starting point for risk management. It is possible that the Partnership's code could yet be broadened to incorporate more elements of proactive hazard identification and risk management thereby elevating it to a full water safety approach. That is not to say that the Partnership does not reduce risks. Indeed, the system is a proactive optimisation programme that encourages good practice and, if successful in effecting net reductions in turbidity, for example, should lead to significant lowering of microbial risk at high risk works. Moreover, the quality assurance provided by the Partnership is deemed to be highly credible, having been informed and authenticated by an independent third party group. Arguably, in a regulated system, it is unlikely that all optimisation programmes will be determined uniquely through companies' own risk assessment projects. Works' design and operation will continue to be influenced by new regulatory standards and 'good practice' guides such as that provided by the Partnership and other expert groups, reviews and inquiries (e.g. Badenoch, 1990, 1995; Bouchier, 1998). This suggests that although initiatives such as the Partnership for Safe Water may benefit from a stronger focus on risk, conversely they may also themselves contain elements that would be useful additions to any water quality management system.

5. An integrated approach to water safety

In order to fully provide *"good, safe drinking water that has the trust of customers"*, water companies need to adopt an integrated approach to managing their supplies, one that not only includes a water safety plan at its core, but that also encompasses a suite of other monitoring, control and other risk assessment initiatives. One way in which this can be conceptualised is to use the framework proposed in Fig. 2. Its premise is that an effective approach to water quality management is characterized at least by the following seven elements:

- *Risk assessment* — A sensible approach to water safety should proactively and continuously seek out threats to water safety and assess risks in terms of perceived likelihood and consequence. This process typically includes activities such as hazard identification and semi-quantitative risk ranking, but could feasibly encompass a range of other analytical tools e.g. complex GIS models (MacGillivray et al., 2006).
- *System controls* — Risks can be reduced or eliminated only by improving the water supply system from catchment to tap, according to time and cost constraints. This can include tightening management controls (e.g. staff training) as well as operational controls (process design and operation) as promoted in AWWA (2005).
- *System monitoring* — a key component of water safety is the monitoring (through sample testing and on-line monitors) of water quality indicators at different stages in the water supply system. This may be conducted to meet legislative and regulatory requirements or for companies' own purposes of internal quality control or research. "Monitoring" can also include qualitative assessments of water quality (e.g. taste and odour tests) as well as routine spot checks of equipment, constructions and areas (e.g. security checks, reservoir inspections and catchment surveys).
- *Risk controls* — These refer to control measures undertaken specifically as part of a risk management programme. Not all of these can or need to be monitored. These may include absolute barriers where the hazard is removed or eliminated.

- *Risk monitoring* — Conversely, not all risks deemed to be significant may be controlled. These can include 'watched risks' believed by the supplier to be borderline, or high risks where no adequate controls currently exist. The risk monitoring process can be complemented by quantitative techniques (e.g. extreme value probability plotting for microbial pathogens, Ongerth, 1989). This can be useful as long as the 'systems-view' ethos of water safety plans is not compromised i.e. that suppliers do assume that a supply is safe solely from its monitoring record.
- *Monitor-based controls* — It is proposed that some of these initiatives (e.g. statistical process control, turbidity improvement programmes, works intake protection monitoring) have such an importance within the field of quality management that they should be considered in their own right, irrespective of whether or not they are explicitly 'risk-based' and included within water safety plans.
- *Barrier validation* — The continuous validation of barrier integrity is a key part of water safety plans. This process can include conventional CCP monitoring as well as quali site inspections, for example. Aspects which arguably be given greater emphasis in water safety plans importance of 'bad days and bypass' with regard integrity, the possible interaction between cert and the level of residual risk in the system.

In terms of water safety plans, the area management del are the m predicated is the proac aspects of that are w features or . However, other out as part of 'good practice' can also play an i quality management. The conceptualisation provided used as a framework for organising and integrating all the initiatives.

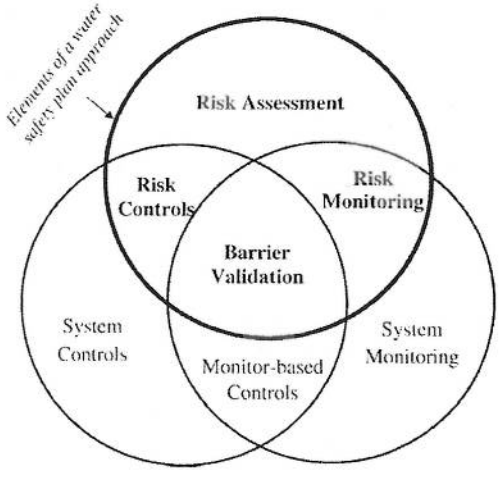


Fig. 2. A conceptualisation of different water quality management initiatives and their inter-relationship.

6. Links to other areas of business

As with many other utility sectors, water suppliers are increasingly seeking to establish sound risk governance throughout all levels of the business to safeguard the interests of their customers and investors. To this end, different risk assessment tools and techniques have been developed that facilitate a consistent approach to risk management across companies, thereby promoting an 'integrated' approach where risk information can be read across from one business area to another.

In England and Wales, for example, water companies are required to adopt a risk-based approach in other areas of regulated business, such as in their obligation to develop and implement 'Distribution Operation and Maintenance Strategies' (DOMS) for the proactive management of drinking water distribution systems (Drinking Water Inspectorate, 2002). A risk analysis approach is also advocated by the financial regulator as a means to prioritise future capital maintenance (Office of Water Services, 2002). Because of the similarity of the risk scoring systems used in these and other initiatives, it would be sensible for a company to standardize its approach to assessing risk in these areas and, where ible, to encourage 'read-across' between them. To this end, panies are now developing their own asset and/or oring systems that allow them to prioritise risks to . Leverett (2003) details how Severn Trent Water iously assesses routine and non-routine tasks in four according to their likelihood and impact on water water quantity, health and safety, and the environment. risks considered to be significant are linked to the any's risk management database, allowing information to shared across the company, and a central tracking of risk anagement actions. Similarly, Scottish Water have developed an nterrelated asset risk and criticality scoring mechanism that assesses the 'total business impact' of asset failures across the company in relation to its core business objectives (Lifton and Smeaton, 2003, 2005). This is in essence a source-to-tap FMECA (Failure Mode and Effects Criticality Analysis) approach, but with the addition of a business impact scoring system that assigns a points' score to different asset failure scenarios according to criteria such as loss of service, environmental impact, and loss of reputation. The result is an integrated system that extends across all levels of the business with the same tools used to prioritise capital investment, plan capital maintenance, as well as develop plant maintenance schedules to minimise the risk of electrical and mechanical failure. Ultimately, the exact shape and form of water safety plan adopted by water companies should be designed with these wider risk management practices in mind.

7. Conclusions

The way in which the international water sector manages risk is becoming integrated with other business processes and made more explicit. Risk management is becoming recognised as central to the provision of safe drinking water.

Water suppliers are increasingly seeking to develop and implement proactive and preventative water safety plans in addition to compliance monitoring regimes to improve water safety.

HACCP can be a useful tool in establishing and tightening treatment process controls, but most modern water safety plans have typically sought to extend this further and have adopted a wider-ranging, multiple barrier approach, that looks at a broad range of 'preventative measures' for managing risks from catchment to tap.

The concepts of bad days and bypass are important within the field of water safety as is barrier independency. A different mindset may need to be taken by water companies and regulators alike to ensure that risks are managed in an effective and transparent way.

Other risk management, optimisation and monitoring initiatives are also important in protecting water supplies. A framework provided can be used to for organising these into an integrated system.

As the industry moves towards a more integrated approach to managing its risks, the ways in which risk information and strategies are 'read across' to other business areas e.g. capital investment planning is also becoming increasingly important. This should also be a prime consideration for companies when developing their water safety plans.

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Recent developments in the application of risk analysis to waste technologies

S.J.T. Pollard [a,*], R. Smith [a], P.J. Longhurst [a], G.H. Eduljee [b], D. Hall [c]

[a] Integrated Waste Management Centre, School of Industrial and Manufacturing Science, Cranfield University, Cranfield Bedfordshire, MK43 0AL, UK
[b] SITA Limited, Maidenhead, SL6 1ES, UK
[c] Golder Associates (UK) Ltd., Nottingham, NG12 4DG, UK

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Abstract

The European waste sector is undergoing a period of unprecedented change driven by business consolidation, new legislation and heightened public and government scrutiny. One feature is the transition of the sector towards a process industry with increased pre-treatment of wastes prior to the disposal of residues and the co-location of technologies at single sites, often also for resource recovery and residuals management. Waste technologies such as in-vessel composting, the thermal treatment of clinical waste, the stabilisation of hazardous wastes, biomass gasification, sludge combustion and the use of wastes as fuel, present operators and regulators with new challenges as to their safe and environmentally responsible operation. A second feature of recent change is an increased regulatory emphasis on public and ecosystem health and the need for assessments of risk to and from waste installations. Public confidence in waste management, secured in part through enforcement of the planning and permitting regimes and sound operational performance, is central to establishing the infrastructure of new waste technologies. Well-informed risk management plays a critical role. We discuss recent developments in risk analysis within the sector and the future needs of risk analysis that are required to respond to the new waste and resource management agenda.
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Keywords: Risk; Analysis; Waste; Management; Developments; Process; Technology

1. Introduction

Environmental risk assessment is an established feature of modern environmental decisions and has been used successfully to target risk management actions on the key drivers of risk across a range of anthropogenic and natural hazards (European Environment Agency, 1998). The basis of risk assessment (Vose, 2000) is an evaluation of the connectivity between the source of a hazard and an environmental receptor — something one wishes to protect. Without a "dose" — an amount or duration of exposure to a harmful agent, there can be no harm at the receptor and one purpose of risk assessment must, therefore, be to evaluate the likelihood and consequences of determining this harm. Many regulators now promote a tiered approach to risk assessment that allows for an initial screening and prioritisation of risk prior to undertaking more detailed assessments (DETR et al., 2000). This assists in ensuring that problems are well-defined, that potential sources, pathways and receptors are comprehensively considered and that subsequent risk assessment effort and resources are focussed on the key risks identified at a screening stage.

The waste management sector applies risk assessment widely to issues such as the risks to groundwater from landfills (Environment Agency, 1996; Hall et al., 2003), the potential risks to human health from continuous stack emissions (Harrop and Pollard, 1998; Eduljee, 2001) and to the potential health impacts from exposures to landfill gas (Attenborough et al., 2002). The development of conceptual models, site-specific exposure scenarios and application of the source-pathway-receptor approach (DETR et al., 2000; Environment Agency, 2000; WHO, 2000), supported by quantitative analysis (Vose, 2000) where appropriate, is now commonplace. Environmental risk tools are based upon models that characterise pollutant pathways in open environmental systems and assume, or model, the release of the source of a hazard to the environment, be it through mechanisms such as liner failure, the episodic flux of emissions to air, or diffusive flow through a landfill cap. Modern groundwater risk assessments for landfills couple a performance assessment of the liner system (Environment Agency, 2001; Hall

* Corresponding author. Tel.: +44 1234 754101; fax: +44 751671.
E-mail address: s.pollard@cranfield.ac.uk (S.J.T. Pollard).

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et al., 2003) with a contaminant transport model to assess potential risks to receptors such as downgradient abstraction boreholes (Fig. 1). The numerical approach to characterising pathways of environmental exposure (e.g. groundwater dispersion or air diffusion) and modelling the distribution of contaminants in the environment, has proved powerful for the developers and operators of waste facilities in securing environmental permits (Garrick, 2002).

A shift within the sector towards waste process technologies, and the attending concerns raised about the potential environmental harm (Dolk, 2002; Defra, 2004) that may result from routine, unmanaged or accidental releases to the environment however, is forcing a widening of the portfolio of risk tools required (National Research Council, 2000; Environment Agency, 2000). Furthermore, we are witnessing a more joined up approach to the assessment of risks from waste facilities (Environment Agency, 2004a), with a growing need to assess a larger set of causal events and subsequent exposures that might result in detrimental impacts — including issues of odour nuisance, exposure to trace components in landfill gas and to airborne microorganisms from biological waste treatment, losses in slope stability at landfills and risks from process failures in engineered systems. This paper discusses these developments and attempts a synthesis of the role of risk assessment in the modern waste and resource management sector.

1.1. Risk analysis tools

Risk assessment tools can be categorised by reference to the nature of the risk problem they are used to assess. Generally, risk analysts are concerned with three categories of risk problem that can be considered as part of a causal chain of events (Pollard and Guy, 2001; Fig. 2):

(i) *source term* risks associated with the risk of an *initiating event* or combination of events that deviate from normal operating conditions and may result in a *release* to the environment (e.g. fire risk; the loss of flame at a pumped landfill gas flare unit; the catastrophic release of fire wash down from an on-site collection tank; the risk of mixing incompatible wastes; a catastrophic landfill liner failure; inventory loss of treatment reagents or stored wastes; inappropriate mixing of hazardous wastes during treatment; CIRIA, 1997);

(ii) *pathway* risks that address the likelihood of a certain *exposure* of an environmental receptor to a hazard following an initial release (e.g. grounding of a plume downwind of an incinerator stack; movement of a leachate plume towards and abstraction point; off-site bioaerosol exposure from the turning of windrows at a composting facility; Pollard et al., 1999); and

(iii) the risks of harm to *receptors* that might occur as a result of the exposure (e.g. adverse human or ecological health effects as a result of exposure to toxic/asphyxiant gases; a toxic overload to biological wastewater treatment plant as a result of a shock load of hazardous waste illegally disposed to foul sewer; occupational health effects experienced by workers at enclosed composting facilities; needlestick injuries and their consequences to medical waste management operatives).

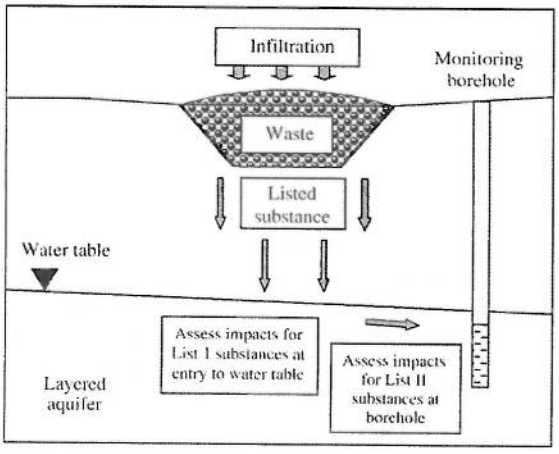


Fig. 1. Basis for the combined performance and risk assessment of landfills and their potential impact on downgradient abstraction points, here by reference to listed substances in the EC Groundwater Directive (Environment Agency, 2000).

Each of these types of problem has associated with it certain categories of risk analysis tools (Fig. 2) that tend to dominate for the analysis in each case. In part, because of the regulatory separation between health and safety and environmental concerns, these tools have historically developed in isolation of one another with little connection between the outputs of one analysis and the input requirements of another. In the future, the integrated pollution and prevention control will ensure that these aspects are more integrated.

Risk analysis tools are also available at a range of tiers of technical sophistication (qualitative, semi-quantitative, quantitative-deterministic, quantitative-probabilistic; DETR et al., 2000; Pollard et al., 2002) and, in deciding on the application of techniques, risk analysts need to consider both (i) the appropriate tool by reference to the type of risk problem being studied (Fig. 2); and (ii) an appropriate level of sophistication selected as needs, complexities, priorities and data allow (Pollard et al., 1995). Changes occurring within the sector are likely to remove the historic barriers between these types of risk problem and their analysis. New guidance for landfill operators in the UK, for example (Environment Agency, 2004a), promotes assessing and presenting the risks for a site as a whole, rather than considering the significance of risks from individual hazards in isolation of one another. This will allow operators and regulators to focus on the priority risks to health and the environment and identify common research needs for the improved understanding of landfill process, for example. Integrated pollution prevention and control is also forcing consideration of risk management at source (pollution prevention) as well as a comparative analysis of risks to the multimedia environment. Under these developments, a broader set of risks (other than just to the aquatic and atmospheric environment) require analysis and comparison.

2. Developing a portfolio of risk analysis tools

2.1. Process risk analysis

In the modern waste sector, much of the waste processing required prior to residuals management will occur in engineered systems, with linked unit processes. Whilst not at the scale or sophistication of the chemicals process sector, waste technologies adopt process engineering principles in their design and optimisation. Here, material flows and mass balances are represented by process flowsheets (Fig. 3) and system layout diagrams. The performance of, and risks from, unit processes can be assessed using tools such as failure mode and effects analysis (FMEA) and event tree analysis (ETA). These tools, used widely in the chemical, oil, nuclear and water sectors, are increasingly applied to waste process flowsheets. They offer the advantage of representing the process system in its entirety and allow vulnerabilities to process failure to be assessed. Though not infallible and requiring application with strict reference to operational expertise (HSE, 2003), these tools can be used to infer the key routes of environmental exposure following a release, providing the system is properly represented, and so inform the prioritisation of risk management actions, including contingency planning in the future. One might reasonably imagine that some of the more common waste management facility incidents experienced in the UK (the inappropriate mixing of wastes during treatment, loss of stored wastes to the aquatic environment) might have been avoided through the active adoption of process risk analysis during design, plant layout and operation.

Fault tree analyses select an undesired event (such as an engineering failure, a fire or an inadvertent mixing of incompatible wastes) and trace it back to the possible system causes, which can be component failures, human error or other factors that could lead to the undesired 'top' event. The causes are related using Boolean logic relationships (i.e. AND/OR 'gates') to allow the root causes of the failure of the system to be identified and modelled (Fig. 4). Where quality reliability data are available, quantitative FMEA allows conditional probabilities to be assigned to the various failure modes.

The nuclear sector has made long-standing and extensive use of FMEA in its performance assessments of radioactive waste repositories (Watts, 2001; BNFL, 2002) and some of these engineering risk tools are now being applied to conventional hazardous waste management facilities in the US and Europe (Garrick, 2002; Shaw et al., 2002).

In contrast, event tree analysis starts with the initiating event (e.g. the failure of a leachate treatment system, the release of a cloud of hazardous gas; the overflow of an oil/water interceptor) and sets out the onward consequences of the release — the environmental consequences of a process accident, for example. As with many risk techniques, fault and event tree analyses require process data to quantify the contributory causes and consequences and their contingent probabilities, though both may be used qualitatively. Data can be difficult to source and quantification relies on expert judgments made on the basis of performance data and long-standing operational expertise. Event tree analysis is seeing particular use for quantitative microbial risk assessment (Fig. 4); for example, in the assessment of pathogenic risks from the disposal of sewage sludge to land on which crops may be grown for human consumption (Gale, 2001), in assessing the pathogenic risks of composting of meat-containing catering wastes, and in assessing the potential risks to human health from the disposal and onward environmental fate of transmissible spongiform encephalopathy (TSE) agents (Hirschhorn, 1999; BRS, 2001; WRc, 1998; Fig. 5). Whilst offering presentational clarity, however, the application of tools used conventionally for closed engineered systems to open environmental settings has its limitations, in that a certain uniformity of structure is imposed on the fate and transport of agents within the environment. The construction of event trees for environmental exposures is open to conceptual bias in this sense and one must be especially cautious of quantitative tools in this regard, because mass balances treated as single 'legs' in an event tree may in reality be dispersed among several environmental compartments.

The requirements of the European Council (EC) Landfill Directive (1999/31/EC) on the progressive reduction of biodegradable waste, the growth in waste processing and the additional requirement under integrated pollution, prevention and control to assess the risks of accidents and their consequences for waste management installations are likely to encourage greater use of risk tools for assessing process failures (e.g. of leachate treatment plant, of gas collection and combustion systems, of

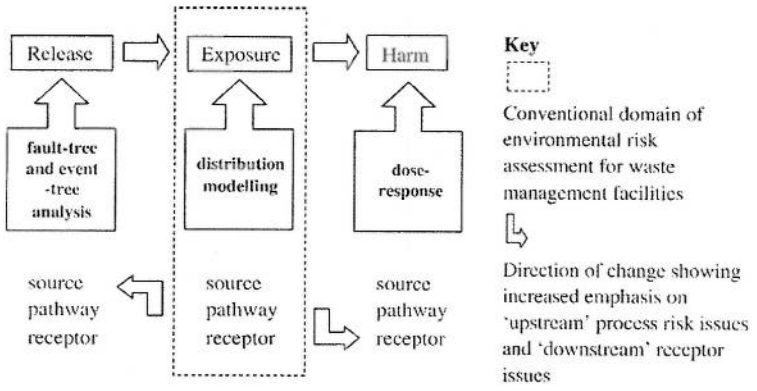


Fig. 2. Basic typology of risk assessment tools and emphasis.

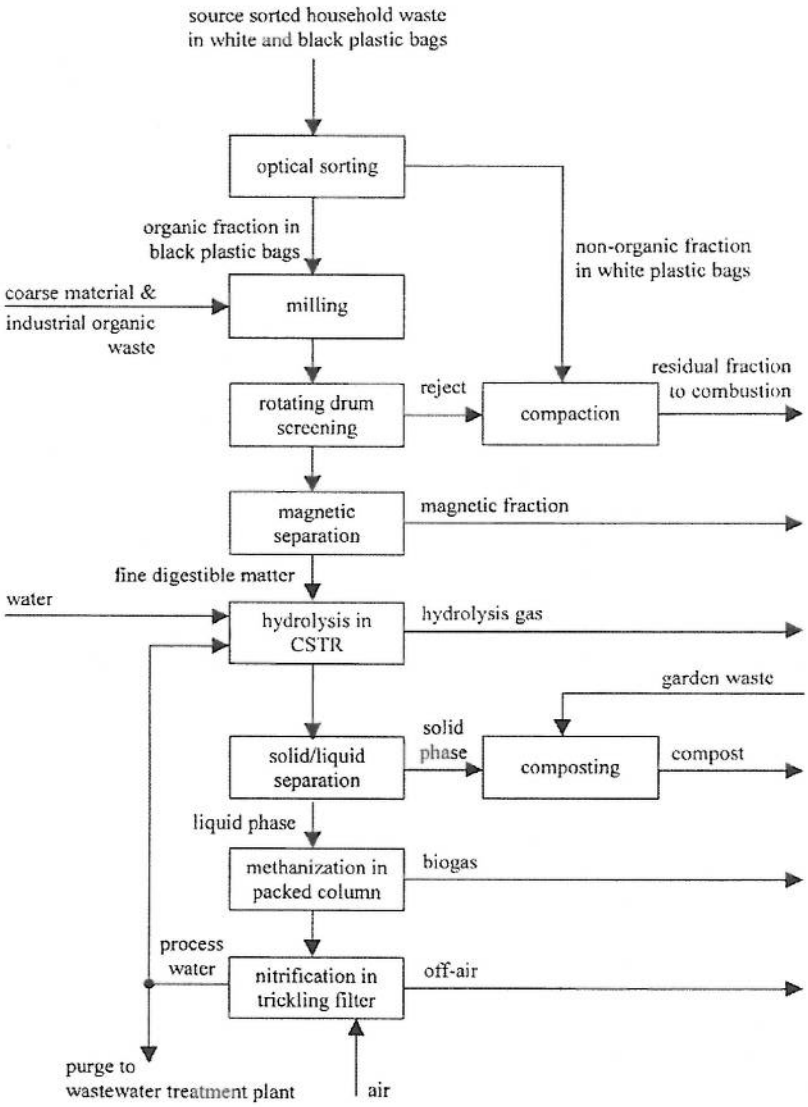


Fig. 3. Simplified process flowsheet for the two-step anaerobic degradation plant, Sobacken, Borås, Sweden for wet organic household waste (after Ecke, 1997). The unit process sequence includes a mixing tank, a hydrolysis reactor, dewatering, a methanogenic filter and a nitrification tower. The plant started operation in 1995 with an annual capacity of ca. 9000 t of organic waste fraction. The digestate is post-treated by composting.

emissions control equipment) and the significance of risks from combined hazards, such as from flooding at hazardous waste storage treatment facilities. In this regard, hazard and operability (HAZOP) tools for assessing process safety, and hazard analysis critical control point (HACCP) frameworks for identifying risk-critical points in multi-unit systems can also be applied to waste processing. The latter approach, adapted from the food technology literature and reviewed for the water sector in this volume, features in European proposals for the management of pathogenic hazards from biosolids (Godfree, 2001) and composting practices under proposed European legislation.

2.2. Environmental exposures and risk

Environmental systems are open, complex, dynamic and heterogeneous. Risks to and from the environment are determined within a combined spatial and temporal context. Models of the environment for its analysis (Schnoor, 1996) often belie this reality but, in simplifying the system, offer the benefit of rational analysis within the confines of the model constructed. Using conceptual models it is possible to assess exposures within the system boundaries and postulate the relative probabilities of exposure mediated through environmental systems. In doing so, risk analysts aim to identify and prioritise key routes of exposure and, where exposures are found to be unacceptable, propose management responses accordingly. Given the complexity involved, practitioners often resort to numerical approaches that allow subtle distinctions between the drivers of exposure to be explored by sensitivity analyses. Conventionally, but by no means universally, quantitative risk assessment is reserved for exposures that are already deemed significant.

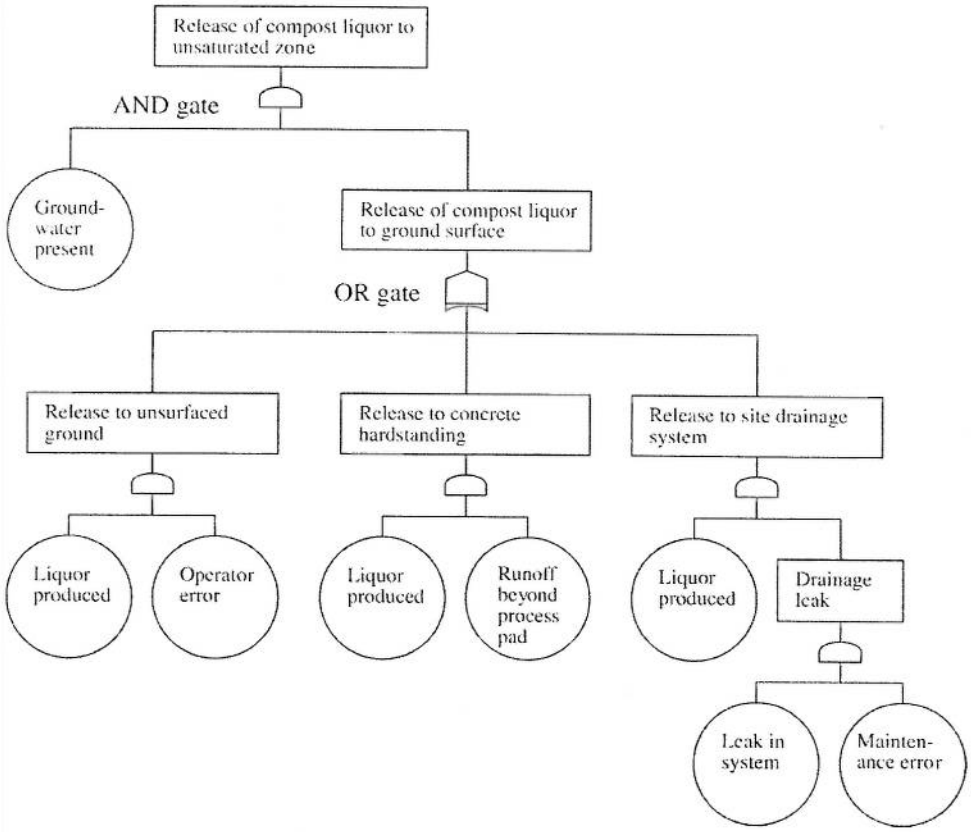


Fig. 4. Illustrative and qualitative fault-tree for release of compost liquor to groundwater at a composting plant showing AND and OR gates.

With respect to the exposure dose, the magnitude, frequency, timing and duration of exposure are important concepts in determining the extent of potential harm from waste processing operations. The presence and maintenance of barriers (physical, engineered, biological, environmental, behavioural) to exposure can often be important in minimising public health risks and when removed or bypassed by accident or design, can dramatically increase the likelihood of exposure by orders of magnitude. Examples might include the ingress of gas into buildings through poor service pipe installations, poor liner welds in engineered landfill liners, an absence of security to land contaminated with hazardous waste. Direct pathways involve exposure to the medium in which the source resides — the direct inhalation of hazardous vapours, for example. Indirect pathways usually involve transport of the source between media, such as the leaching of contaminants from a landfill site through permeable strata to a groundwater aquifer, or the carry over of persistent compounds through the various unit processes of a poorly performing leachate treatment works. Whilst concern is usually reserved for direct exposures through inhalation and ingestion routes, risks may be driven by direct or indirect exposure to the source of the hazard.

Dispersion modelling is one approach to quantifying the spatial extent of exposures to the wider environment from a point or area source. Human health and amenity risk assessments that assess the impacts of odour and particles downwind of landfills and other operating installations adopt such approaches (Hester and Harrison, 2002; Taha and Pollard, 2004). Many treatment processes such as windrow composting and the bioremediation of organic wastes emit odours, bioaerosols and/or volatiles (Steinheider et al., 1998). The off-site impacts of these hazards are conventionally assessed by reference to exposure point concentrations or doses experienced by a receptor at distance from the source. Fig. 6 illustrates this type of assessment used in support of an environmental statement, where odour unit concentrations are specified as a percentile of total hours in the year to interpret levels of annoyance that could be experienced by a local population. Risk assessments for bioaerosols, dust, and odour frequently have to account for the significance of such impacts by defining permissible emission limits at source, through back-calculation, or reverse modelling of an exposure point concentration. As with noise limit models, these approaches attempt to define maximum permissible levels by accounting for the existing baseline of impacts from other nearby sources as well as the incremental impacts from the facility in question. Disaggregating these individual contributions is methodically complex and frequently not possible.

Controlling detrimental impacts from pollutants is further complicated where exposure limits are not defined but where annoyance impacts may still be significant. The need to assess the significance of low concentrations of pollutants in the ambient environment is especially evident where impacts on local amenity arise, because communities may assume that presence of an odour confirms exposure to hazardous

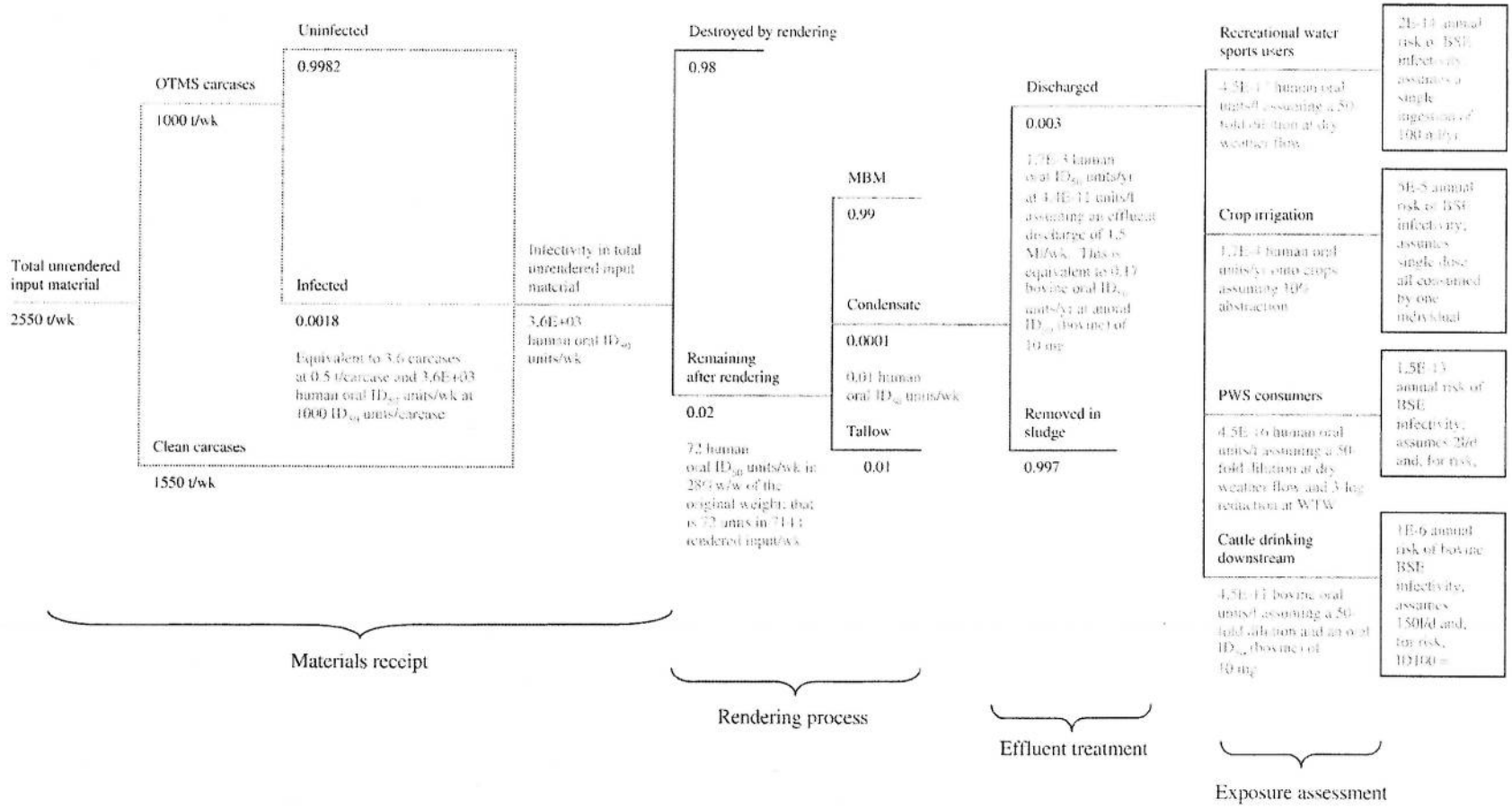


Fig. 5. Illustrative event tree for the fate of infective doses (ID) of pathogenic agents during the proposed rendering of over thirty month scheme (OTMS) material in a fictitious rendering plant (adapted from WRc, 1998, used with permission).

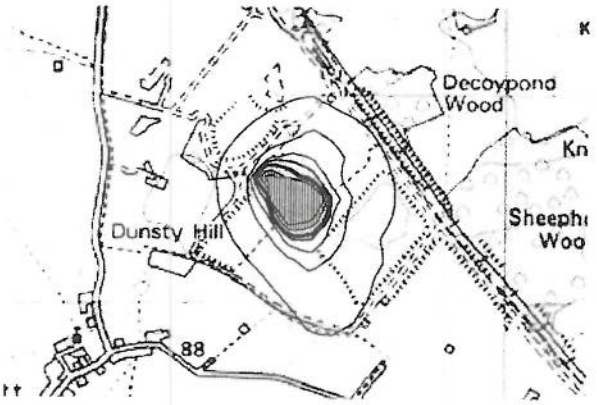


Fig. 6. The application of distribution models in exposure assessment for amenity risk assessment. Map shows contours of increasing odour units (ou; from outer contours, inward) of 1, 3, 5 ou/m^3, presented here as boundaries beyond which values are not exceeded for more than 2% of the time (Shanks Waste Services, 2003; location plan reproduced from the revised 1998 Ordnance Survey 1:50 000 Landranger map No. 153 with the permission of the Controller of Her Majesty's Stationery Office, © Crown copyright.)

compounds. Risk-based approaches, evident within the forthcoming European Directive on Noise, provide a consistent policy for operators to define process design standards. Harmonised approaches using risk tools to inform odour management plans are being established across international companies (Senante, 2004) and promoted during policy development (Van Broack, 2004).

Modelling the environmental distribution of contaminants from waste management facilities has highlighted the susceptibility of environmental risk assessments to the availability and quality of data on source terms (Environment Agency, 2004b). Notwithstanding the widely acknowledged difficulties encountered in measuring releases from these types of facility, bioaerosol, gas and vapour emissions at waste installations are frequently episodic (rather than continuous) and often related to operational process cycles, diurnal and daily fluctuations in air temperature and pressure or phase changes in contaminant behaviour (Rabl and Spadaro, 2002). Under these circumstances, conventional dispersion models may prove inappropriate for estimating off-site exposures (Hobbs et al., 2003; Taha and Pollard, 2004) especially over short distances and may require amendment.

Within regulatory risk assessment, there is a need to scrutinise the total mass balance of waste systems and account for total losses to the full set of environmental compartments, so that whilst one aspect of the impact is fully assessed (and regulated), other pathways are not inadvertently ignored (e.g. Mills et al., 2004). For example, the impact on groundwater of new landfills rarely assesses the other routes that contaminants might take, such as bulk flows to a treatment plant, volatile emissions to the atmosphere, or discharges to surface water. The single environmental compartment approach historically adopted by many risk assessments has been in response to regulation of the specific receiving body (groundwater, surface water, air), but in future, risk assessments for waste installations under integrated pollution prevention and control will adopt a more integrated approach, that views potential impacts by reference to multimedia (air, water, land, biota) routes of exposure (Environment Agency, 2004a) to a range of receptors within the environmental setting. Further, with the emphasis now firmly on pollution prevention, risk assessments can be expected to better inform *preventative* pollution strategies and risk management plans rather than focusing on the impacts of releases post-event.

Understanding the temporal aspects of exposure is equally important — for example, characterising the long-term risks to the environment during the management of treatment residuals and understanding the episodic nature of exposures, highlighted above. The sustainable development agenda has forced a consideration of intergenerational timeframes within the performance assessment of the engineered landfill environment, with 30 years being frequently considered as a regulatory benchmark for risks into the future. Whilst knowledge of leachates from conventional (largely municipal solid waste co-disposal) landfill sites in the UK is considerable, the UK has far less experience at hand to inform the management of risks associated with leachate from post-Landfill Directive sites (Environment Agency, 2004b). Unlike several EU Member States, where national legislation has required alternatives to landfill for a number of years, the UK has not relied heavily on incineration and mechanical and biological pre-treatment. The expectation is that post-Landfill Directive sites will be characterised by significantly reduced degradable carbon loadings and dominated by chemical rather than biological processes, but there is considerable uncertainty surrounding the characterisation of environmental fate processes, emissions and long-term risks. Adaptation of risk analysis approaches used elsewhere in radioactive waste performance assessment however, is demonstrating that much longer management timescales than those considered to date are likely to be relevant (Fig. 7). When the long-term fate of contaminants in landfill is modelled beyond the current regulatory requirement of 30 years, extended periods of operational and institutional control may be required (Hall et al., 2004).

Hall et al. (2004) suggest that for true landfill equilibrium status, where each and every contaminant in the landfill

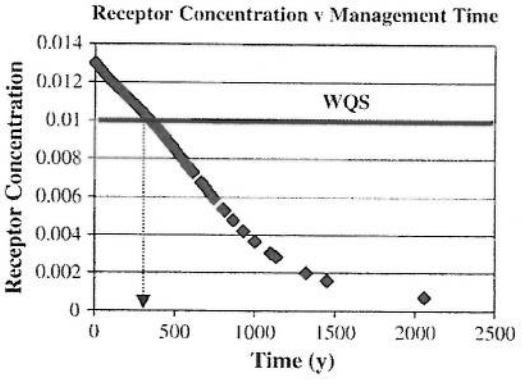


Fig. 7. Estimated management period of 340 y for a non-flushing landfill accepting raw municipal solid wastes (MSW) and meeting the water quality standard (WQS) for lead at a groundwater receptor (after Hall et al., 2004).

environment meets a required assessment endpoint, that maximum management periods in excess of 2000 years for persistent contaminants in certain residues may be required. These timescales raise important regulatory and operational issues over operational, post-operational, post-closure and post-institutional control periods and the timing and nature of regulatory interventions for managing risk. Drawing on decades years of international experience in the development of safety cases for radioactive waste repositories Nuclear Energy Authority (1999), Yearsley and Summerling (2002) conclude:

- The possibility of impacts arising in the far future is an inevitable consequence of the decision to concentrate and contain waste. The observation that any repository can be sited and designed such that significant impacts are estimated to only occur at very long times in the future is a positive feature and measure of success of the waste management solution.
- No single timescale is likely to be acceptable to all audiences of a risk assessment or for all the motivations that underlie the use of long timescales. Safety cases need to use different arguments, lines of evidence and calculations at different timescales to provide confidence.
- Common sense should be exercised in the presentation of risks over extended time periods and if results to long timescales are presented then the associated uncertainties and their interpretation should be explained.
- Dialogue with the wider scientific community and the public could inform the safety case and the timescales adopted. Whilst the public is recognised a heterogeneous group that will bring a wide range of personal values to any dialogue process, such dialogue might lead to different emphases on the timescales adopted in safety assessments, possibly with less emphasis on extremely long timescales (100,000 years for radioactive waste).

These observations offer important lessons for the non-radioactive waste community as they formulate the approach to assessing exposures in the long term and the consequences and timing of environmental harm. The adoption of integrated waste management that delivers the waste hierarchy would likely address the health risks associated with individual waste management options (South West Public Health Observatory, 2002), through process control. But this also requires the segregation and treatment of waste at co-located facilities, and risk management upstream in the process cycle. Many of the risks that arise in the latter stage of the process cycle, i.e. during waste management, are a consequence of actions taken at earlier stages of design, production, packaging and marketing. Ultimately, chemical hazards from waste residues must be managed at source through the elimination of hazardous components from the design process.

2.3. Environmental harm

For environmental receptors, the risk of potential environmental harm following a release (accidental or consented) and a subsequent exposure (Fig. 2) is characterised by the dose–response curve (Fig. 8) the relationship between the exposure to or intake of a hazardous agent and its toxicological (or chemical, or physical) effect on the receptor (Dolk, 2002).

Dose–response curves embody both the likelihood and consequences of an effect given that an amount (dose) or duration (time) of exposure occurs. The potency of a hazard on individual receptors is understood by reference to the gradient of dose–response relationship, in that for the same amount of exposure, different sources of a hazard can pose different levels of harm. With respect to sensitivity, some receptors are less resilient to hazards than others. This could be because of their sensitivity to the specific hazard or because they are vulnerable by their very nature. With respect to the magnitude of harm manifest following exposure, we often consider the number of receptors at risk — the population, or 'stock at risk'. Consequences are generally considered to be more significant if a large population of receptors is at risk rather than a small number. This may not be universally applied, however, as we may attach substantial value to even a small number of receptors: single representative habitats, for example.

The requirements of the EC Seveso II (COMAH) Directive to large waste management installations and of the EC Habitats Directive to licensed facilities act as specific drivers for broadening the emphasis of risk management to the off-site receptor (e.g. ecosystem) components of the environment and considering the implications of ecological harm (DETR, 1998, 1999a,b). Furthermore, changes to the human population profile in many countries (increased age, more immunosuppressed people and sensitised sub-populations) have given rise to a greater awareness of sensitive and vulnerable sub-populations. The emphasis for receptor-focused risk studies is on assessing the significance of potential harm at the receptor. This is not trivial and for ecosystems in particular, there is a wide ranging debate over the level at which serious impairment to ecosystem function should be assessed (Smith et al., 2006) and, for human

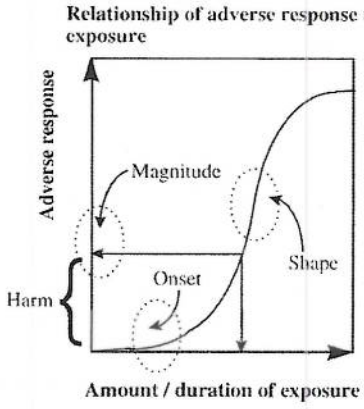


Fig. 8. The dose–response curve determines the relationship between exposure (amount or duration) and the harm manifest at the receptor. Dose–response curves have varying (i) gradients representing the potency of the hazard per unit exposure; (ii) points of departure from the *x*-axis, representing threshold or non-threshold behaviour (or latency where expressed in terms of exposure duration); and (iii) reversibility, representing system recovery as exposure ceases.

receptors at what level (95%, 99% of the populations) protection should and can be afforded.

3. Integrated risk assessment for multiple receptors

The future of risk analysis for waste management installations is likely to focus on (i) assessing an expanded set of hazardous circumstances (slope stability, landfill gas, hazardous trace components, issues of odour, risks from unit processes, combined events, such as flooding and inventory loss) from individual facilities; (ii) on aggregated risks at integrated, multi-process facilities; and (iii) on the integration of risks that have historically been assessed singularly by reference to individual legislative demands (e.g. Waste Management Licensing (UK), EC Groundwater Directive, EC Habitats Directive). Whilst integration is to be welcomed, its implementation will raise a number of technical and practical challenges for risk analysts, operators and regulators, including:

- a step change in the complexity and likely costs of risk work required of operators;
- the need for commensurate regulatory appraisal of risk assessments submitted in support of environmental permits and, arguably an independent assessment function;
- increased challenges to operators and regulators over the communication of risks to multiple receptors and their relative importance;
- the development and application of new skills in process risk modelling and ecological risk assessment;
- new metrics for the aggregation of risks from multiple technologies and the comparison of risks between distinct endpoints;
- heightened awareness and likely discussion of the potential risks to human health from waste management activities;
- debates about the complex issues involved in comparing risks to different receptors and definitions of risk significance; and
- deciding on appropriate timescales for risk assessments.

Many of these challenges are not new, have been worked through elsewhere internationally and do not require a priori treatment. However, with a more complex picture on the assessment of risk from waste management installations and the increased application of these tools upstream within the decision process during planning, there is a need for a 'route map' detailing the relative positioning of various tools within the broad context of environmental legislation.

4. Risk analysis: from strategic to project risk

Finally, risk analysis is increasingly being used beyond the site-specific project level within (i) the strategic planning of projects; and (ii) for the assessment of risks to and from policies, programmes and plans of work, in a similar way to many environmental appraisal tools (Pollard et al., 2004b). This shift recognises that decisions made at the site-specific level often flounder because of inadequacies in strategic waste planning. Risk assessment becomes fundamental to all phases of the development of waste management facilities. At the strategic 'macro' scale, risk assessments inform strategic decisions about land use planning relying on zoning and vulnerability maps. At an 'intermediate' scale, risk assessments underpin an assessment of the potential impacts associated with a facility's environmental setting, considered through the development planning process. At the project-specific ('micro' scale) and in the context of environmental permitting, risk assessment is used to enable the operator and regulator to identify the risk management options required to prevent, control, minimise and/or mitigate the risks to the local environment, these becoming stipulated as permit conditions. The increased use of risk assessments at the strategic and development planning stages, usually in support of environmental impact assessments and statements, raises issues about the interface between the assessments submitted at these stages and, where effort is best placed for the benefit of improving overall decisions.

The planning regime generally seeks to avoid commentary on issues that are the preserve of the environmental permitting process although for practitioners, there is merit in developing risk assessments from the strategic to the project level as the site-specificities become clearer. There is a natural progression in the detail and sophistication of assessment as development proceeds. In this context, the spatial dimension of risk is increasingly recognised, and as national, regional and sub-regional waste strategies progress towards implementation and the logistics of waste movements and the siting of new facilities is discussed, the spatial and temporal profile of risks from the new facilities will require analysis.

5. Conclusions

Risk-based decision making in waste management is increasingly used outside the established sectors of landfill and hazardous wastes (Milke, 2003). Integrated environmental regulation is leading to risk-based approaches being adopted for site management and the setting of priorities for regulatory inspection (DETR, 1999a,b; Environment Agency, 2004c). However, with increased emphasis on risk-based regulation, a tension exists for practitioners (Tromans, 2004) because concurrent with this expansion is a growing call for simpler, quicker and less costly risk assessments. Balancing the practical value of risk-informed decisions against the resources required to complete complex studies must rank among our future research priorities. Reflecting on current practice, however, we conclude that:

- recent developments in the sector offer a pivotal opportunity to review the application of decision tools for those responsible for managing risk;
- a more diverse palette of risk tools is required for decision makers wishing to optimise risk management at waste facilities;
- many of these tools can be 'read across' from other disciplines and tailored for the waste sector's needs (Milke, 2003);
- in terms of developing an integrated suite of tools, analogues already exist in the radioactive waste community for the prioritisation of source-pathway-receptor linkages;
- tools for the aggregate and comparative assessment of risks from various waste management options are required by

decision-makers optimising the delivery of a mix of management options co-located at single integrated facilities;
- comparative and integrated options appraisal tools exist for the relative evaluation of environmental, social and financial risk (Pollard et al., 2004a) that have direct application within the waste sector.
- integrated risk assessments addressing, and allowing the prioritisation of, the risks to a range of environmental receptors are likely to represent the future;
- benefits to be seized include the reduced costs of gaining environmental permits, improved regulatory and public confidence and the development of a sound and structured approach to managing environmental risk within the sector; and
- sound and well-informed risk management is critical to securing confidence in, and establishing new technologies in a rapidly developing marketplace.

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Modeling human exposures to air pollution control (APC) residues released from landfills in England and Wales

Christopher Macleod [a], Raquel Duarte-Davidson [b], Bernard Fisher [c], Betty Ng [d], David Willey [d], Ji Ping Shi [d], Ian Martin [e], Gillian Drew [f], Simon Pollard [f,*]

[a] *Institute of Grassland and Environmental Research (IGER), North Wyke, Devon, EX20 2SB, UK*
[b] *Health Protection Agency, Chemical Hazards and Poisons Division Headquarters, Chilton, Didcot, Oxon, OX11 9RQ, UK*
[c] *Environment Agency, Environmental Policy, Risk and Forecasting, Reading, Berks, RG1 8DQ, UK*
[d] *Environment Agency, Air Quality Modeling and Assessment Unit, Cardiff, CF24 0TP, UK*
[e] *Environment Agency, Science Group, Human Health, Solihull, West Midlands, B92 7HX, UK*
[f] *Cranfield University, Integrated Waste Management Centre, School of Industrial and Manufacturing Science, Cranfield, Beds, MK43 0AL, UK*

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Abstract

Human exposures to air pollution control (APC) residues released from 6 landfills were modeled and assessed. Following a qualitative risk characterisation, direct and indirect exposures were quantified. Site-specific air dispersion modeling was conducted for PM_{10}, PCDDs/PCDFs, Pb, Cd, As and Cr^{VI} concentrations at the closest residential points of exposure for 4 landfill sites accepting, in total, 75% w/w of the APC residues disposed of in 2000–2001 (UK). Inhalation risks, assessed by reference to air quality standards at residential exposure points, were assessed as insignificant. Preliminary modeling suggested that indirect exposures from PCDDs/PCDFs at the 95th percentile level for the site where APC deposition rates were highest could potentially exceed the tolerable daily soil intake (TDSI) but this warrants further study given the model limitations. These results offer an initial screen of the significance of potential risks from APC disposal, which is of value in addressing concerns about the uncertainty of potential risks to human health from bulk APC disposal at strategic locations.
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Keywords: Air pollution control residues; Risk; Air quality impact; Landfill; Health

1. Introduction

This study models human exposures to the air pollution control (APC) residues from municipal waste incinerators in England following their disposal to landfill. The research was initiated to help ensure the safe and effective management of these hazardous wastes at receiving landfill sites (Environment Agency, 2002). There are 11 municipal waste incinerators in England (Environment Agency, 2002). Most are located in and around major conurbations where landfills are more distant; with ca. two-thirds of the incineration capacity in England in London and the west Midlands (38.5% w/w and 30% w/w respectively). Each of the 11 facilities has been either recently (since 1996) commissioned or significantly modified to meet the requirements of the Waste Incineration Directive (2000/76/EC; European Parliament and Council of the European Union, 2000). The incinerators are employed at their design capacity, burning a total of ca. 2.65 MTpa (2002) of municipal solid waste (MSW). Between them, they recover heat to raise steam and generate a total of 197 MW_e of electricity for the national grid. In 2002, MSW accounted for ca. 90% w/w of the waste burned by municipal waste incinerators, the rest being non-hazardous commercial and industrial waste, the greatest quantities of which were burned at the Edmonton and Lewisham sites in London (Environment Agency, 2002).

The potential public health risks from incinerators have been extensively reviewed (Rabl and Spadaro, 2002). Combustion

* Corresponding author. Tel.: +44 1234 754101; fax: +44 1234 751671.
E-mail address: s.pollard@cranfield.ac.uk (S. Pollard).

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gases from MSW incineration are acidic because materials in MSW contain chlorine and sulphur. The gases contain dioxins and furans (PCDDs/PCDFs) and high concentrations of fine particles (Basher and Whitwell, 1999; Weber et al., 1999; Ma, 2002). Adding lime to neutralise excess acid cleans the exhaust gases and finely divided carbon is employed to remove dioxins and metals (Brna and Kilgroe, 1992). The fine ash particles, carbon and lime are removed by high efficiency bag filters. The carbon and fly ash contain most of the dioxins produced. The solid residues from municipal waste incinerators, (i) bottom ash; and (ii) APC residues (the subject of this paper) are controlled wastes and regulated by the Environment Agency under the Environmental Protection Act, 1990. Methods for the safe disposal of these wastes have been summarised by Hjelmar (1996). Operators of landfills and treatment plant accepting bottom ash or APC residues require a permit from the Agency and are under a specific duty to ensure their activities do not harm the environment or human health.

1.1. Problem formulation and study rationale

This study was initiated before recent changes to hazardous waste legislation have reduced the number of available outlets for APC residues. In 2002 within England and Wales, bottom ash was either landfilled, processed to produce an aggregate substitute or used in treatment plants. APC residues were either landfilled or used in licensed waste treatment plant to neutralise and/or solidify other hazardous wastes. In 2002, 88% w/w of APC residues went directly to landfill (Environment Agency, 2002). The study reported here was initiated to assess the significance of the off-site risks associated with the landfill disposal of APC residues at the principal sites of bulk disposal. Off-site exposure may occur through APC residues becoming airborne with onward inhalation, or through indirect exposure at some point distant from the site of disposal (Kosson et al., 1996). On-site occupational risks were not the subject of this study.

To identify the disposal locations for APC residues, incinerators and energy-from-waste (EfW) plants in England and Wales were contacted and the relative amounts of APC residues disposed to a number of licensed landfills estimated. The Environment Agency (2002) identified 18 destinations for the disposal of APC residues—12 landfill sites and 6 waste treatment plants. Of the 12 landfills, 6 received APC residues directly and 6 received treated wastes incorporating APC residues. The principal sites accepting APC residues (as of September 2001; Table 1) were selected on the basis of available information on the relative amounts of APC residues disposed of in the years 2000–2001. Between them, the sites identified received 75% w/w of the total weight of APC residues (England and Wales) disposed of.

Having identified the principal locations, the study applied Government guidelines on environmental risk assessment and management (DETR et al., 2000; Fig. 1) and, in the latter stages, focused on the generalized assessment of potential exposures at key sites of concern using the best available data and a defensible, albeit conservative, modeling approach. The aim of the study was to assess the significance of these potential exposures by adopting a modeling approach.

Table 1
Summary of APC residue disposal at landfill sites in 2000–2001 (April–April), based on 10/12 returns from incinerators as of 14th September 2001

Landfill site	Type of landfill	APC receipt (t/year)	% E and W total	Method of disposal
Wigmoor Farm	Monofill hazardous waste landfill, lined with clay	32,479	41.3	Pre-treated on site and disposed of to open cells
Sidegate		5331	6.8	Arrives in dry form and treated on site prior to disposal
Dorkethead	Engineered	4433	5.6	Buried immediately on deposit and covered immediately
Bilsthorpe		1816	2.3	–
Himley Wood[a]		8828	11.2	Delivered in nylon bags
Meece[a]	Mixed disposal site with composite liner of engineered clay and Bentomatt	6472	8.2	Delivered in nylon bags and buried in trench and covered in MSW

[a] Not considered for detailed risk assessment.

2. Methodology

2.1. Risk screening

A tiered risk assessment approach to the study was adopted consistent with current guidance in England and Wales (DETR et al., 2000; Fig. 1). Relevant baseline information, e.g. volumes of APC disposed of, chemical characteristics, potential human exposure pathways and the proximity of potential receptors was collated from the published literature (Greenberg et al., 1978; Kosson et al., 1996), interviews with operational and technical staff and site visits. Summary information (Tables 2 and 3) was used to assemble a generalised conceptual model of exposure and to inform a qualitative risk screening in which key exposure pathways, comprising source–pathway–receptor relationships of relevance, were identified. Environment Agency staff with regulatory responsibilities for these sites considered the applicability of the conceptual model to the APC landfill for which they had responsibility and confirmed, or otherwise, the likely existence of pollutant linkages at the sites. A sub-set of feasible pollutant linkages with a 'medium' or 'high' interim risk characterisation (Table 4) was examined in more detail. Air dispersion modeling was employed to estimate air quality impacts and screen for the significance of exposures through direct inhalation. Indirect exposures were then assessed using a generic soil exposure assessment model.

2.2. Generic quantitative risk assessment—inhalation of airborne dusts

For inhalation exposures, two complementary air modeling approaches were adopted to provide a range of estimated dust

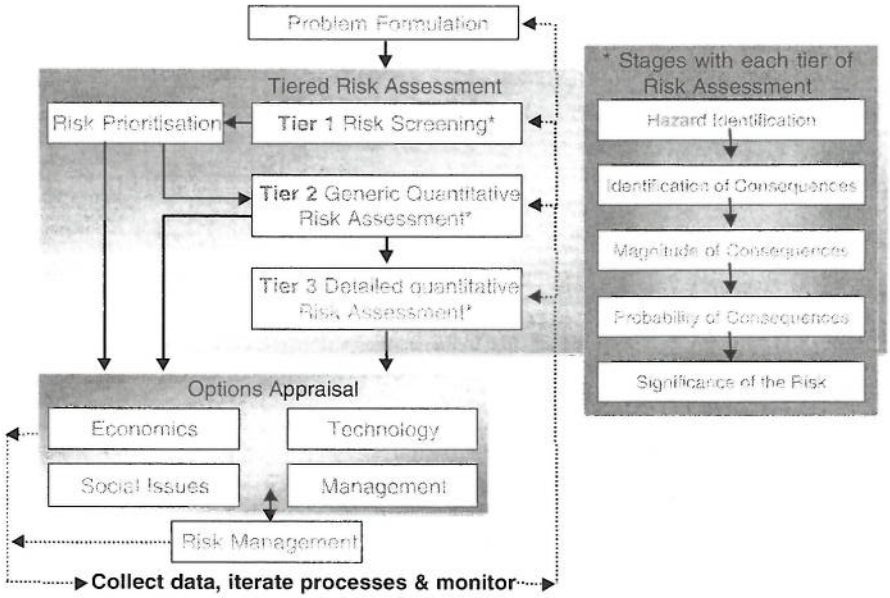


Fig. 1. Approach to the study (after DETR, Environment Agency and IEH, 2000).

emission factors from all of the potential dust release activities that might occur on landfill sites:

(i) a simple dust blow model incorporating deposition and dispersion components based on the USEPA's fugitive dust model (FDM), used widely to assess the influence of fugitive dust emissions from landfills and similar industrial activities (Fisher and Macqueen, 1981; Cowherd et al., 1982) and
(ii) the application of AERMOD (Cimorelli et al., 1998), a USEPA air dispersion model designed to predict pollutant concentrations from continuous point, area and open pit sources. This enables the concentrations of windblown APC dusts and contaminant concentrations at nearby human receptors to be estimated. Application of the two approaches is described below.

2.2.1. Simple dust blow model (SDBM)

Defensible source term data are essential for risk assessment but difficult to obtain on account of the complexities of site topography, waste characteristics and local meteorological conditions. The generation of windblown dust is an important release mechanism for inhalation exposures and has historically been characterised by an analytical model describing the dispersion and settling of dust particles (Fisher and Macqueen, 1981). The relationship is described by a single formula (Ermak, 1977) and the sensitivity of results to assumptions regarding the dispersion and deposition of particles can be tested with ease. The formula (Ermak, 1977) provides the theoretical basis of the USEPA fugitive dust model (FDM), a computerised Gaussian plume dispersion model developed by the USEPA for estimating airborne particulate concentrations (USEPA, 1995). The FDM employs an advanced gradient transfer particle deposition algorithm (Horst, 1977; Hanna et al., 1982) but no explicit expression of the dust source term – this has to be supplied by the user.

Here, the analytical formulae in the dust blow model were setup in an EXCEL™ spreadsheet. Site operations that lead to the generation and emission of dust include (i) vehicle movements over previously deposited waste; (ii) wind erosion from recently deposited friable waste (before natural crusting of the surface binds material together); and (iii) release when the waste is deposited on the landfill (DoE, 1994; Table 2). Estimates of the potential dust emission factors from wind erosion of deposited APC residues were made using USEPA (1995) and DoE (1994) for both storage piles and exposed surfaces. It was assumed that daily disturbance of deposited piles would allow the surface to dry sufficiently for erosion to occur. The simple dust blow model calculates the wind shear stress at the surface and the threshold velocity above which erosion and dust release takes place. The simple dust blow model uses the AP-42 emission factors (USEPA, 1995) for dust blow including the particle size relationship (Table 5). The relationship (USEPA, 1995) was used to estimate the emissions (Table 6) of PM_{10} and PM_{30} particles, taking no account of dust suppression or rainfall. Generally, significant emissions of dust were associated with wind erosion from APC residues when wind speeds were greater than 6 m/s and where recently deposited waste piles were spread to form an even layer. The amounts of APC residues released per disturbance event were expressed as an emission rate per day (Table 6) in order to generate downwind concentrations of respirable dust and contaminants, and to allow comparisons with air quality standards for airborne dust (Table 7).

2.2.2. Limitations in the estimation of source terms

Significant approximations are entertained when applying these modeling techniques to episodic source terms to generate

Table 2
Information on generic APC disposal practice pertinent to qualitative risk assessment including that summarised in Environment Agency (2002)

(A) Source of hazard

APC residues are transferred from incinerators to treatment sites and treated before final disposal at licensed landfill sites, the treatment site may or may not be in the same location as the landfill site.

Treatment of APC residues varies with location. Treatment involves the controlled mixing of the APC residues with a variety of waste liquids, including landfill leachates and industrial waste fluids.

To reduce the source of the hazard 'ordinary control procedures' are required, for example use of daily and intermediate cover.

Assessment of the source needs to include all potential dust releasing operations and scenarios where emissions can take place, for example, disposal of APC residue to a raised void will increase potential for wind erosion of material.

(B) Hazard

APC residues are potentially hazardous due to their: high pH (pH 11–12.5); high levels of PCDD/F 2500 ng I-TEQ/kg; Pb 5000 mg/kg; Cd 250 mg/kg; As 200 mg/kg; and Cr (vi) 116 mg/kg (maximum concentrations taken from analysis).

APC residues are 'dust like' due to their particulate nature with small diameters (<100 μm), with the potential for atmospheric transport under energetic conditions. Data from one analysis indicates that 100% of APC residues were smaller than 63 μm, with 50% smaller than 12 μm.

Waste management licenses may have protocols for sampling APC residues and determining their chemical content. This should be performed by the producer at the waste disposal site.

(C) Transport mechanisms

Potential sources for atmospheric APC residue release include: accidental release from APC residue delivery vehicles; waste transfer stations; loading waste treatment silos; loading open dumper trucks; transfer to active landfill cells; and activities at active landfill cell.

Have insufficient volatility [some dioxins, i.e. the lower chlorinated ones are semi-volatile] for appreciable evaporation

The potential and extent of any dust release is based on the amount of APC residues being disposed and the method of disposal.

Depending on whether the APC residues are mono- or co-disposed influences the potential for the transport of APC residues off site. Co-disposed APC residues tend to be covered daily. Mono-disposal sites may not use daily cover.

(D) Pathways

Atmospheric transport of dusts is the main potential pathway for identified hazards reaching a nearby human receptor.

Appreciable exposure is only likely to occur when a young child is present on the site, perimeter fences should mitigate against this.

Leachates recirculated or collected for off-site disposal.

All potential exposure pathways need to be included in risk assessments.

(E) Targets/receptors and exposure

Risk assessments and license conditions need to include fundamental aspects of current operations and monitoring programme, e.g. they need to include dust sources other than active cell and minimum moisture content of 20%.

Predicted APC deposition rates are well below nuisance threshold quotes for all receptors at Wingmoor Farm landfill site.

Use of 'more realistic' scenarios in applicants risk assessment may not be conservative enough. Evidence is needed that these accurately represent the operations of the site.

Dispersion modeling based on a Gaussian decay curve indicate an approximately 100-fold reduction in dust levels over the minimum distances between the tipping face and the perimeter of the site.

estimates of the impact on air quality (Sax and Isakov, 2003). Generalised assumptions included in the empirical relationship of dust generation include the silt and moisture content of the surface material and the mean vehicle weight. The resulting source term estimate is presented as a mass of APC residue emitted per vehicle-kilometre. Uncertainties in the source term model and in approximating the operating area of the landfill propagate further once air dispersion modeling is undertaken using a simple dust blow model (SDBM). Further, the particle size determines the likely distance that particles will travel. Large particles greater than about 100 μm diameter are likely to be deposited within a few tens of metres of their point of release. Given the necessities of approximation, verification of the model was attempted through comparison with a risk assessment already undertaken for the Wigmoor Farm Landfill, Bishops Cleeve and available site monitoring data (Applied Environmental Research Centre, 2001). The simplifications mask an important reality that source term generation at operational waste management facilities is mostly episodic and short-term, consistent with operational cycles. Thus, comparing averaged concentrations to long term air quality standards, therefore, must be undertaken with caution.

2.2.3. Estimating dust emissions using AERMOD

AERMOD, the American Meteorology Society-Environmental Protection Agency Regulatory Model, is a stationary new generation dispersion model designed to predict pollutant concentrations from continuous point, flare, area, line, and volume sources. Terrain effect was modeled and dust deposition was predicted at selected receptor locations downwind of the landfill site (Table 7). Concentrations were compared, where available, to the statutory UK air quality objectives (Table 7) and, for PM_{10}, to background concentrations at the nearest automatic monitoring network location (Table 8).

Amenity impacts from waste management activities are of increasing interest. The lower nuisance threshold for dust deposition is often taken to be 200–350 mg/m^2/day averaged over a month (Anon, 1986; Bate and Coppin, 1990; North Ayrshire Council, 2000), with a 'likely nuisance' level of 650 mg/m^2/day. Here, the lower threshold was used as a criterion for assessing the nuisance potential of APC deposition rates (Table 9).

2.3. Generic risk assessment—indirect exposures through ingestion and consumption

Whilst inhalation offers a direct route of exposure for airborne dust, indirect exposures may also occur through the deposition and subsequent uptake of contaminants from the soil (Harrop and Pollard, 1998). Here, the Contaminated Land Exposure Assessment (CLEA) (Defra and Environment Agency, 2002) model was used to estimate indirect exposures to key contaminants in APC residues deposited at receptor locations downwind of disposal sites. CLEA has been developed to generate generic soil guideline values for contaminated land in the UK. Information can, however, be incorporated into the model to inform estimates of exposure from more specific

Table 3
Composition of selected APC residues from a range of literature sources

Determinand	Study reference					
	WRc (2000) (range)	Tyseley (range)	EA S-90456	EA S-90455	Bolton (hall)	SELCHP
pH	12.2–12.5	–[a]	12.4	12.5	–	–
Organic carbon (% w/w)	1.6–4.0	–	–	–	–	1.7–2.0
Dioxins I-TEQ (ng/kg)	–	2402–2598	4180	88	450–653	1256
Polynuclear aromatic hydrocarbons (mg/kg)	–	–	–	–	–	270
Chloride (mg/kg)	111,000–207,750	197,100–236,000	–	–	–	–
Sulphate (mg/kg)	2600–14,250	58,800–94,900	–	–	–	–
Iron (mg/kg)	646–7844	3900–7800	4400 (0.7)[b]	1700 (0.42)	–	3740
Manganese (mg/kg)	94–486	268–404	280 (<0.5)	210 (<0.4)	297 (<0.03)	431
Copper (mg/kg)	37–769	623–1067	370 (0.7)	66 (<0.4)	435 (<0.08)	386
Zinc (mg/kg)		12,600–17,600	8100 (40)	650 (<0.4)	–	6580
Nickel (mg/kg)	329613,950	<1–89	20 (<0.5)	9 (<0.4)	19 (<0.33)	22
Chromium (mg/kg)	11–113	51–324	100 (0.7)	41 (<0.4)	68 (1.04)	12
Lead (mg/kg)	422–5331	4300–6000	2000 (280)	140 (1.4)	2420 (215)	2690
Cadmium (mg/kg)	20–215	190–516	94 (<0.5)	5 (<0.4)	122 (<0.06)	103
Mercury (mg/kg)	11–30	2–25	6 (0)	<2	11 (<0.27)	12
Arsenic (mg/kg)	200	2–166	<20	<20	24 (<0.9)	14
Aluminium (mg/kg)	17,000	17,300–29,700	28,000 (0.8)	9000	–	–
Barium (mg/kg)	250	147–952	–	–	–	72
Cobalt (mg/kg)	10	9–620	–	–	–	9
Antimony (mg/kg)	450	–	–	–	–	–
Tin (mg/kg)	500	940–1438	–	–	60 (<1.7)	271
Vanadium (mg/kg)	30	16–175	–	–	–	–
Fluoride (mg/kg)	1500	2–54	–	–	–	–

[a] Not determined.
[b] As leachable (mg /kg).

circumstances; for example, the consumption of allotment grown vegetables. CLEA was employed to estimate daily intakes for receptors of concern (e.g. a local child) and exposure estimates for evaluating the significance of potential risks to human health.

The CLEA model consists of a number of generic fate and transport algorithms that are normally reviewed and adapted, where necessary, to the requirements of a specific compound before the soil guideline value is produced. Whilst this process has been carried out for the metals (lead, cadmium, chromium and arsenic), this is not the case for dioxins and furans. Hence, the model has not been properly validated for dioxins and the results should therefore be treated with caution. CLEA does not allow consideration of a source term increasing over time (such as annual deposition for a number of years) nor take account of changing fluxes in the source term. Further, at present, a critical pathway, the deposition of particulates on the leaves of fruit and vegetables, was not modeled in this screening assessment. A number of critical adaptations and assumptions were therefore required:

(i) it was assumed that deposition occurs at a constant annual rate and that deposited dust is mixed evenly into the top 0.1 m of the soil;
(ii) a 6-year deposition period was assumed with the concentration at the end of the sixth year being assumed to have been present from the start. This is a conservative assumption and consistent with the exposure duration used in CLEA to assess risks to children from exposure to soil contamination;
(iii) local onward mobilisation of contaminated dusts was assumed to be negligible compared to the primary flux to the site and the relative contribution from other exposure pathways such as ingestion;
(iv) the most sensitive receptor and standard land-use was considered to be a female child aged 0–6 in a residential setting where the family consumes its own homegrown produce.

3. Results and discussion

3.1. Generic risk screening

From 31 potential pollutant linkages identified from the prior literature, reports and through initial interviews with Agency staff in the risk screening stage, seven were assessed as key, with risk rankings of medium or high (Table 4). These were used as the basis for undertaking the generalized assessment.

3.2. Generic risk assessment—inhalation of dusts

Application of the key generic linkages (Table 4) to individual site (Table 1) by regulatory staff resulted in only four of the six sites being considered for site-specific assessment (Table 7). Two sites, Meece and Himleywood, had APC residues delivered and disposed of in sealed nylon bags with the reasonable presumption that a negligible probability of exposure to nearby human receptors existed.

Table 4
Summary of key pollutant linkages identified from the qualitative risk screening exercise

No.	Source of hazard	Pathways	Receptors	Probability of exposure[1]	Consequences[2]	Interim qualitative risk characterisation[3]	Justification for interim risk characterisation
1	PCDD/Fs	Inhalation of airborne dust	Local residents/ workers	Medium	Severe	High	Direct pathway, high load, assumes close proximity to site and outdoor exposure, high potency
2		Incidental ingestion of soil, dust	Local residents, particularly children	Medium	Severe	High	Indirect pathway, low load dispersion but local hot spots, limited intake, high potency
3		Ingestion of maternal breast milk	Local breast-fed babies	Medium	Severe	High	Indirect pathway, low load, limited uptake and storage by mothers, local hotspots where mother is long-term resident regularly consuming home grown produce, bioaccumulation in fatty tissue and release through breast feeding, high potency
4		Consumption of contaminated produce	Residential consumers of home grown produce (fruit and vegetables)	Low	Severe	Medium	Indirect pathway, low load, removal due to rainfall and washing produce, assumes root crops unpeeled, limited contribution to diet, high potency
5		Consumption of contaminated dairy and meat products	Consumers of locally produced dairy and meat products (eggs and poultry)	Medium	Severe	High	Indirect pathway, low load but local hotspots adjacent to site, limited transfer to dairy and meat products, evidence of bioaccumulation in eggs and poultry, high potency
6	As, Pb, Cd, Cr^{VI}	Inhalation of airborne dusts	Local residents	Medium	Severe	High	Direct pathway, high load, assumes close proximity to site and outdoor exposure, known health effects
7		Incidental ingestion of soil, dust	Local residents	Medium	Severe	High	Indirect pathway, low load, dispersion but local hotspots, limited intake, known health effects

(1) Key: probability of exposure
Probability of exposure is defined as the likelihood of the receptors being exposed to the hazard.
High: direct exposure likely with no/few barriers between hazard source and receptor; medium: feasible exposure possible, barriers to exposure less controllable; low: several barriers exist between hazards source and receptors, to mitigate against exposure; negligible: effective, multiple barriers in place to mitigate against exposure.
(2) Key: consequences
The consequences of a particular hazard being realised may be actual or potential harm to human health, incorporating spatial and temporal extents of potential harm and reversibility. Assumes child as most sensitive human receptor.
Severe: there is sufficient evidence that short- or long-term exposure to chemical may result in serious damage to health (e.g. death, clear functional disturbance or morphological changes which are toxicologically significant). Latency of effect and irreversibility (during or following exposure) should be considered here; moderate: there is sufficient evidence that exposure to chemical may result in health effects that are not severe in nature and are reversible once exposure ceases (e.g. irritant); mild: health effect not apparent though chemical exerts reversible physiological and/or pathological changes (e.g. biochemical, haematological changes or enzyme induction but no other apparent effect); negligible: no evidence of adverse health effects and/or physiological and pathological effects following exposure to chemical.
(3) Qualitative evaluation of the significance of the risk
Determined by combining the probability of the consequences (i.e. probability of (a) the hazard occurring; (b) the receptor being exposed to the hazard and (c) harm resulting from that hazard) and the magnitude of the consequences.

3.2.1. Simple dust blow model

The emission rates in Table 6 were associated with wind erosion from APC residues in the case where recently deposited waste piles were periodically spread to form an even layer. These were in agreement with previously reported studies on the transport of APC residues from landfill sites (AERC, 2001). Through sensitivity testing with the SDBM (not presented here for brevity), it was established that:

(i) the particle sizes of the APC residues released from the landfill sites determine, in part, the distance the particles will travel;
(ii) moisture contents less than 20% w/w result in increased dust release;

Table 5
Emission factors used for a range of particle sizes

Particle diameter (μm)	30	<15	<10	<2.5
Emission factor	1.0	0.6	0.5	0.2

Table 6
APC source term release assumptions adopted

Dust sources	PM_{10} ($mg/m^2/day$)[a]	PM_{30} ($mg/m^2/day$)[a]	Landfill average and range ($\mu g/m^3$)[b]
Total	1000	3000	13 (0–158)

[a] Reasonable worst case emission rates calculated using the simple dust blow model.
[b] Values measured at other landfill sites and comparable industrial sources.

Table 7
Pollutant concentrations at receptor locations from primary landfill source estimated using site-specific emission terms

Landfill	Human receptors at (location; m from source)	PM_{10}		Annual mean				
		90.2 percentile of daily mean ($\mu g/m^3$)	PM_{10} annual mean ($\mu g/m^3$)	PCDD/F(μg I-TEQ/m^3)	Pb ($\mu g/m^3$)	Cd ($\mu g/m^3$)	As ($\mu g/m^3$)	Cr^{VI} ($\mu g/m^3$)
AQ stds/objectives		50	40	none set	0.5	5.0×10^{-3}	0.2	0.1
Source		DETR air quality strategy objectives 2000				WHO (2000)	EA assessment level	
Wigmoor Farm	Wigmoor farm; 100	5.5	2.1	5.1×10^{-9}	1.0×10^{-2}	5.1×10^{-4}	4.1×10^{-4}	2.4×10^{-4}
	Glebe farm; 690	2.0	7.0×10^{-1}	1.8×10^{-9}	3.5×10^{-3}	1.8×10^{-4}	1.4×10^{-4}	8.2×10^{-5}
	Hayden; 450	5.5	1.8	4.4×10^{-9}	8.9×10^{-3}	4.4×10^{-4}	3.5×10^{-4}	2.1×10^{-4}
	Court farm; 610	7.2×10^{-1}	3.2×10^{-1}	8.0×10^{-10}	1.6×10^{-3}	8.0×10^{-5}	6.4×10^{-5}	3.7×10^{-5}
	Rugby ground; 570	1.7	5.4×10^{-1}	1.3×10^{-9}	2.7×10^{-3}	1.3×10^{-4}	1.1×10^{-4}	6.3×10^{-5}
	Cattery; 500	1.2	4.6×10^{-1}	1.1×10^{-9}	2.3×10^{-3}	1.1×10^{-4}	9.1×10^{-5}	5.3×10^{-5}
Sidegate	Hillside farm; 960	1.3×10^{-3}	4.0×10^{-4}	1.0×10^{-12}	2.0×10^{-6}	1.0×10^{-7}	8.0×10^{-8}	4.6×10^{-8}
	House 1; 375	3.5×10^{-3}	1.5×10^{-3}	3.8×10^{-12}	7.5×10^{-6}	3.8×10^{-7}	3.0×10^{-7}	1.7×10^{-7}
	Finedonhill farm; 450	1.2×10^{-3}	5.7×10^{-4}	1.4×10^{-12}	2.9×10^{-6}	1.4×10^{-7}	1.1×10^{-7}	6.6×10^{-8}
Dorkethead	Road; 185	1.9×10^{-2}	7.5×10^{-3}	1.9×10^{-11}	3.8×10^{-5}	1.9×10^{-6}	1.5×10^{-6}	8.7×10^{-7}
	Jenned road; 495	2.0×10^{-3}	8.0×10^{-4}	2.0×10^{-12}	4.0×10^{-6}	2.0×10^{-7}	1.6×10^{-7}	9.3×10^{-8}
	Surgey's lane; 445	3.0×10^{-3}	1.1×10^{-3}	2.8×10^{-12}	5.5×10^{-6}	2.8×10^{-7}	2.2×10^{-7}	1.3×10^{-7}
	Dorket Head farm; 435	2.7×10^{-3}	1.0×10^{-3}	2.5×10^{-12}	5.0×10^{-6}	2.5×10^{-7}	2.0×10^{-7}	1.2×10^{-7}
	Quarry; 17	2.7×10^{-3}	1.0×10^{-3}	2.5×10^{-12}	5.0×10^{-6}	2.5×10^{-7}	2.0×10^{-7}	1.2×10^{-7}
Bilsthorpe	Manor farm; 500	1.9×10^{-3}	8.0×10^{-4}	2.0×10^{-12}	4.0×10^{-6}	2.0×10^{-7}	1.6×10^{-7}	9.3×10^{-8}
	Houses; 750	7.1×10^{-4}	3.0×10^{-4}	7.5×10^{-13}	1.5×10^{-6}	7.5×10^{-8}	6.0×10^{-8}	3.5×10^{-8}
	Scrapyard; 235	7.9×10^{-3}	2.4×10^{-3}	6.0×10^{-12}	1.2×10^{-5}	6.0×10^{-7}	4.8×10^{-7}	2.8×10^{-7}
	Industrial depot; 350	5.8×10^{-3}	1.6×10^{-3}	4.0×10^{-12}	8.0×10^{-6}	4.0×10^{-7}	3.2×10^{-7}	1.9×10^{-7}
	Footpath; 205	9.4×10^{-3}	4.3×10^{-3}	1.1×10^{-11}	2.2×10^{-5}	1.1×10^{-6}	8.6×10^{-7}	5.0×10^{-7}

(iii) wind speeds greater than 6 m/s are needed for significant erosion of dusts from active landfill cells; and
(iv) vehicle movements across bare APC residue leads to increased dust release.

The main uncertainties in the model are the source terms describing the amount of material becoming airborne and the size distribution of these particles. The source terms used were conservative and did not allow for rainfall that would contribute to dust suppression.

3.2.2. AERMOD dispersion of APC residues

Data from the AERMOD air dispersion modeling are presented in Table 7. The air quality standards or objective were not exceeded at any human receptor for any of the landfill sites studied (using 1997 meteorological data) based on the site-specific emissions rates. Additional analysis using meteorological data from 1995, 1996 and 1997 indicated pollutant concentrations typically <10% of the air quality strategy objectives at the 90th percentile. Using a reasonable worst case scenario of two source areas of 14,560 m^2 (88 m×145 m and 40 m×45 m) emitting 1000 mg APC residue/m^2/day, the PM_{10} air quality objective was not exceeded. Predicted PM_{10} concentrations in Table 7 were, at maximum, ca. 10% of the measured annual mean background PM_{10} concentrations close to these sites (Table 8).

3.3. Generic risk assessment—indirect exposures

Deposition data for APC residues in soils are presented in Table 9. For Pb, Cd, As and Cr^{VI}, volume averaged soil concentrations are very low. Assuming a uniform mixing of APC residues in the top 0.1 m of soil for 6 years resulted in concentrations for most contaminants of <1 mg/kg, and in many cases, <100 μg/kg. The estimated soil concentrations for the site with the highest predicted deposition rates are presented in Table 10. The highest soil concentration is for Pb at ca. 15 mg/kg and this can be compared with typical soil lead concentration of between 10 and 30 mg/kg in many areas of the UK (Davies, 1995).

Comparison of these modeled metal concentrations to UK soil guideline values indicate that these concentrations would not present regulatory concern with respect to risks to human health. For the highest deposition rates, in excess of 100 years' deposition would be required for Pb and Cd and more than 1000 years for As and Cr^{VI} for concentrations to meet the soil guideline values. This said, two issues warrant further consideration. The calculations above, for a hypothetical site, assume that the soil is not already contaminated with metals found in the APC residues. It might be the case that background or point-source contamination of the soil could be close to, or above the levels indicated by the soil guideline values, in which case further deposition of dust may be more significant. In addition, both As and Pb are considered to be non-threshold substances by the UK Department of Health under which concentrations in soil are subject to ALARP risk management principles where even small additions to the soil must be considered by reference to the cost and benefits of control.

In the case of dioxins (expressed in terms of 2, 3, 7, 8-TCDD toxic equivalents; TEQs), CLEA was used to assess exposure at Glebe Farm (Table 10). The CLEA model has not been externally validated for

Table 8
A summary of background PM_{10} concentrations at representative PM_{10} monitoring points

Landfill	Automatic monitoring network site	Annual mean ($\mu g/m^3$)	
		1999	2000
Wigmoor Farm	Leamington Spa	22	20
Sidegate	Leamington Spa	22	20
Dorkethead	Nottingham centre	25	24
Bilsthorpe		–	20–23 (projected 2004)

dioxins. The results are tentative and demand qualification. The estimated, conservatively modeled, soil concentration for the highest deposition rate was 8 ng TEQ/kg of soil. This is within the typical mean soil concentration of 3 to 23 ng TEQ/kg reported in the UK and elsewhere for PCDD/PCDFs in rural and urban soils (Duarte-Davidson et al., 1997). The average daily human exposure (ADE) to the critical receptor was estimated to be 0.8 pg TEQ/kg bw/day, which is twice the health criteria value derived for dioxins (0.4 pg TEQ/kg bw/day; Defra and Environment Agency, 2003). Based on this initial assessment, it would be useful to explore this exposure assessment further using more realistic parameters and to refine the CLEA model to allow for the derivation of soil guideline values for PCDD/PCDFs and this is currently under consideration.

3.4. Key limitations and uncertainties

An exposure assessment was undertaken for a representative number of sites using a limited data set. There are a number of uncertainties that affect the results of any such assessment and these could lead to a larger or smaller risk of exposure. The results presented here can only be described as an indication of the potential risks posed by the contamination. Further sampling, analysis, and a more detailed risk assessment would increase the confidence in these results. However, the assumptions underlying exposure assessment were carefully selected, making it necessarily conservative at this stage. A number of important uncertainties that need to be considered when considering the outcome of this study are:

(i) *Source term considerations*—estimating the mass of APC residue likely to be lost from the site has large levels of uncertainty associated with it. The main contributors to the source term are included and are hypothetically large and designed to incorporate smaller non-quantifiable sources.

(ii) *Dispersion and indirect exposure modeling*—modeling is reliant on the quality and quantity of the data supplied. Key parameters have been estimated and would need to be refined to reduce uncertainties associated with the estimates. A conservative approach was taken to counter these uncertainties.

(iii) *Contaminants assessed*—only a few selected contaminants were assessed. These were selected on the basis of concentrations reported in APC residues and the health effects that might result from exposure to these contaminants. The reported TEQ levels, for example, only account for dioxins and furans. The contribution of dioxin-like PCBs was not considered. If incorporated, this would lead to a higher TEQ daily intake than that estimated here. Similarly only those metals deemed hazardous to human health were assessed.

(iv) *Exposure dynamics*—the CLEA model does not allow any consideration of a soil source term that is increasing over time (such as continuation of annual deposition for a number of years) nor does it take account of changing fluxes in this source term. CLEA is designed to deal with the risk posed by historical soil contamination.

Table 9
PM_{10} deposition fluxes for receptor locations

Landfill	Human receptors at	Lower range for deposition flux[1]	Upper range for deposition flux[2]
Nuisance threshold 350 mg/m²/day		mg/m²/day	mg/m²/day
Wigmoor Farm	Wigmoor farm	0.12	1.92
	Glebe farm	0.05	0.79
	Hayden	0.16	2.41
	Court farm	0.03	0.44
	Rugby ground	0.09	1.26
	Cattery	0.03	0.52
Sidegate	Hillside farm	3.6×10^{-4}	5.2×10^{-3}
	House 1	1.3×10^{-3}	1.9×10^{-2}
	Finedonhill farm	4.9×10^{-4}	7.4×10^{-3}
Dorkethead	Road	6.6×10^{-3}	0.10
	Jenned road	6.8×10^{-4}	0.01
	Surgey's lane	9.6×10^{-4}	0.01
	Dorket Head farm	8.8×10^{-4}	0.01
	Quarry	8.8×10^{-4}	0.01
Bilsthorpe	Manor farm	6.8×10^{-4}	0.01
	Houses	2.6×10^{-4}	3.8×10^{-3}
	Scrapyard	2.1×10^{-3}	0.03
	Industrial depot	1.4×10^{-3}	0.02
	Footpath	3.8×10^{-3}	0.05

[1]A value of 1 cm/s is used as a lower range value for the dry deposition velocity and [2]a value of 15 cm/s is used as an upper range value for the dry deposition velocity. In both cases, particles have a diameter of 10 μm, a density of 2.55 kg/m³ and wet deposition is not included.

Table 10
Modeled indirect exposure assessment for windblown APC residues at Glebe Farm

Contaminant	Deposition rate (mg/m²/year)	Total deposition after 6 years (mg/m²)	Concentration in 0.1 m of soil (mg/kg[1])	Deposition to exceedance[3] (year)
Pb	420	2520	15.75	152
Cd	2	13	0.08	130
As	2	10	0.06	1905
Cr	1	6	0.04	8214
PCDD/PCDFs	210×10^{-6}	1260×10^{-6}	8×10^{-6}	2.04[4]

[1]Assumes even mixing; [2]uses blood lead concentration as health criteria value; [3]based on time to exceed SGV at current deposition rate; [4]that is the ratio of the average daily human exposure of dioxins from the site divided by the tolerable daily soil intake.

4. Conclusions

A generic risk screening approach was developed for the potential pollutant linkages that exist at landfill sites accepting APC residues. Potential exposures were modeled using data from the literature, not site monitoring data. The results provide an indication of the relative magnitude of the risks posed. They are generic, and do not reflect all exposure circumstances at all locations. The following conclusions demand qualification given the assumptions adopted.

1. Seven important pollutant linkages were identified with medium and high risk to human health. These considered the atmospheric transport and subsequent direct and indirect exposure to nearby workers and residents. The key pollutant linkages were potentially present at 4 of the 6 landfill sites studied.
2. Direct exposure through ingestion and inhalation are the critical exposure pathways.

3. Dust does not appear to be of major concern given the deposition rates modeled. However, it would be prudent to control dust release through the enforcement of control measures in the permit conditions and working plans.
4. The main APC landfill site (>40% of the total APC residues disposed in 2000–2001) was found not to cause significant release of APC residues that reached the nearby receptors. The predicted annual mean of PM_{10} at the nearest sensitive human receptor was 1.8 $\mu g/m^3$, significantly lower than the air quality strategy objective of 40 $\mu g/m^3$.
5. The long term accumulation of dioxins from deposited dust are tentative and warrant further study. Indications in this work are that indirect exposures require more detailed investigation.
6. On the basis of this preliminary analysis, the disposal of APC residues at landfill sites does not appear to pose significant harm to nearby human receptors. However, this assessment was made using a restricted data set and more information is required to fully understand the nature of the hazard.
7. Future work will have the opportunity to utilise updated research on APC residues and their characteristics (WRc, 2004).

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Weathered Hydrocarbon Wastes: A Risk Management Primer

K. J. BRASSINGTON and R. L. HOUGH
Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, United Kingdom

G. I. PATON
Department of Plant and Soil Sciences, School of Biological Sciences, Cruickshank Building, University of Aberdeen, Aberdeen, Scotland, United Kingdom

K. T. SEMPLE
Department of Environmental Sciences, Institute of Environmental and Natural Sciences, University of Lancaster, Lancaster, United Kingdom

G. C. RISDON
TES Bretby, Burton-on-Trent, United Kingdom

J. CROSSLEY
Dew Remediation Limited, Royds Works, Sheffield, United Kingdom

I. HAY
Sustainable Manufacturing, PERA, PERA Melton Mowbray, Leicestershire, United Kingdom

K. ASKARI
SLR Consulting Limited, Nottingham, United Kingdom

S. J. T. POLLARD
Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, United Kingdom

We provide a primer and critical review of the characterization, risk assessment, and bioremediation of weathered hydrocarbons. Historically the remediation of soil contaminated with petroleum hydrocarbons has been expressed in terms of reductions in total petroleum hydrocarbon (TPH) load rather than reductions in risk.

Address correspondence to S. J. T. Pollard, Centre for Resource Management and Efficiency, Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, UK. E-mail: s.pollard@cranfield.ac.uk

There are several techniques by which petroleum hydrocarbons in soils can be characterized. Method development is often driven by the objectives of published risk assessment frameworks. Some frameworks stipulate analysis of a wide range of petroleum hydrocarbons; for example, the United Kingdom (UK) approach suggests compounds from EC_5 to EC_{70} be examined. Methods for the extraction of petroleum hydrocarbons from soil samples have been reviewed extensively in the open literature. Although various extraction and analytical methods are available for petroleum hydrocarbons, their results suffer from inter-method variation, with gas chromatography methods being used widely. Currently, the implications for risk assessment are uncertain. Bioremediation works well for remediating soils contaminated with petroleum hydrocarbons. As a result, the optimization of environmental conditions is imperative. For petroleum hydrocarbons in soil, international regulatory guidance on the management of risks from contaminated sites is now emerging. There is also growing support for the move toward compound-specific risk-based approaches for the assessment of hydrocarbon-contaminated land.

KEY WORDS: environmental, hydrocarbons, remediation, risk management, weathered

1. INTRODUCTION

Contamination of land due to anthropogenic activity, both present and historical, is a global problem. It is estimated there may be as many as 100,000 contaminated sites in England and Wales alone. Contamination has become a subject of social, legal, environmental and economic concern within many of the world's industrialized countries.[108] Land may be contaminated because of past industrial activity, historic disposal practices, or due to an adverse event such as a chemical spill.[63] Although a large proportion of contaminated land may be attributable to historical practices, modern industrial processes also produce potential contaminants, and thus contamination of land is an ongoing problem that requires active management.

Petroleum continues to be a widely utilized resource throughout the world. Its use has resulted in contamination through accidental spillage and leakage.[72] Certain components of petroleum contamination may pose risks to human health, property, watercourses, ecosystems, and other environmental receptors.[34,30] Petroleum in its natural state is a highly complex mixture of hydrocarbons with minor amounts of other heterogenic compounds such as nitrogen, oxygen, and sulfur.[34] The composition of petroleum hydrocarbon products can vary substantially, depending on the nature, composition, and

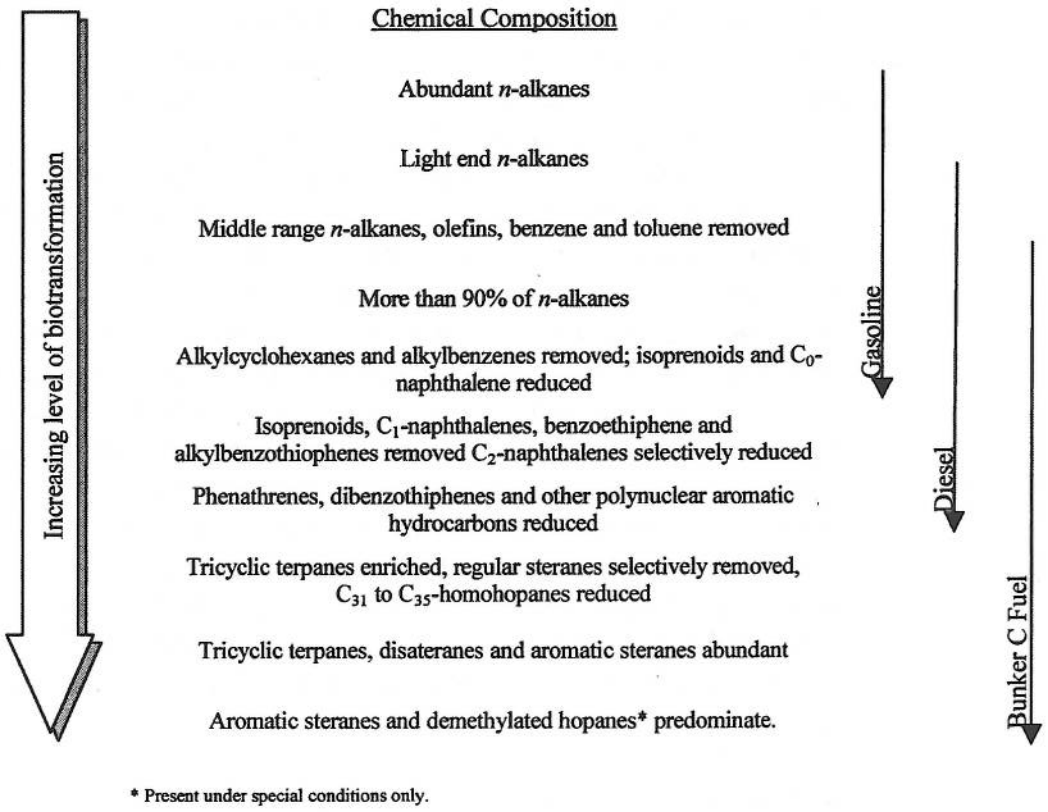


FIGURE 1. General petroleum hydrocarbon degradation pattern. Modified after Kaplan et al. (1996).[50]

degree of processing of the source material.[70] Once released into the environment, petroleum products are subject to physical, chemical, and biological processes that further change their composition, toxicity, availability, and distribution (partitioning) within the environment (Figure 1). Such degradation processes include adsorption, volatilization, dissolution, biotransformation, photolysis, oxidation, and hydrolysis.[9,30,50,70,87] The extent of weathering experienced is particularly important when characterizing petroleum contamination prior to remediation.[107] While there is a large literature describing the composition and properties of petroleum products,[87] there is a relative paucity of information on the toxicity, distribution, transport, and availability of weathered hydrocarbons in the environment.[71,87] Here, we provide a primer and critical review of the characterization, risk assessment, and bioremediation of weathered hydrocarbon fuel products. Current issues are discussed.

As with all contaminants, their chemistry determines which environmental compartment they are found in and thus analyzed and is also responsible for their environmental fate and transport characteristics. Analytical methods for determining concentrations of hydrocarbons in the soil need to be technically and economically feasible and capable of analyzing the

range of compounds key to the risk management protocols applied.[30] Although various extraction and analytical methods are available for petroleum hydrocarbons, their results suffer from inter-method variation as illustrated by Buddhadasa et al. (2002).[16] Additionally, as discussed by Whittaker et al. (1995),[109] methods can suffer from both positive and negative analytical bias.[86] Gas chromatography is a widely used technique for the analysis of petroleum hydrocabons.[46,103,105] Biodegradation of more amenable components of the petroleum mixture leads to relative enrichment of the more recalcitrant species. Incomplete resolution of this more recalcitrant mixture leads to a characteristic "humped" appearance of the gas chromatograms output. The "hump" is the resulting signal produced by many hundreds of components such as cyclic and branched hydrocarbons and is widely referred to as the unresolved complex mixture (UCM). The shape and position of the UCM is not constant and depends on the nature of the original petroleum contamination and the extent of degradation that has taken place in the ground. These issues need to be addressed when implementing a national risk-based framework, as differences in analytical approach may inadvertently result in excessive or inadequate remediation being performed.

Risk assessment is now a well-established requirement for the management of contaminated land[4] and a support tool for environmental management decisions. It is widely used as a means of assessing and managing potential impacts to human and ecosystem health.[4,100] Several risk-based frameworks for petroleum hydrocarbons in soil have been published under the auspices of the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG[88]), the American Society for Testing and Materials (ASTM[5]), the Massachusetts Department of Environmental Protection (MaDEP[55]), the Environment Agency of England and Wales (EA[32]), the American Petroleum Institute (API[3]), and the Canadian Council of Ministers of the Environment (CCME)[18], each reflecting national legislation and socioeconomic issues.[3,100,101] These frameworks, and the exposure assessment methods embedded within them, do not specifically address weathered hydrocarbons, although many acknowledge that petroleum products released to the environment will have undergone some degree of degradation.[3,6,30,32,55,87] Weathering of fresh petroleum product makes it very difficult to accurately predict the composition, toxicity, and distribution of petroleum at a given site.[53]

Historically the remediation of soil contaminated with petroleum hydrocarbons has been expressed in terms of reductions in total petroleum hydrocarbon (TPH) load rather than reductions in risk. This still remains as standard practice in a number of countries, including Portugal and the United Kingdom.[30,35] Recent stakeholder consultations in the United Kingdom and subsequent publications from the Environment Agency aim to adopt a risk-based framework where remediation is expressed in terms of

risk, consistent with other countries (e.g., the United States[85] Canada,[18] and the Netherlands[10]).[30–32]

There are a plethora of approaches to, and techniques available for, the remediation of contaminated land.[13,20,28,33,49,63,109,111] Choice of approach depends on a number of environmental, economic and human health considerations.[51] The United Kingdom adopts the "suitable for use" approach as the most appropriate strategy for the sustainable development of contaminated sites.[23,44] Within the land remediation sector, the EU Landfill Directive[81] is now encouraging the development and implementation of alternative remediation techniques[63] and is expected to further increase the cost-effectiveness of bioremediation technologies.[69,77] This has resulted in increased interest in and use of the technique for the remediation of hydrocarbon-contaminated soils.

A complete understanding of the contaminant in question is a key component when estimating potential risks to human health. To achieve this, adequate information regarding a substance's environmental fate, behavior and distribution, toxicity, concentration, and potential exposure at a site is essential[30] (Figure 2). In this review, then, we critically review these considerations for the successful implementation of a risk assessment framework for the bioremediation of weathered petroleum hydrocarbons.

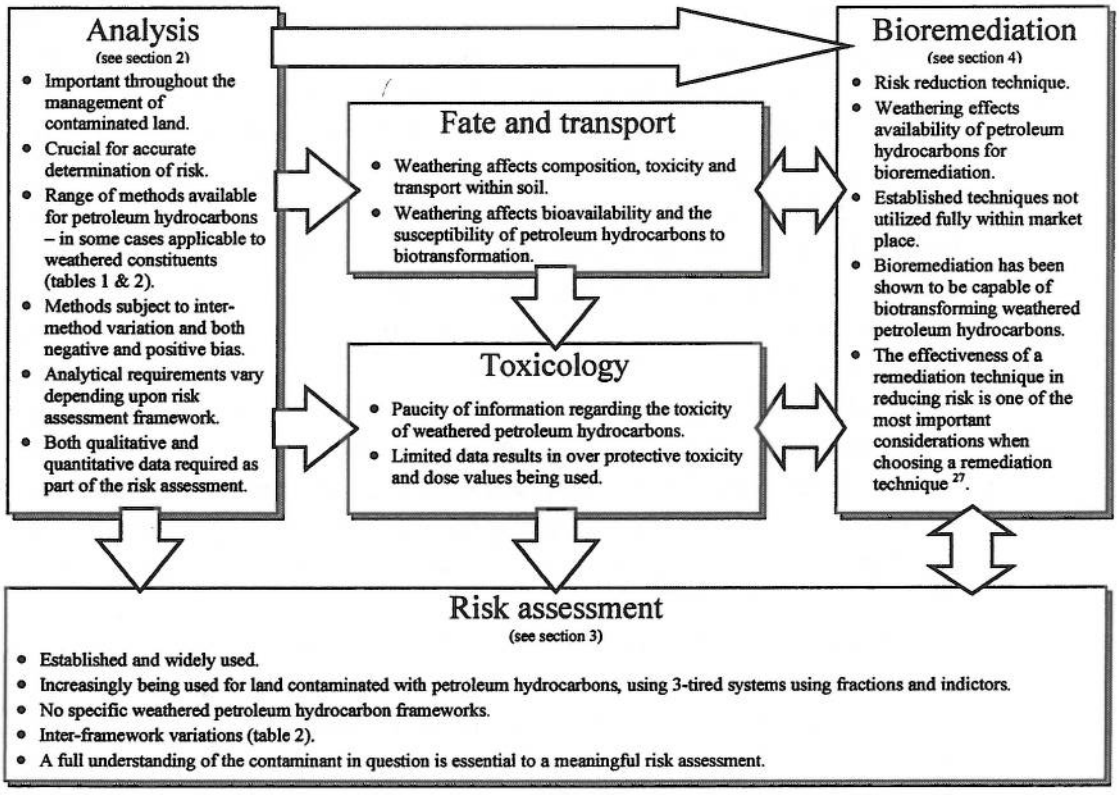


FIGURE 2. Illustration of the interactions of the key elements involved in remediation of weathered petroleum hydrocarbon-contaminated land.

2. CHARACTERIZATION OF WEATHERED HYDROCARBONS

2.1. Extraction and Analysis

There are several techniques by which petroleum hydrocarbons in soils can be characterized. Method development is often driven by the objectives of published risk assessment frameworks (Table 1).[3,5,6,17,54,88] Many frameworks (e.g., TPHCWG, API, CCME, MaDEP) require the quantification of specific indicators and/or fractions, while others consider indicator compounds or chemicals of concern (e.g., ASTM)[3,17,54,87] (Section 3). It is necessary to use analytical techniques capable of analyzing specified aromatic and aliphatic "fractions" as well as the specific indicator compounds selected by the different protocols (summarized in Table 1 and Section 3 of this review). These compounds are known carcinogens, including benzene, toluene, ethylbenzene, and xylene (BTEX), and the 16 U.S. Environmental Protection Agency (EPA) polynuclear aromatic hydrocarbons (PAHs).[1,17,30,54] Some frameworks stipulate analysis of a wide range of petroleum hydrocarbons; for example, the UK approach suggests compounds from an equivalent carbon number (see Section 3) of 5 to 70 be examined (Table 1).

2.1.1. Extraction of Petroleum Hydrocarbons From Soil and Class Fractionation

Methods for the extraction of petroleum hydrocarbons from soil samples have been reviewed extensively in the open literature. They include purge and trap (volatiles), headspace (volatiles), manual shaking, Soxhlet, ultrasonic extraction, pressurized fluid extraction, microwave-assisted extraction, and supercritical fluid extraction.[86] For heavily weathered fuel oils, extraction of volatile hydrocarbons is rarely considered. Soxhlet extraction is commonly used in research, yet several risk assessment frameworks adopt manual shake methods, for example, TPHCWG, the Agency for Toxic Substances and Disease Registry (ATSDR), and the Texas Natural Resource Conservation Commission (TNRCC).[1,6,84,86] This method involves shaking or vortexing 10 g (typically) of soil with 10 ml of an appropriate solvent (typically *n*-pentane) for 1 h, after which an aliquot is drawn for analysis.[1,58] The popularity of manual shake/vortex methods is due to a combination of convenience and cost, being quicker, easier, more accessible, and cheaper than Soxhlet extraction, with no concentration step required prior to analysis.[34,86] Additionally, legislative analysis requirements within some countries can be met using this method rather than a more exhaustive technique.

Soxhlet extraction[34,86] is the benchmark method for the CCME C_{10}–C_{50} hydrocarbon range and a component of the U.S. Environmental Protection Agency (U.S. EPA) methods for semi- and nonvolatile organics in soil.[19,93] Soxhlet extraction is a highly exhaustive extraction technique and can handle both air-dried and field-moist samples, with the latter being facilitated

TABLE 1. Summary of the Analysis Methods Developed for Several Risk Assessment Frameworks

	Massachusetts Department of Environmental Protection[54]	Total Petroleum Hydrocarbon Criteria Working Group[85–89]	Canadian Council of Ministers of the Environment[18]	New Zealand[61]	New South Wales[64]
Description	Use of two methods. Volatile petroleum hydrocarbon (VPH) method[58] and extractable petroleum hydrocarbon (EPH) method[57] developed by MaDEP. The EPH method refers to U.S. EPA methods for sample extraction.[57,99]	Use of "The Direct method" (AEHS)[1] developed for the TPHCWG framework. Based upon U.S. EPA SW-864 test methods[99] and MaDEP EPH method.[57]	Recommends the use of benchmarked methods[19]; however, also allows the use of nonbenchmarked methods providing that validation data demonstrate that the substitute method provides data comparable to the benchmark method.	Permits the use of a variety of methods, including those prepared by the Oil Industry Environmental Working Group (1999),[67] which outlines methods for several different petroleum products often referring the reader to U.S. EPA documentation.[67,99]	Recommends the use of methods specified in the National Environmental Protection Councils (NEPC) Schedule B(3): Guideline on Laboratory Analysis of Potentially Contaminated Soils (1999)[64]. Where no suitable analytical method is available it recommends the use of U.S. EPA[99] or equivalent methods.[64] All chemical analysis should be carried out in laboratories currently accredited by the national association of testing authorities (NATA).
Reported range	C_5 to C_{36}	$C_6$to C_{35}	C_6 to C_{50}	C_6 to C_{36}	$C_7$to C_{36}
Sample collection	EPH method uses amber glass wide mouth sample jars with Teflon lined screw caps. These are cooled immediately after collection and extracted within 14 days of receiving the sample. VPH method uses specially designed air tight collection vials with Teflon-lined septa screw caps stored at 4°C and preserved with methanol before analysis within a maximum of 28 days.	Wide mouth glass jars with Teflon lined caps stored at 4°C. Analysis must be performed within 14 days of sample collection.	Wide-mouth glass jars with aluminum foil or Teflon-lined lids. Samples must completely fill the jars. Samples are not chemically preserved but are cooled to 4°C. Laboratory sample handling procedure is also outlined.	100 ml (volatiles) and 250 ml (semivolatiles) Borosilicate jars with Teflon-lined cap and completely filled. Stored at 4°C in the dark.	Use of U.S. EPA[99] or equivalent methods

(Continued on next page)

TABLE 1. Summary of the Analysis Methods Developed for Several Risk Assessment Frameworks *(Continued)*

	Massachusetts Department of Environmental Protection[54]	Total Petroleum Hydrocarbon Criteria Working Group[85–89]	Canadian Council of Ministers of the Environment[18]	New Zealand[61]	New South Wales[64]
Extraction technique	VPH method uses purge and trap with methanol. EPH method uses DCM for extraction and solvent exchanges into hexane. Using U.S. EPA methods 3540C[93] (Soxhlet), 3545A[94] (pressurised fluid extraction (PFE)), 3541[91] (automated Soxhlet extraction), 3546[96] (Microwave extraction) and 3570[97] (microscale solvent extraction (MSE)).	Vortex or shaker method using *n*-pentane.	Purge and trap for C_6 to C_{10} range using methanol. Soxhlet is the benchmarked method for the C_{10} to C_{50} range.	For the C_{10} to C_{36} range any method that can be demonstrated to meet the performance criteria can be used. For the C_6 to C_9 range purge and trap is used.	U.S. EPA methods 3540B[99] or C[93] (Soxhlet extraction), 3550B[95] (sonication extraction) or sequential bath sonication and agitation described by NEPC.[64]
Evaporation	The EPH method uses those specified by the U.S. EPA. However, after fractionation the use of gentle stream of air or nitrogen is recommended to bring the sample to the required volume. Evaporation is not applicable to the VPH method.	N/A	Uses an evaporation vessel after extraction for the C_{10} to C_{50} range. After silica gel cleanup rotary evaporator is the benchmarked method to reach the required sample volume.	Permits the use of any method that can be demonstrated to meet the performance criteria.	U.S. EPA methods specified for extraction using Kurderna–Danish (K-D) evaporation.
Cleanup/fractionation	Silica gel cleanup for EPH method. Not applicable to VPH method.	Extract fractionation using alumina or silica.	One of two specified clean up steps for C_{10} to C_{50} range, not fractionated.	Clean up steps and fractionation are optional as this may not be required for each sample/analytical approach.	Solvent exchange into hexane followed by K-D evaporation and treated with silica gel as described in U.S. EPA method 1664.[64,99]
Analysis technique	EPH uses GC/FID.* VPH may use either GC/FID* or GC/PID.#	GC/FID*	GC/FID*	For the C_{10} to C_{36} range GC/FID* is used and for the C_6 to C_9 range GC/MS$ is used.	GC/MS$, or GC/FID*, however the use of GC/MS$ to identify unusual mixtures is noted as being necessary when analysing by GC/FID.*

*GC/FID refers to gas chromatography with flame ionization detection.
#GC/PID refers to gas chromatography with photoionization detection.
$GC/MS refers to gas chromatography with mass spectroscopy detection.

through the addition of chemical drying agents, such as anhydrous sodium sulfate, prior to extraction. A wide range of solvent types can be employed, making this technique versatile for different chromatographic endpoints. The Soxhlet method generates a relatively large volume of extract requiring concentration prior to chemical analysis. This may be seen as a disadvantage due to potential contamination and losses during concentration steps.[86] However, losses can be minimized through the use of methods such as Kuderna Danish.

The time taken to extract a sample using Soxhlet extraction and ultimately its cost have initiated investigations into alternative methods. Hawthorne et al. (2000),[42] for example, reviewed methods available for the extraction of PAHs from historically contaminated soils. Methods reviewed included Soxhlet extraction, pressurized liquid extraction (PLE), supercritical fluid extraction (SFE), and subcritical water extraction (at 300 and 250°C) (SWE). Comparisons were made between hydrocarbon recovery, the effects on the sample matrix, the presence of co-extracted (non-target) matrix material, and the relative selectivity for extracting different classes of target organics.

The authors concluded that extraction methods that are relatively simple to perform yield the "dirtiest" extracts, while those yielding cleaner, more specific extracts required methods that are relatively complex.[42] Soxhlet and PLE yielded much darker and turbid extracts, whereas subcritical water extracts were orange to dark orange in color with moderate turbidity. SFE extracts were light yellow in color and clear. Soxhlet and PLE yielded more artifact peaks in the gas chromatogram and, due to the extracts from these methods having a high soil matrix content, more frequent cleaning of gas chromatograph (GC) injection ports was required in comparison to SFE extracts.[42] However, the development of GC techniques negates this issue due to enhanced sensitivity allowing the analysis of more dilute samples. Although there were minor differences in extraction efficiencies, the quantitative agreement between the methods was reportedly good.[42] It has also been shown by Hollender et al. (2003)[45] that ultrasonic extraction and accelerated solvent extraction can achieve higher extraction efficiencies when extracting PAHs than Soxhlet extraction can. Saifuddin and Chua (2003)[75] compared Soxhlet extraction to microwave-assisted extraction (MAE).[75] Here, MAE was quicker (~33 min vs. 24 h for Soxhlet extraction), used less solvent (4 ml solvent compared to 20 ml for Soxhlet extraction), and was capable of slightly higher extraction efficiencies (82% rather than 77% for Soxhlet extraction). However, samples needed to be free from metallic particles, which clearly limits application of this technique to contaminated soils.[22,34] Additionally, although MAE achieved higher extraction efficiencies, there was no significant difference between the data for MAE and Soxhlet extraction ($\alpha = .05$); thus the benefit of a slight increase in extraction efficiency is questionable.[75]

Soxhlet extraction is considered a harsh method that extracts a fraction closer to the full capacity of the soil for hydrocarbons, rather than a

more biologically relevant analogue of extractability.[74] It has been suggested that methods that only extract environmentally relevant pollutant molecules should be used.[42,74] Although any concentration determined by extraction is operationally defined, it may be more appropriate to employ a "weaker" extraction that may determine a closer analogue of bioavailability and hence potential risk, depending on the use of the data.

Non-petroleum-based hydrocarbons may result in spurious or elevated TPH concentrations, especially when remediation methods employ the use of bulking materials such as wood chips. In order to limit interference, it is necessary to purify samples prior to analysis.[107] The most commonly used methods of cleanup employ alumina or silica gel (U.S. EPA methods 3611B and 3630C, respectively), used by the TPHCWG, ATSDR, TNRCC, CCME, and MaDEP risk assessment frameworks.[1,19,30,54,84] This cleanup method also facilitates fractionation into aliphatic and aromatic fractions, which is required by MaDEP, TPHCWG, ATSDR, and the EA.[6,30,32,54,85] However it is likely that any moderately polar compounds will be retained in the silica matrix, including any that increase in polarity as a result of biotransformation. This may be an issue when analyzing weathered hydrocarbon wastes and those undergoing remediation. Attempts to automate the fractionation procedure have resulted in incomplete resolution of the aliphatic and aromatic fractions. While some well-resolved components could be eliminated by subtraction, incomplete separation does not address any UCM present. The key fractions affected involve the mono- and diaromatics.

Extracted samples often need to be concentrated prior to analysis, and before and/or after cleanup steps where an unacceptable level of dilution may be introduced, such as Soxhlet extraction[34,86,93] and class fractionation.[34,86,98] There are several concentration methods that can be used: Kuderna Danish concentration, nitrogen evaporation, and rotary evaporation. A concentration step is a further source of error. For example, identification errors may occur if samples are evaporated too exhaustively during sample preparation using methods such as rapid nitrogen evaporation, where volatile components are most likely to be lost.[54] The use of a keeper solvent such as acetonitrile and methods such as Kurderna Danish, as specified by the U.S. EPA Soxhlet extraction protocol, is considered to minimize such losses.[86]

Due to the wide carbon range covered by hydrocarbon products and the tiered nature of some risk assessment frameworks, it is clear that no single analysis technique is likely to be sufficient for analyzing soil samples. It would seem sensible that if a tiered risk assessment is used then a systematic tiered analysis strategy be matched to it, as progression to higher tiers and thus higher levels of analytical complexity may not in all situations be necessary. Tiered analytical approaches are increasingly being applied in oil spill identification.[103,104] For example, Wang et al. (1997)[103] used a five tiered analytical approach that enabled the identification of oil type, degree of weathering, and biodegradation.

Many of the risk assessment frameworks for petroleum hydrocarbons specify preferred extraction and analytical techniques; some have published their own recommended methods (CCME, TNRCC, TPHCWG, and MaDEP[19]; Table 1[1,57,58,84]). The majority specify manual shake or vortexing methods with an appropriate solvent to extract the sample, followed by alumina or silica gel clean up and fractionation into aliphatic and aromatic compounds.[1,30,54,84] The MaDEP approach specifies volatile petroleum hydrocarbon (VPH) and extractable petroleum hydrocarbon (EPH) determinations. The VPH method uses a purge and trap approach, whereas the EPH method specifies extraction using dichloromethane (DCM), cross-referring to the U.S. EPA extraction method followed by silica cleanup and fractionation prior to analysis.[57,58] The CCME method specifies purge and trap for the fraction range C_6–C_{10}, or Soxhlet extraction followed by silica-gel cleanup and fractionation for the C_{10}–C_{50} range.[19] However, it is stated that suitable alternative techniques can be used on the condition that validation data can demonstrate that the alternative method provides data comparable to the benchmark protocol.[19] The CCME method allows for use of U.S. EPA methods, adding further quality control measures.[19] Although in prescribing methods the CCME is also allowing laboratories to use in-house methods, the validation requirement of these methods should ensure the production of comparable data across laboratories with the presumption of comparable risk assessment and remediation outcomes. Neither the EA nor the ASTM specifies methods for the extraction of petroleum hydrocarbons in risk assessment; however, the EA is to adopt performance criteria rather than prescribing specific approaches.[5,32] Here, as with the CCME, the emphasis is on quality and reliability of data rather than the use of specific "gold standard" techniques.

2.1.2. Methods for Analysis of Petroleum Hydrocarbons

The techniques used for the analysis of petroleum hydrocarbons can be grouped by their measurement outcome: quantitation of the petroleum hydrocarbon load, of the concentration of different groups of hydrocarbons, or the concentration of specific target compounds.[87] There are also methods for rapid on-site screening of contaminated soils. However, the majority of these are based on the measurement of vapours derived from the vadose zone by either in situ soil gas measurements or headspace analysis. In the case of weathered petroleum hydrocarbons, the relevance of such methods will depend on time and alteration mechanisms. Further analysis would also be required to enable the analysis of components with low volatility present within weathered hydrocarbons.[107]

Methods that generate total petroleum hydrocarbon concentrations and group (fraction) concentrations are considered to be nonspecific techniques.[103] These generate basic information that is a surrogate for contamination, such as a single TPH concentration. Such data are not

suitable for risk assessment in isolation.[34,87] However, they are inexpensive, quick, and easy, and, as such, can offer a useful screening tool.[34,87] The most commonly used specific methods include gas chromatography (GC), gas chromatography–mass spectrometry (GC-MS), gas chromatography with flame ionization detection (GC-FID), infrared spectrometry (IR), thin-layer chromatography (TLC), and gravimetric analysis.[87] Gas chromatographic methods are the most preferred TPH measurement techniques, as they offer relative sensitivity, and selectivity and can be used to identify risk critical compounds. As the composition of crude oil and petroleum products are highly complex and display a high degree of between-oil variation, unique chemical "fingerprints" for each oil can be isolated. These can be used to aid identification of the source of weathered oil contamination.[104] Techniques such as GC require additional skills/experience compared to other methods and require that samples are volatile at the operating temperature of the column.[22] Issues also arise with co-elution of compounds, as petroleum hydrocarbons comprise many isomers with similar boiling points and thus retention times. Weathered hydrocarbons typically exhibit low volatility and high boiling temperatures and require high column operating temperatures. This can vary depending on the starting product and whether sorbed or mobile fractions are under analysis. GC techniques can be adapted to enable the analysis of specific hydrocarbon ranges, such as gasoline range organics (GRO) and diesel range organics (DRO),[34] but are often unable to resolve a large proportion of UCMs, characteristic of weathered petroleum hydrocarbons.[108] This may become an issue as more toxicological data becomes available in the future.

Gas chromatography coupled with mass spectrometry detection (GC-MS) is routinely applied for the identification and measurement of individual petroleum hydrocarbons. These methods have a high level of selectivity, with the ability to confirm compound identity though the use of retention time and unique spectral patterns. GC-MS requires specialist operation and interpretation of the data, and, as such, it can be more expensive that other GC methods depending on the market forces. GC-MS offers target analyte confirmation and non-target analyte identification, and can be used to separate hydrocarbon classes.[48] Even with ready benchtop availability, some jurisdictions have felt unable to recommend GC-MS analysis of petroleum hydrocarbons to inform risk assessments.[48] The analysis requirements of current frameworks can be easily met, relatively cheaply, by GC-FID. The MaDEP method adopts GC-FID methods, along with the majority of risk assessment frameworks.

In response to the difficulties with traditional methods for the analysis of weathered petroleum hydrocarbons, alternative and specialized methods have been developed.[109] Whittaker et al.,[109] in reviewing both conventional and novel analytical techniques for the characterisation of refractory wastes, highlighted several of these, including simulated distillation gas chromatography (GC-SIMDIS), thin-layer chromatography with flame ionization detection

(TLC-FID), high-performance liquid chromatography (HPLC), and laser desorption laser photoionization time-of-flight mass spectrometry (L^2TOFMS).[109]

The coupling of Curie point pyrolysis to GC-MS (Py-GC-MS) is an alternative method to conventional techniques for the analysis of nonvolatile compounds such as rubbers, paints, and synthetic plastics and has been applied to several sample matrices, including soil.[15] Recently, Buco et al.[15] evaluated this technique for the analysis of the 16 PAHs included in the U.S. EPA priority pollutant list, and demonstrated repeatability within the range of classic techniques (RSD = 3.4%) with good accuracy for the measured PAHs.[15] This technique is quick, involves no cleanup, and does not require an extracting solvent. It is particularly effective for low-molecular-mass PAHs; high-molecular-mass PAH quantification was complicated by reduced sensitivity. This may limit Py-GC-MS use for analysis of weathered petroleum hydrocarbons.[15] Additionally, the small sample volume used makes the homogenization of samples critical for accurate analysis.[15] These authors concluded that Py-GC-MS is suited to use as an alternative screening method for contaminated soil or sediment.[15]

3. RISK MANAGEMENT FRAMEWORKS FOR HYDROCARBONS

Risk assessments should provide an "objective, scientific evaluation of the likelihood of unacceptable impacts to human health and the environment".[66] Where a "pollutant linkage" between the source of a hazard and a receptor is present,[3,71,101,102] estimates of exposure are often used to characterise risks to human health, comparing the potential intake of contaminants with acceptable or tolerable intakes inferred from toxicological or epidemiological studies. Many risk assessment frameworks adopt a three tiered approach with increasingly sophisticated levels of data collection and analysis.[5] As assessors move through the tiers, the generic and conservative approach of the earlier tiers is replaced with more detailed and site-specific assumptions[3,5,30], although each tier aims to be protective of human health.[3–5,30,32,55] The progression to higher tiers involves additional cost due to increased analytical and site investigation requirements. This expenditure enables a more complete characterisation of contaminants resulting in a more comprehensive risk assessment and more cost-effective corrective action (risk management) plans.[5] Site-specific assumptions resulting from use of the higher tiers may increase the cost-effectiveness of the remediation, so assessors need to balance the increased cost and time against potential benefits before proceeding to the next level.[5] Cost-benefit analysis techniques are built into some risk assessment frameworks to facilitate decision making for tier transition.[3]

Different countries and organizations consider aspects of risk assessment frameworks differently. For example, residential exposure scenarios have not been considered as relevant in the API framework.[3] This is because the most

realistic future uses for exploration and production (E&P) sites are ranch, agricultural, or parkland.

Hydrocarbon-contaminated soils contain many hundreds of different compounds. Although it may be feasible to identify each of the compounds present, this would be unnecessarily time-consuming. Further, data describing the toxicity, partitioning, fate, and transport characteristics of the different compounds are not currently available.[3,55] Identification and assessment of all compounds would be burdensome, which would not be practicable for stakeholders.[30,32] Therefore, surrogate measures for carbon fractions of toxicological significance, such as boiling point and carbon number ranges, have been used to simplify the assessment process.[5] Furthermore, risk management frameworks have focused on a limited subset of key components, using broad observations regarding the characteristics of known petroleum hydrocarbons to group compounds into fractions and identify key toxic compounds for use as indicators.[3,5] Typically, petroleum fractions are used to consider threshold health effects while indicator compounds are used to evaluate non-threshold health effects.[32]

Approaches such as the ASTM[5] risk-based corrective action (RBCA) framework use indicator compounds as a surrogate for risk. This approach was deemed by MaDEP[54] as insufficient for characterising risks posed at a petroleum hydrocarbon release site and fractions were introduced. The definitions of specific fractions are derived from either the carbon number (C_n) or equivalent carbon (EC_n) number. For example, MaDEP uses fractions to evaluate the threshold contaminants and indicator compounds (or "target analytes") to evaluate non-threshold toxicity.[5,30,54] The MaDEP approach is one of the few approaches that use carbon numbers. Here TPH fractions are based on "chemical structure, carbon number, and structure activity relationships."[54] The majority of frameworks use equivalent carbon numbers (EC_n), for example, TPHCWG,[30] because these are considered more closely related to the mobility of a compound in environmental media.[30] As such, EC_n are based on "a range of physical-chemical properties and simple partitioning models."[85] In practice, the boiling point of the compound of interest on a non-polar GC column is used to derive EC_n, assuming the relationship between boiling point and EC is the same for both aromatics and aliphatics. In characterizing the toxicity of a fraction, surrogate compounds or mixtures that are well characterized and characteristic of a particular fraction are often used.[30,87]

The validity of the equivalent carbon number may be challenged. For example, the TPHCWG derive EC_n using a simple empirical binomial model parameterized using data describing the boiling point (T_B, °C) and carbon number of 75 key hydrocarbons, where K_1 and K_2 are empirical constants, and C is the intercept:

$$EC_n = K_1[T_B]^2 + K_2[T_B] + C \quad (1)$$

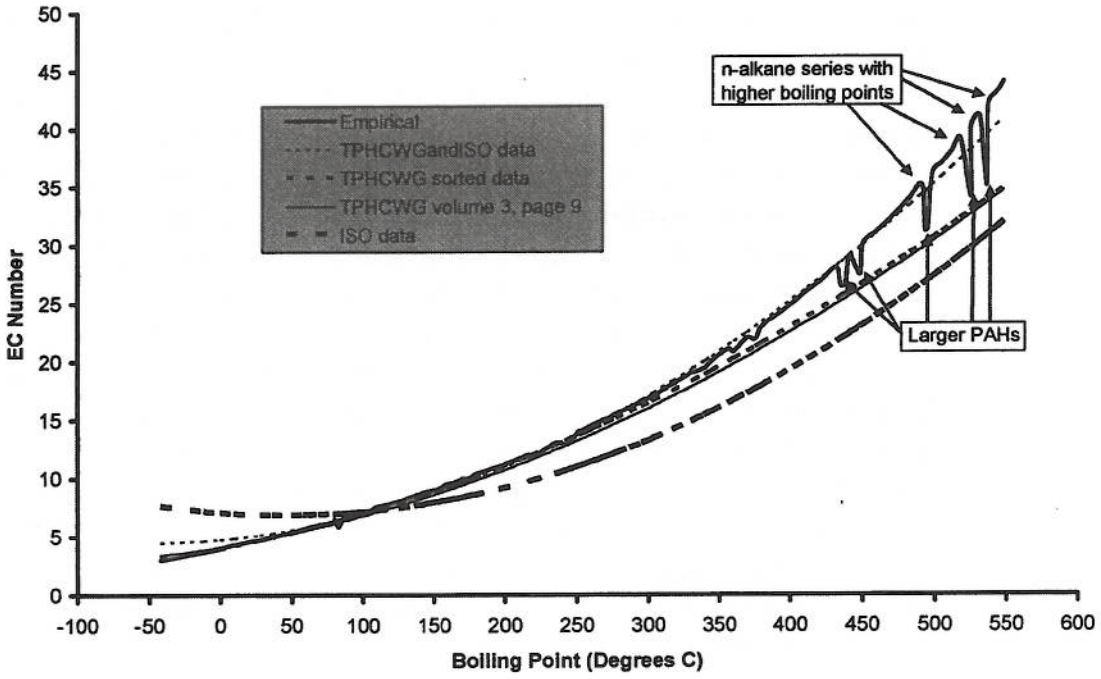


FIGURE 3. Estimated equivalent carbon number using Eq. (1) parameterized with four different data sets. The measured data are also provided for comparison.

At best, this provides only a rough estimate of EC_n (e.g., a measured EC value of 31.3 for benzo[a]pyrene compared to the calculated value of 30.0 using eq. 1). Also, a T_B of 548 should relate to EC_{44}; however, calculating this from eq. 1 provides a value of $EC_{34.6}$. Clearly there is a disparity between the TPHCWG model and the empirical data. Different parameterizations will have an effect on calculated EC_n. Figure 3 shows a series of fitted binomial models based on four different parameterization data sets. As the boiling point increases, a clear disparity emerges between the *n*-alkanes and the PAHs. This can be seen most clearly in the "empirical" plot (Figure 3), between boiling point 450 and 550°C, where PAHs have markedly lower EC numbers than the *n*-alkanes. Figure 3 suggests that the EC_n approach is unsuitable, particularly for substances with $EC_{>20}$. Simple empirical models, such as Eq. 1, do not hold true, and the theory that T_B can be used to calculate EC_n representative of normalization to the *n*-alkanes appears to be incorrect. However, the implications for risk assessment are likely to be minimal, considering the heterogeneity of soils.

Aromatic and aliphatic compounds differ in their toxicity, solubility, and fate and transport characteristics.[55] Because of this, and the evidence shown in Figure 3, some frameworks employ fractions where aliphatic compounds are considered separately to aromatic, which are further fractionated by (equivalent) carbon number (Table 2). Each fraction may then be treated as if it were a separate compound in the environment.[3,54,87] However, the

TABLE 2. Summary of Risk Assessment Used by Several Different Jurisdictions (Modified After Environment Agency, 2003[30])

	American Society for Testing and Materials[5]	Massachusetts Department of Environmental Protection[54]	Total Petroleum Hydrocarbon Criteria Working Group[85–89]	Agency for Toxic Substances and Disease Registry[6]	Canadian Council of Ministers of the Environment[18]	American Petroleum Institute[3]	Environment Agency[32]	New Zealand[61]	New South Wales[64]	National Institute for Public Health and the Environment[10]
Indicator compounds	Uses "chemicals of concern" only.	Use most toxic and those most frequently tested for	Uses most toxic compounds only	Uses most toxic compounds only	Uses most toxic and those most frequently tested for	Uses most toxic compounds only	Most toxic and most prevalent in petroleum hydrocarbon-contaminated environment	Use of "contaminants of concern" to address most toxic substances and aromatics	Individual compounds identified	Uses most toxic and those most frequently tested for
Fractions										
Number	None	6 Analytical fractions (3 aromatic, 3 aliphatic), using 4 toxicity values(3 aliphatic, 1 aromatic.	13 Analytical fractions (6 aliphatic, 7 aromatic), using 7 toxicity values (3 aliphatic, 4 aromatic).	Similar to TPHCWG. Minor modification to aromatic groups to include BTEX compounds in same fraction	4 Fractions, based on TPHCWG, separate evaluation of aliphatic and aromatic compounds not required	14 Fractions based on TPHCWG (7 aromatic, 6 Aliphatic and 1 aliphatic and aromatic combined)	16 Fractions based on TPHCWG and API (7 Aliphatic, 8 Aromatic and 1 aliphatic and aromatic combined)	3 Aliphatic fractions	2 Petroleum hydrocarbon fractions	7 fractions based on toxicity values (3 aliphatic and 4 aromatic)
Basis	N/A	Carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Equivalent carbon number	Not defined	Equivalent carbon number
Application of approach	RBCA 3 tiered look-up tables for tier 1 and increasing use of site-specific information in tiers 2 and 3.	Not tiered as appropriate method is selected prior to assessment. 3 methods can be used—increasing specificity with methods 1 generic 3 site-specific.	RBCA 3 tiered look-up tables for tier 1 and increasing use of site-specific into in tiers 2 and 3.	RBCA 3 tiered look-up tables for tier 1 and increasing use of site-specific into in tiers 2 and 3.	RBCA 3 tiered look-up tables for tier 1 and increasing use of site specific information in tiers 2 and 3.	Modified TPHCWG approach.	Modified TPHCWG approach within UK context.	Use of a 3-tiered approach, moving from generic guidelines to less conservative values using site-specific information.	None specified	Use of a tiered approach, moving from generic to less conservative values using site-specific information in tiers 2 and 3.

Analysis	No recommended method of analysis	Use of two methods developed by MaDEP for volatile petroleum hydrocarbons (VPH) [58] and Extractable petroleum hydrocarbons (EPH)[57]	The "Direct Method," developed by AEHS.[1]	The "Direct Method"[1]	Benchmarked methods for the C_6 to C_{10} and C_{10} to C_{50} ranges.[19]	Modified "Direct Method" for C_{44}+ range.	No specified methods, however, are to adopt performance criteria—MCERTS[32]	Use of method prepared by the Oil Industry Environment Working Group.[67]	Dependent on source of threshold concentration. Using NEPC methods.[64]	Single analytical method (NEN 5733) recommended.
Additivity effects	Not recommended	Precautionary based on addition of hazard quotients across fractions	Precautionary based on addition of hazard quotients across fractions	Precautionary. Developing index of concern based on addition of hazard quotients across fractions for compounds affecting same target organs of systems	Not advised due to different toxicological endpoints and exposure pathways of different fractions	Precautionary based on addition of hazard quotients across fractions	Assumes additivity of toxicological effects across all fractions, unless there are scientific data to the contrary.	Additivity of excess lifetime cancer risk for non-threshold substances. Precautionary approach, as for ATSDR	Not discussed in guidance document	Precautionary approach, based on addition of hazard quotients across fractions
Range		nC_5–nC_{36} Aliphatics, nC_9–nC_{22} Aromatics	EC_5–EC_{21} Aliphatics, EC_5–EC_{35} Aromatics	EC_5–EC_{21} Aliphatics, EC_5-EC_{35} Aromatics	EC_6–EC_{50}	EC_6 to EC_{44+}	EC_5 to EC_{70}	EC_7 to EC_{36}	EC_6 to EC_{40}	EC_5 to EC_{35}

"New Zealand Approach"[61] only considers aliphatic fractions while the aromatic faction is addressed separately by direct measurement of BTEX and PAH concentrations.[30]

Toxicity values are assigned to the fractions and indicators used. This is achieved through the process of review and/or extrapolation of available toxicological data on hydrocarbon mixtures and specific hydrocarbon compounds.[54] The number of fractions and their ranges vary between frameworks (Table 2), and in general build on or adapt the fractions defined by TPHCWG and MaDEP. Various bodies have adapted these ranges. For example, The New Zealand approach uses three aliphatic fractions, while the TPHCWG approach employs 13 analytical fractions (6 aliphatic, 7 aromatic) covering the range from EC_5 to EC_{35}.[30,55,84,85]

The API extended the fractions used by the TPHCWG so that there is a $>EC_{21}$–EC_{44} aromatic fraction and a $>EC_{16}$–EC_{44} fraction along with an additional EC_{44+} combined aliphatic and aromatic fraction (as it is not physically possible to separate hydrocarbons of this size into fractions)[3] (Table 2). This step was taken due to the TPHCWG fractions not encompassing hydrocarbons with carbon numbers greater 35 which can make up to 60% by weight of some crude oils[3] and is characteristic of weathered hydrocarbons. It was also considered that the TPHCWG fractions were appropriate for most refined products but not the crude oils present at the majority of E&P sites.[3] Toxicological and fate and transport data for these heavier hydrocarbons ($>EC_{35}$) are sparse.[55] As such, the API assigned the characteristics of the next closest aliphatic or aromatic carbon number fractions to the EC_{35}–EC_{44} aliphatic and aromatic ranges[3,6,30,54,87] deriving oral and dermal reference doses of 0.03 mg/kg/day and 0.8 mg/kg/day, respectively (as EC_{44} has extremely low volatility no inhalation reference dose was set by API[3]). The EA approach extends these carbon ranges further (Table 2), resulting in 16 fractions, giving an overall range from EC_5–EC_{70}. Further, to the TPHCWG fractions, the EA added an aromatic EC_{35}–EC_{44} range, an aliphatic EC_{35}–EC_{44} range, and a combined aromatic and aliphatic EC_{44}–EC_{70} range.[30,32] Research is currently underway to examine the implications of this extended set of hydrocarbon ranges.[69] The use of surrogate data from the next closest hydrocarbon fraction may be overly conservative and thus not cost-effective. In the case of the API approach, the next closest fraction usually encompasses petroleum hydrocarbons with lower molecular weights, and as such would be characterized by a greater degree of mobility within the environment.[3] Further research into the characteristics of heavier compounds may provide a more complete understanding of their behavior within the environment and potential risks to human health. It could also potentially result in a reduction in the analysis and remediation requirements, enabling the risk assessment to become more streamlined.

4. BIOREMEDIATION

The bioremediation of contaminated soils has been extensively reviewed. Bioremediation methods utilize naturally occurring biological processes to transform, decrease, or eliminate polluting substances.[13,28,33,41,63] Theoretically, optimal conditions are provided for bacteria or fungi to degrade or transform more complex compounds (e.g., contaminants) into relatively simple constituents that may pose a lesser potential risk to humans or ecosystems. An idealized bioremediation method would use harmless reagents, enable the process to be carried out quickly and efficiently (on site), and result in an acceptable soil product that can be reused with little/no further modification.[16] Compared to other remediation approaches, bioremediation often has greater analytical and process control requirements. From an engineering perspective, the processes and logistics of bioremediation are relatively simple.[33] Any increased expense due to greater analytical and process requirements is usually offset by lower capital costs.[20,33] In 2000, an EA survey indicated that organic pollutants accounted for 83% of contaminants remediated at contaminated sites in England and Wales,[27] demonstrating the applicability of bioremediation within the UK land remediation sector.

The disadvantages of bioremediation include the potential unpredictability of performance, difficulties in scaling up from laboratory to field and relatively long (weeks/months) remediation times. Bioremediation is not universally suitable for all contaminants.[49] High concentrations of heavy metals and other highly toxic compounds can be prohibitive of microbial growth,[49] or still leave the remediated soil unfit for purpose and classed as contaminated due to the residual presence of inorganic contaminants. Although bioremediation can breakdown potentially toxic contaminants, this process may result in the formation of metabolites that are toxic in their own right.[33] Contaminants need to provide an energy and carbon source to enable microbial growth, and so need to be biologically degradable or transformable.[27,49] Hence, biological remediation systems are more suited to organic contaminants, including weathered petroleum hydrocarbons.[48]

4.1. Bioremediation Techniques

The choice of bioremediation technique can depend on a number of site-specific factors, including the type, mobility, concentration, and volume of a contaminant, the soil structure, surrounding geology, the proximity to structures and potential receptors, and intended end use.[13,20,28,33,63] There is no single method for every situation, and often combinations of techniques are implemented at sites with multiple contamination sources. Bioremediation processes can be divided into in-situ and ex-situ. In-situ methods include monitored natural attenuation,[12,13,28,43,49,59,63] biosparging,[13,25,63] and bioventing.[13,33,36,49,63] They have the advantage of not requiring the

excavation or removal of soil.[13,20,33,63] They are able to deal with deep contamination and enable remediation both under and around buildings.[20] These techniques minimize problems with dust, and hence worker exposure may be reduced.[20,33,63] In-situ techniques can adapt, enhance, and control bioremediation conditions. However, they are limited by the degree of process control that can be used. In comparison, ex-situ methods are contained and offer a higher degree of process control with greater control over time.[27] Techniques can be performed on or off site, depending on the restrictions present at a particular site.[20] Overall, ex-situ methods are considered to be more efficient than *in-situ* techniques[13] and can deal with higher concentrations of contaminants.[27] Ex-situ techniques include landfarming, composting, biopiling and bioreactor treatments.[33]

"Landfarming" (also known as "land treatment") is a simple technique used to treat large areas of land. Landfarming has been used for the remediation of many waste types, but mainly for the remediation of hydrocarbon contaminated soils.[13,20] Landfarming involves the excavation and spreading (to 0.3–0.5 m thickness[28]) of contaminated soil over a bunded area (incorporating a leachate collection system and impermeable liner material[13,28,63]), which is tilled to aerate the soil at regular intervals.[20,28,33] Composting is an aerobic process using systems that involve the construction of piles, often using bulking agents to increase porosity and facilitate airflow.[13,33] Anaerobic conditions can also be used to compost wastes; however, this can result in the synthesis of unpleasant odorous compounds such hydrogen sulfide[20] and the generation of methane. Purpose-built closed reactor composting systems can be used to compost wastes, and have been used as the basis of soil treatment centers in mainland Europe.[13,20,63] Here, the soil is combined with water to form a slurry, which is continuously mixed using mechanical agitators, giving rise to improved contact between the pollutants and the microorganisms.[33,63] Closed systems provide a high degree of process control over environmental conditions and allow for the control and treatment of volatile compounds. However, they are more expensive than open systems such as windrows.[33]

Engineered biopiles are an intensive static pile version of composting that enable greater control over important environmental factors that effect biotransformation rates (i.e., oxygen, water and nutrient levels[13]) compared to other methods. This intensive method is especially useful when space is limited[13]. Details regarding biopile design and operation can be found elsewhere.[11,13,20,28,40]

As highlighted by some of the responses to the EAs survey,[27] the time scale in which pollutants can be remediated is an important consideration when selecting the most appropriate remedial treatment to use at a given site. Cost, guaranteed insurance, and risk reduction were also cited as reasons for not using bioremediation methods. Engineered biopiles offer a high degree of control, have a smaller footprint, and are comparatively quick, yet they

are not as expensive as closed bioreactor systems (~£10–40 m^3 vs. ~£30–150 m^3).[13] This makes biopiling attractive to contaminated land remediation specialists, especially as the high degree of control allows the processes to be optimised for biotransformation of specific pollutants of interest.

Bioremediation works well for remediating soils contaminated with petroleum hydrocarbons .[36,49] Most studies have reported biotransformation to be rapid in the initial stages of bioremediation, with rates seen to move to an asymptote as the weathered proportion is biotransformed.[26,37,111] Weathered petroleum hydrocarbons have typically been present in the soil for a long period of time; they display relatively low bioavailability, and thus are more recalcitrant in the environment.[40] As a result, the optimization of environmental conditions is imperative for the remediation of land contaminated with weathered petroleum hydrocarbons.[40] Giles et al. (2001) studied the bioremediation of weathered oil sludge (C_{20}-C_{38}) in composting piles. A biotransformation of 97% by weight of TPH was achieved after 10 weeks. This study showed that indigenous bacterial populations were more suited to biotransforming the sludge.[39] Unexpectedly, the bulking agent used had a greater effect on biodegradation than augmentation with a consortia of oil-degrading bacteria. The authors suggested that the bulking agent achieved higher degradation rates (complete compost) due to the presence of indigenous hydrocarbon-degrading microorganisms. However, this may have been due in part to the increased adsorption capacity of the amended soil matrix. It was suggested that this material was effective at modulating the temperature, thus maintaining the bacteria within their optimal range.[39]

4.2. Optimizing Bioremediation

Contaminated soils usually contain a number of microbial species capable of degrading the contaminants present.[28] The degradation process can be enhanced through biostimulation and bioaugmentation. The former refers to the enhancement of the bioremediation process by optimising specific environmental parameters such as temperature, pH, oxygen partial pressure, moisture, and nutrient levels.[33,63] The latter describes the augmentation of bioremediation systems with commercially available microbial cultures which, in some cases, perform specific functions.[13,28,40,63] Bioaugmentation may be required where native microbial populations are insufficient to achieve effective biotransformation. For example *Phanerochaete chrysosporium* (white rot fungus) can aid in the degradation of problematic recalcitrant compounds.[28] However, it should be noted that resulting increased costs are rarely justified by the benefits.[28] Additionally, it was shown by Trindade et al. (2005)[90] and Giles et al. (2001)[39] that indigenous micororganisms can be better adapted and more resistant to the contaminants present, with greater remediation potential than foreign organisms.[28,39,90] Typically, the addition of foreign organisms are not required when degrading hydrocarbons.[11]

To grow, microorganisms require an electron donor (source of energy) and an electron acceptor as a means of extracting energy from the electron donor. Thus, electron acceptors play a key role in the biotransformation of a contaminant (the energy source–electron donor). Potential electron acceptors for microbial activity are (in order of energy yield, highest first): oxygen, nitrate, iron, manganease, sulfate, carbon dioxide, and organic carbon.[49] Clearly, as oxygen yields the highest amount of energy, it is the preferred electron acceptor, and it is important to optimize its diffusion into and concentration within the soil matrix (typically need to keep oxygen in the soil gas >2%).

Different bacterial classes require different temperature ranges to achieve optimum growth. For example, mesophiles grow from about 15 to 45°C,[49] whereas thermophiles grow best between 45 and 65°C.[33,49] Typically during bioremediation mesophilic temperatures are common, with Giles et al. (2001)[39] having found optimum growth for the bacteria present during the bioremediation of a weathered oil sludge to be less than 45°C.[39]

The pH of the soil can inhibit microbial activity and also can affect the solubility of important nutrients such as phosphorus.[33,49] The typical optimum pH range for bioremediation is pH 5.0–9.0, with a pH of 7.0 being preferable. Giles et al. (2001)[39] reported a soil pH of 6.1 during the bioremediation of a weathered oil sludge, suggesting that the "typical" bioremediation pH range is likely to be suitable for weathered petroleum hydrocarbons.

Water is essential for microbial growth and maintenance and also serves as a transport medium though which organic compounds, contaminants, and nutrients are transported into the cells and waste products from the cells.[33,49] Achieving a suitable water balance within the biopile can be critical, as dry zones may result in decreased microbial activity.[33] Conversely, saturation inhibits gas exchange, resulting in anaerobic conditions.[33] The typical optimum water content range is within 55–80% by weight of the water-holding capacity.[13,49] Bacteria also require nutrients (carbon, nitrogen, phosphorus, and in lesser quantities potassium, sodium, magnesium, calcium, iron, chloride and sulfur[13]) for the assimilation and synthesis of new cell materials.[13,33,49] The depletion of nutrients can effect the biotransformation of contaminants; in response, biroemediation systems can be amended with fertilizers containing appropriate quantities of the rate-limiting nutrients.[11,40]

It is clear that successful bioremediation relies on the optimization of several parameters. Thus, prior to the remediation of contaminated land it can be useful to assess the treatability of the soil and identify requirements for bioremediation.

5. DISCUSSION

The preceding sections of this review have provided an overview of the issues for the management of risks from weathered hydrocarbons. Summarizing this material is insightful in that it illustrates trends and approaches from

a variety of perspectives. The view expressed is that 30 years of research into petroleum microbiology and bioremediation have bypassed an important observation: that many hydrocarbon-contaminated sites posing potential risks to human health harbor weathered, "mid-distillate" or heavy oils. These sites present considerable challenges to remediation over and above those posed by fresh or more refined petroleum distillates. Critically, there are important scientific components that drive risk management for these wastes and specifically the partitioning of risk-critical compounds within the oil/soil matrix.

While early work suggested the recalcitrance of these wastes to microbial breakdown, we now know that the risks from these wastes can be actively managed through optimizing treatment process parameters during bioremediation. This said, the "in-field" verification of ex-situ technologies such as biopiling continues to be expressed in many countries in terms of reductions in total petroleum hydrocarbon (TPH) load, or "losses" from the soil being treated, rather than by reference to reductions in risk. An observation from the United Kingdom is that the absence of risk from the vocabulary of many remediation operators and remediation projects reduces stakeholder (regulatory, investor, landowner, and public) confidence in technology performance, and in doing so, limits the market potential of these technologies.

For weathered hydrocarbon wastes, risk management decisions are complicated by the gross complexity of the source term, the effects of weathering on the bioavailability of risk critical contaminants, and the variable performance of remedial technologies under authentic site conditions. For heavy oils (the viscous [50–360 mPa s], high-boiling [300 - > 600°C] products such as number 6 fuel oil with carbon ranges in excess of C_{20}), their inherent complexity is further compounded as they weather in the environment on account of biotic and abiotic losses that shift their chemical composition toward recalcitrant, asphaltenic products of increased hydrophobicity.

These changes raise an important feature of hydrocarbon contaminated land that is often overlooked—that the source term, the oil matrix, is itself a strong partition medium for risk critical compounds and weathering imparts further hydrophobicity to the oil matrix. Compositional changes dramatically affect the partitioning behavior of these source terms prior to, during, and following biological treatment. Risk critical components (e.g., the higher ring polynuclear aromatic hydrocarbons [PAH]) in weathered oils are less bioavailable because they are effectively partitioned within the source term in accordance with Raoult's Law. Sun and Boyd (1991)[79] first suggested the concentration of residual oil within a oil–soil matrix required for it to act as a discrete partition medium (~1000 mg/kg) and suggested that this residual oil, as the original source of priority contaminants, could typically be 10 times more an effective partition medium than soil organic matter for hydrophobic organics. This is rarely represented within the fate and transport models that support the environmental exposure assessment of hydrocarbons, with the

possibility that regulatory exposure assessment models may dramatically over estimate the availability of risk-critical compounds through exposure routes. There is prior art here. Zemanek et al. (1997)[115] showed that between 71–96wt% of PAH in weathered diesel-contaminated loam soils was partitioned to residual oil (at 2–6wt% of the total soil composition) in petroleum and weathered creosote-contaminated soils, with 84wt% of benzo[a]pyrene partitioned to the residual oil phase. Woolgar and Jones (1999)[112] estimated oil–water partition coefficients (termed log K_{mw}) for a series of PAH to be between 4.5 and 6.5, dependent on the source term. Under these conditions, highly partitioned constituents in weathered hydrocarbon waste matrices may be biologically inaccessible to microbial communities and resistant to biotransformation. However, their very inaccessibility may, but not necessarily, also restrict the dose available to receptors. Clearly, attempts to improve the bioavailability of these components to microorganisms during bioremediation may also result in increased human exposure. In estimating the fate of pollutants in complex environmental matrices, the application of fugacity models[53] for predicting the relative phase distributions and concentrations of contaminants and their metabolites during treatment[76,77] is now proving valuable for informing exposure assessments and the optimization of in situ remediation. These approaches have yet to be applied to the biopiling of weathered oils or to account for the partitioning behavior of PAH in weathered non-aqueous phase liquid (NAPL) within the unsaturated zone. In short, the relationships between chemical presence, toxic response, bioavailability, and risk for weathered hydrocarbons have yet to be fully elucidated and coupled into a meaningful risk management framework, though work is progressing.[29–32,82] One of the obvious research needs is to authenticate human exposures to oil/soil matrices in the context of contaminated land and, in particular, to explore the bioavailability of risk–critical compounds (benzene, benzo[a]pyrene) in light of these newly revealed partition relationships.

The regulation of site remediation now requires adoption of a risk-based approach and this extends to technology verification.[29] Although the effectiveness of an environmental technology in treating pollution has historically been expressed as a percentage reduction in the pollutant concentration released to, or found in, a medium of concern, regulators are increasingly concerned with mass, toxicity, and risk reductions within the multimedia, multiphase environment. For petroleum hydrocarbons in soil, international regulatory guidance on the management of risks from contaminated sites is now emerging. As shown in this review, much of this guidance promotes the use of risk management frameworks to guide decision making, the application of reference analytical methodologies, and the derivation, and use of acute, subchronic, and chronic toxicological criteria for these wastes. These frameworks adopt a variety of approaches to the evaluation of risk-critical components within the hydrocarbon waste–soil matrix.

In the United States, a substantive research effort has focused on integrating hydrocarbon fate and transport, petroleum microbiology, and environmental diagnostics to inform regulatory processes for site management under the Superfund Program. ThermoRetec (2000),[82] reporting for the Petroleum Environmental Research Forum (PERF), provided an authoritative account of the central importance of partitioning within soil-bound hydrocarbons in developing environmentally acceptable endpoints (remedial objectives). Drawing on a detailed understanding of NAPL and residual oil fate and behavior, this work is now influencing the development of remediation criteria for petroleum hydrocarbons in soils in the United States for human health, groundwater and ecological receptors, and a reappraisal of the level of residual petroleum hydrocarbons that can be left at remediated sites without posing an unacceptable risk. In contrast, weathered, mid-distillate and heavier oil sources are generally given a narrow treatment by these reviews and frameworks. The Environment Agency (2003)[30] has recognized this in its recent consultation on principles for evaluating the human health risks from petroleum hydrocarbons in soils, and has called for views. One of the few environmental exposure assessments explicitly to address heavy oils has been discussed in a recent article relating to worker and visitor exposure following the wrecking of the oil tanker *Erika*, 65 km south of the Brittany coast.[7] Here, inhalation, dermal, and oral PAH exposures from beached no. 6 fuel oil were estimated and found to be negligible for beach cleaners and tourists (occasional visitors) coming into to contact with heavy oil, demonstrating the feasibility of this level of risk analysis for these problematical wastes.

The move toward risk-based corrective action (RBCA) has been slow in the United Kingdom and whilst some progress has been made in integrating the aspects of analysis, exposure assessment, and technology verification,[29] there are gaps in the current knowledge base. Specifically, (1) analytical strategies in the United Kingdom are not generally targeted at the bioavailability of risk-critical components; (2) risk assessments do not regularly account for highly weathered residues encountered at many sites (API, 2001); and (3) treatment "success" is still supported by reductions in hydrocarbon load in isolation of combined reductions in toxicity, chemical mass and risk. In a typical study, Al Awadhi et al. (1996)[2] report an 80wt% reduction in oil from heavy oil-laden landfarming plots in Kuwait over a 15-month research period, and Milne et al. (1998) report between 30 and 50 wt% reductions in TPH from heavy refinery sludge treated in amended composting plots over the treatment period. Guerin (2000)[40] reports a 5-year performance study of a land treatment facility for oil wastes from heavy vehicle maintenance. Most of these studies and many of those since (e.g., Tien et al., 1999[83] and Owens and Bourgouin, 2003[68]) follow a pattern of reporting reductions in TPH load as a presumed surrogate for risk reduction.

A contributing factor to the over-reliance on TPH as an indicator of treatment performance in isolation of other parameters, has been the cost of implementing more sophisticated diagnostic techniques and their low uptake within the sector. This has been, in part, a result of the absence of a regulatory framework. Nevertheless, researchers have been concerned with improved diagnostics methods (the analysis of specific carbon number ranges); the fingerprinting of hydrocarbon wastes for source identification (for liability disputes) and in tracking biotransformation; and with biological techniques as indicators of the impact of hydrocarbon contamination on soil function. Recent initiatives have included the development of reference methods for the analysis of petroleum hydrocarbons from nC_6-C_{50},[19,84] the application of biomarker analysis (*n*-alkane: substituted *n*-hopane indices) to bioremediation verification,[46,62] and the validation of microbial bioassays for petroleum hydrocarbons in soil.[24,68] Our own work,[46] building on that of Prince et al. (1994),[73] demonstrated that the ratio of total alkanes (Σn-alkanes) to $17\alpha(H)21\beta(H)$-hopane is the most sensitive of a series of biomarker ratios in reflecting oily waste depletion in a 256-day soil microcosm study.

6. CONCLUSIONS

Risk assessment is a well-established paradigm for the management of contaminated land.[4] However, the move toward risk-based corrective action has been slow. Recent stakeholder consultations in the United Kingdom, and subsequent publications from the Environment Agency, aim to adopt a risk-based framework where remediation success is expressed in terms of risk rather than TPH load reductions.

There are several risk assessment frameworks for land contaminated with petroleum hydrocarbons including those published by TPHCWG,[88] ASTM,[5] MADEP,[55] Environment Agency,[32] API,[3] and CCME.[18] However, none of these specifically deal with weathered petroleum hydrocarbons, which are widely acknowledged to have major qualitative and quantitative differences compared to non-weathered petroleum hydrocarbons.[87] Additionally, there are variations between frameworks that may result in different recommendations, such as the level of remediation to be achieved. As shown, the use in some frameworks of deriving equivalent carbon numbers from empirical relationships representative of normalization to the *n*-alkanes appears to be incorrect. In general, variations between frameworks occur in the determination of the range used, how toxicity is assessed, and how soil samples are analyzed.

Beyond the regulatory perspective, researchers have been involved in improving diagnostics methods (the analysis of specific carbon number ranges); the fingerprinting of hydrocarbon wastes for source identification (for liability disputes) and in tracking biotransformation; and with biological

techniques as indicators of the impact of hydrocarbon contamination on soil function. There has also been increased interest in the use of fugacity models for making inferences about the fate and transport of risk-critical compounds within contaminated soils.

Many of these advances have yet to be synthesized into regulatory tools. However, there is growing support for the move toward compound-specific risk-based approaches for the assessment of hydrocarbon-contaminated land.

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APPENDIX OF MAIN ACRONYMS AND DEFINITIONS

API	American Petroleum Institute
ASTM	American Society for testing and materials
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	Benzene, toluene, ethylbenzene and xylene
CCME	Canadian Council of Ministers of the Environment
EA	Environment Agency (UK)
EPH	Extractable petroleum hydrocarbon
GC	Gas Chromatography
GC-MS	Gas Chromatography mass spectroscopy
GC-FID	Gas Chromatography with flame ionisation detection
MaDEP	Massachusetts Department of Environmental Protection
PAH	Polynuclear aromatic hydrocarbons
RIVM	National Institute for Public Health and the Environment
TNRCC	Texas Natural Resource Conservation Commission
TPH	Total petroleum hydrocarbon
TPHCWG	Total Petroleum Criteria Working Group
UCM	Unresolved complex mixture
USEPA	United States Environmental Protection Agency
VPH	Volatile petroleum hydrocarbon

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A SURVEY OF GREEN BURIAL SITES IN ENGLAND AND WALES AND AN ASSESSMENT OF THE FEASIBILITY OF A GROUNDWATER VULNERABILITY TOOL

K-H KIM[1], M.L. HALL[2], A. HART[3] AND S.J.T. POLLARD[2*]

[1]Department of Environmental Horticulture, The University of Seoul, South Korea
[2]Sustainable Systems Department, School of Applied Sciences, Cranfield University, Cranfield, Bedfordshire, MK43 0AL, England
[3]Environment Agency, Science Group, Solihull, UK

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ABSTRACT

Since 1994, 200 'green' or natural burial sites have been developed in the UK and Eire, attracting regulatory attention because of perceived risks to groundwater. Here, a survey of natural burial practice in England and Wales (n=49 of 141 elicited) is presented, providing data on operational trends and supporting the design of a groundwater vulnerability assessment tool. Natural burial grounds are generally small in area (< 0.8 ha), adopt a mean single burial depth of 1.45 m bgl and a mean plot density of *ca.* 1480 graves ha^{-1}. A vulnerability screening tool is described that allows a desk-based evaluation of sites by reference to seven groundwater risk attributes. Initial feasibility is evaluated through application to 131 sites.

Keywords: Cemetery, groundwater, pollution, natural burial grounds, risk, vulnerability.

INTRODUCTION

There are two principal options for the disposal of the dead in the UK: cremation or burial. Cremation has been preferred for 40 years and in 2003 accounted for 75% of the funerals in England and Wales [1]. But there is also considerable pressure for space in cemeteries. Furthermore, a growing demand for a more 'natural' way of burial has led to the development of natural or 'green' burial grounds. Here, graves have no permanent gravestone or they posses an unobtrusive marker. Sites have a natural appearance, often taking the form of a managed woodland or meadow. Since 1994, *ca.* 200 sites in the UK and Eire have joined the Association of Natural Burial Grounds (ANBG) [2], the sector's trade body.

The potential for burial grounds to pollute the environment and the management of this risk is summarised by others (Pacheco *et al.* [3-14] When bodies and grave contents (coffins, coffin liners, shrouds, clothing) decompose, the decomposition products are released to the environment. The human body (*ca.* 70kg) is a complex matrix of organic (17%^{w}/w protein; 17%^{w}/w fat and 6%^{w}/w carbohydrate) and inorganic (N, P, Ca, Na, Sr) constituents. Decomposition poses a microbiological hazard. In risk assessment terms, there is a growing consensus that the principal receptor of concern for the key pollutants (NO_3^- and $NH_4^+{}_{(aq)}$) is the groundwater below the site (Pacheco *et al.*, [3,6,8,15,16].

This study provides the first survey of natural burial practice in England and Wales and describes the initial design of a groundwater vulnerability screening tool. The survey provides a unique snapshot of practices in this industry and the first qualitative information on the potential risks to groundwater. Both site operators and regulators in England and Wales (local authority planning and environmental health departments and their Government consultees, including the Environment Agency) must make decisions on the suitability of individual sites and, or, recommend site investigations where appropriate. In doing so, the first level of risk based decision making relies on screening the site against known likely hazard combinations. The original guidance on this subject (see Environment Agency 2004c) provided a similar framework which has been used in some sites. At this screening stage, a full site characterisation and risk assessment of proposed burial grounds during the planning stages of their development is rarely possible. As a guide to prioritising sites that merit greater attention, this study proposes a risk screening methodology and examines its initial feasibility using a desk-based trial. The costs associated with detailed subsurface assessments are often too high for small sites. In addition, for extant sites there is the

added reluctance of undertaking work that may disturb existing graves. Nevertheless, the method described here is based on bringing together existing tools such as the groundwater vulnerability maps that are widely recognised as appropriate to the screening step and are central to the regulatory response to any new developments that threaten groundwater quality.

MATERIALS AND METHODS

Study Rationale and Natural Burial Ground Survey

Initially, a survey was undertaken to ascertain the state-of-the-art on natural burial grounds in England and Wales. A questionnaire (Table 1) was distributed to burial ground managers between April and June 2005 to characterise natural burial practice. Questionnaires were distributed to 141 members of the ANBG, the aim being to obtain a description of the source term and summarise the practices employed; data not previously compiled for England and Wales.

The questionnaire was designed to elicit information of the operational life (Q1), source term (Q2-6), depth of burial (Q7) and burial specifications (Q8-11).

Groundwater Vulnerability Screening Tool Design

For development of the groundwater vulnerability tool, both active and planned grounds whose location had been established were included. Site postcodes were used to extract the grid coordinates from the UK street map coordinate converter and the coordinates used to reference relevant data from available spatial data sets. A baseline methodology for screening groundwater vulnerability to pollution from cemeteries is described by Young *et al.* (1999).

Table 1. Sample survey questionnaire.

Name and address of burial site(s):					
Postcode of actual burial site (s):					
Contact name and/or email address:					
1. When did the site open for burials?					
Were any environmental surveys done before the site was opened?					
If so, what was the nature of these?					
2. What is the size of the burial site (acres)? (later converted to hectares)					
Approximately what proportion of this is given over to tree cover?					
Are there any intentions to expand the site?					
3. In total, how many potential					
i) grave plots are there on the site?					
ii) ashes plots are there on the site?					
4. How many burials were there at the site in					
	0-5	6-10	11-20	21-50	more
i) 2004	☐	☐	☐	☐	☐
ii) 2003	☐	☐	☐	☐	☐
iii) 2002	☐	☐	☐	☐	☐
iv) 2001	☐	☐	☐	☐	☐
5. How many burials in total have there been to date?					
6. Are graves dug for each coffin, or are multiple coffins interred in single graves?					
If a mixture of both practices is employed, what proportion of single and multiple graves are dug?					
7. How deep are the graves i) for single coffins?					
ii) for two coffins?					
iii) for three coffins?					
I'm also trying to establish whether the policy in burial grounds is to encourage more natural practices, or if the rule:					
at burial sites are more prescriptive (and perhaps less flexible).					
8. Which coffin types does the site accept?					
9. What types of memorials are permitted on the site?					
10. What requests are made of funeral directors using the burial site?					
11. Does the site accept embalmed bodies for burial?					

The parameters used were: superficial deposit type and thickness, depth to water table, flow mechanism, presence and type of aquifer, source protection zone category and distance from watercourses, springs and drains. Since comprehensive data for each of these parameters are not available, the methodology was adapted, as shown in Table 2.

Each parameter (attribute; column 1, Table 2) was subdivided into categories representing an increasing risk to groundwater and a score assigned; 1-2 representing the least threat to groundwater and 9-10 the greatest. Scores for each attribute were equally weighted and summed to provide an aggregate vulnerability score across seven attributes (Tables 2 and 3). Adaptations made to the screening tool for each of the attributes are described below. Important limitations of the tool are discussed later. In some details especially because validation, in a metaphorical sense, is problematic for these scientific locations.

Type and thickness of superficial deposits

Superficial deposits (regoliths) are interpreted as unconsolidated deposits that occur as discontinuous patches and larger spreads, resting on bedrock. Superficial deposit data at 1:50 000 was obtained from the British Geological Survey (BGS) (DiGMapGB-50 v2_11). Additional categories of superficial deposits to those described by Young *et al.* (1999) [7] were assigned a vulnerability score (Figure 2). The thickness of the deposit was obtained from the BGS at the 1:50 000 scale from the GeoSure data set. The data is limited – it is modelled, created by interpolating values from borehole and map measurements. The basic superficial thickness model (BSTM) for deposit thickness was used. Wherever bore data is unavailable, this model uses a minimum mapped thickness of material of 1.5 m.

Hydrology of soil type models (HOST)

While the Environment Agency holds some data on water table depth, a full national coverage is not available. Substitute data sets were therefore sought to provide an improved method for assessing groundwater vulnerability. The Hydrology of Soil Types (HOST) model [17] has merit in this context because it assigns classes to soil types on the basis of their hydrological response and the representative processes occurring in soil (Figure 1). The HOST classes provide an indication of the degree of protection that an overlying soil provides to groundwater. A category of risk to groundwater for each HOST class was therefore assigned (Figure 2).

Briefly, the HOST model catalogues soils on the basis of their physical properties and their effects on the storage and transmission of water. There are 29 HOST classes, based on 11 response models, A-K (Table 2; Figure 2). Each model belongs to one of three groupings (horizontal rows in Figure 2), based on whether an aquifer is present and at what depth it is likely to occur: at more than 2m depth, within 2m, or no

Table 2. Adapted groundwater vulnerability scoring methodology (adapted from Young C.P., *et al* [7].

parameter / score	very low 1-2	low 3-4	moderate 5-6	high 7-8	very high 9-10
regolith type	clay and silt	clay, silt and sand	clay, silt, sand and gravel	Sand sand and gravel	absent
	clay, silt, sand and peat peat (2-3)				
superficial deposits thickness	>5 m	3 - 5m	3 m	0 - 3m	Absent
HOST model classification	H, I, J, K (no significant aquifer or groundwater)	C, D	A, B, (aquifer or groundwater normally present at >2m depth)	E	F, G (aquifer or groundwater normally present within 2m)
flow mechanism	1 (inter-granular)	2	3	4	5 (fissured)
Aquifer	none		minor aquifer		major aquifer
Source protection zone	outside zone III	in zone III	close to boundary of zones II and III	within zone II	within zone I
distance from river lines	>150 m		80-150 m		<80m

significant aquifer or groundwater present.

The HOST model describes the dominant water movement in soils (*i.e.* vertical or lateral) based on the soil properties of depth to gleyed layer, depth to slowly permeable layer, integrated air capacity and the presence of a peaty surface layer.

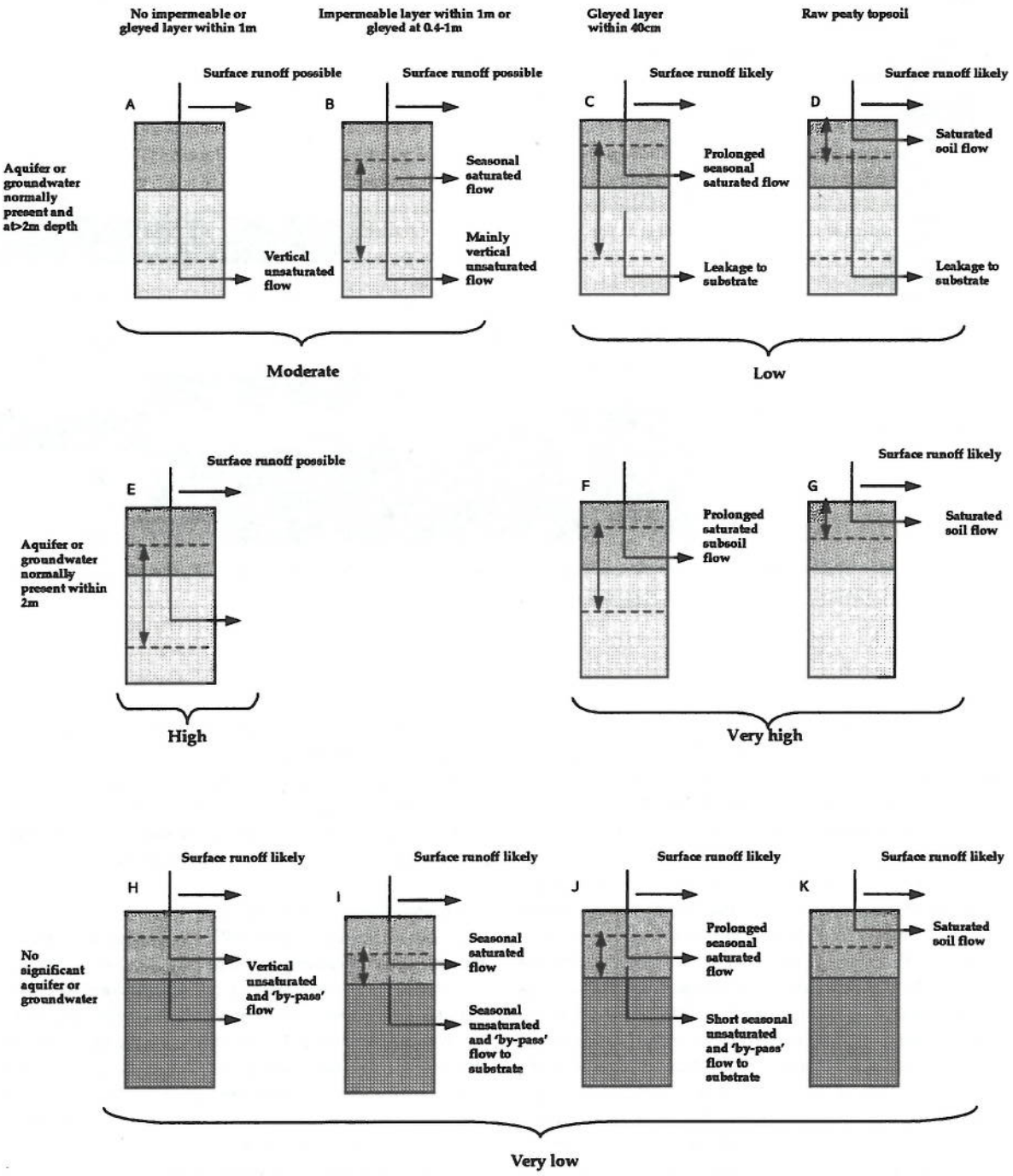


Figure 1. Conceptual models for HOST model classification (after Boorman *et al* [17].

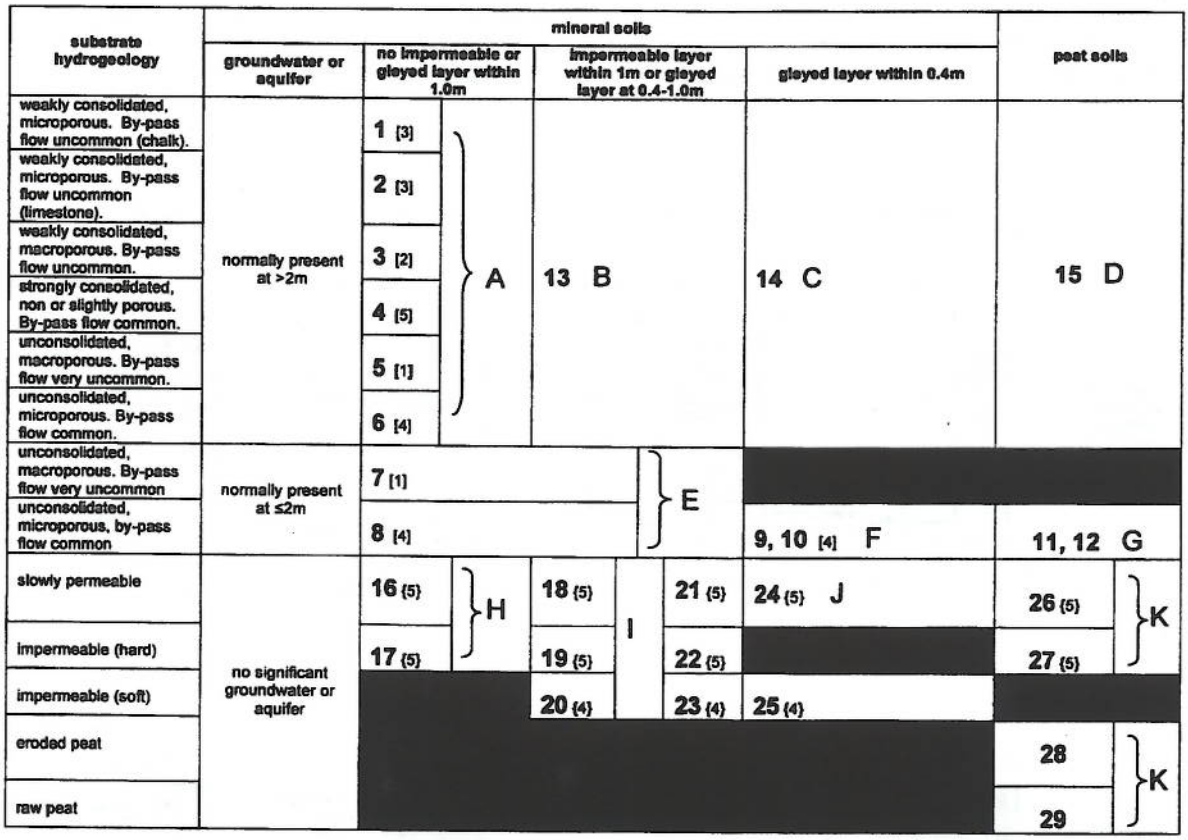


Figure 2. Host classification (1-29; A-K) and flow mechanism values to viable aquifers [in squared brackets] and local wells (in curved brackets) (adapted from Boorman *et al* [17]).

Assignment of flow mechanism values

The mechanism of water movement through soil influences the relative vulnerability of the underlying groundwater to pollutants. Intergranular flow is normally slower in the unsaturated zone than in the saturated zone. Water and dissolved pollutants travel downwards slowly allowing filtration and attenuation and thus providing a degree of protection to groundwater (Figure 1). In contrast, fissured flow enables pollutants to by-pass these attenuating processes. Flow mechanism scores were assigned using the HOST model (Figure 2), reflecting the spectrum of flow types from intergranular (1) to fissured (5). HOST models B and C, which contain an impermeable layer within 1m or gleyed layer at 0.4-1.0 m and a gleyed layer within 0.4 m respectively, represent a range of substrate hydrogeology and no single flow mechanism can be assigned (Figure 2). Fortunately, model B (HOST class 13) and C (HOST class 14) account for only 0.5% and 0.03% of land in England and Wales and none of the burial sites fell into either of these classes. Raw peaty top soils dominate the hydrology of model D (class 15; Figure 2). While the underlying substrate is coarse and relatively permeable, the upper level is saturated. Model E is divided into two HOST classes, 7 and 8. Class 7 soils are made up of coarse textured sands and gravels in which by-pass flow is very uncommon; hence this class was assigned a flow mechanism of 1. Class 8 was assigned a flow mechanism of 4 as it is comprised of loamy and clayey soils, but in which by-pass movement is often common via fissures and macropores.

Source protection zones and aquifer data

Source protection zone (SPZ) and aquifer data, part of the groundwater vulnerability mapping data set for England and Wales, [12]. Burial ground coordinates were compared with the source protection zones, and where the coordinates lay within zones II or III, the distance from the boundary between the two was measured using ArcMap™ software. The category 'close to boundary of zones II and III', not defined in Young *et al.* [7], was taken to be 150 m from the boundary. The sites were scored for groundwater vulnerability for these two parameters as in Table 2.

Distances from watercourses, wpring and drains

Data on distances from drains and field are not collated on a national level. These features are critical and only

identifiable through desk-based research or site investigation. Distances from rivers, canals and lakes at 1:50 000 scale were provided by the Environment Agency. The scoring used in Young *et al.* [7] was adapted: a distance of less than 30m between a burial ground and a river represents a high risk site. However, as the coordinates of the burial sites were generated from postcodes, the location of the sites does not have the required degree of precision to distinguish five different categories of risk. Instead, the sites were divided into three categories (Table 2): within 80 m, between 80 m and 150 m and more than 150 m from a river or spring.

RESULTS

Survey of Natural Burial Ground Practice

To our knowledge this is the first survey of natural burial ground practice beyond the rudimentary information reported in Wienrich and Speyer [2]. Our survey of 141 sites elicited 49 responses. Natural burial grounds are operated privately, or by trusts or by local authorities. Almost 60% of sites in England and Wales are local authority-run and of the 49 respondents, 26 were from local authorities. Members of the ANBG have all opened since 1993 and been subject to modern planning procedures and statutory (Environment Agency) consultation on their siting. The following analysis is based on the 49 responses received.

Site size and density of graves

The area of burial grounds varied from 0.04 to 14 ha. Natural burial grounds are generally small sites, with half of the sites being ≤ 0.8 ha. Only three sites are > 8 ha, the mean size being 1.7 ha. The mean number of potential burials per site is 2637 and the mean plot density is 1478 graves ha^{-1}. The plot density is consistent with the Environment Agency's estimated average of 1580 graves ha^{-1} and lower than the typical density for conventional cemeteries of 1975 graves ha^{-1}. The burial ground with the lowest projected density of burials has 165 graves ha^{-1}; whereas the ground with the highest density has an average of *ca.* 9800 graves ha^{-1} which appears anomalous. To estimate the rate of burial per site, each of the sites were asked how many burials occurred in each of the last four years (Table 1). In 2001, over 50% of burial grounds undertook less than 5 burials. By 2004 this number had dropped to 40% and the percentage of sites with higher burial rates had increased (Figure 3).

Depth of graves

The majority of natural burial grounds (87%) dig graves to a single depth and inter a single coffin. By contrast, conventional cemeteries usually dig graves to inter two coffins. A survey of Danescourt cemetery in Wolverhampton, UK [18] found that 90% of the graves were for two coffins, at 1.8 m below ground level (m bgl). Deeper 'common graves' make up 2-3% of annual interments, typically extending to 2.7 m bgl to contain three coffins. On occasion graves extend to 3.4, 4.0 or 4.6m bgl, for four, five or six burials. The graves are normally filled within one year, so the source term may be treated as a single 'large burial' [19] This survey suggests the mean burial depth in natural burial grounds is 1.45 m bgl. Whilst this is slightly deeper than the Agency model (Young *et al.* [7,20], which assumes 1.3 m bgl, it is shallower than for conventional cemeteries. This potentially results in a slightly

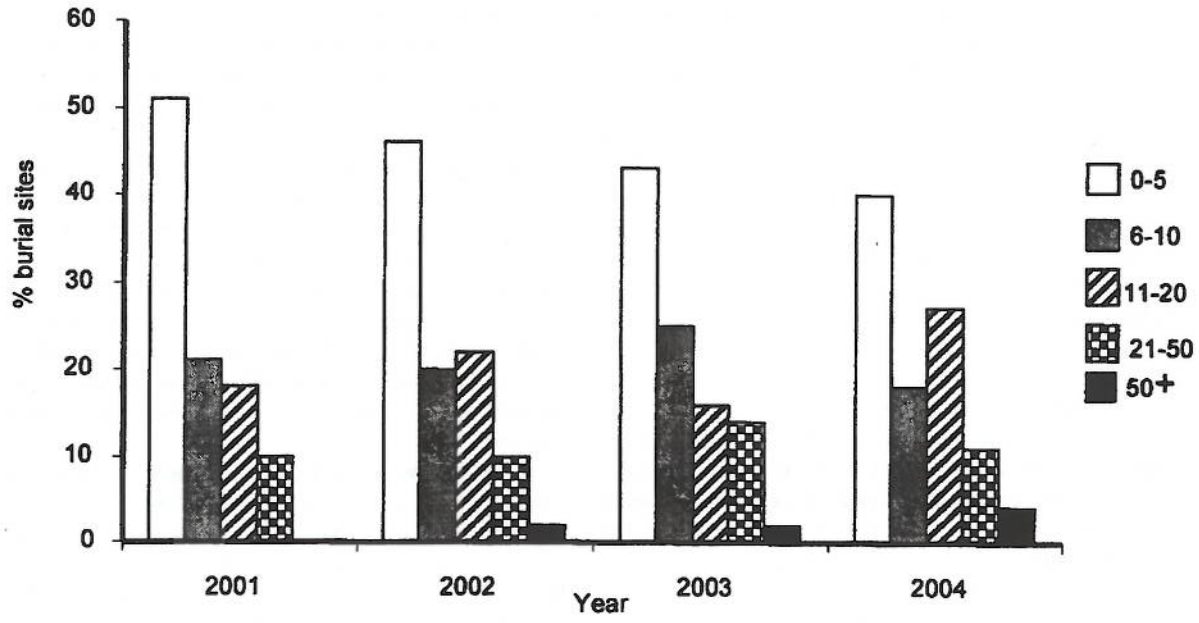


Figure 3. Number of burials per site, 2001-2004 (n= 49 responses).

thicker layer of soil between the base of the grave and any underlying groundwater through which attenuating processes may occur, potentially lessening the potential polluting effects of the products of decomposition.

Prior investigation and survey

Nineteen of the responses indicated that no form of environmental site survey had been conducted before the site was opened. Eighteen respondents were aware of some form of prior investigation: in some cases a desk-based groundwater risk assessment had been conducted, boreholes sunk to monitor water quality or a soil or geological survey performed; in another case the local water utility had identified suitable locations using a desk-top analysis. At six grounds, respondents were unaware whether a survey had been conducted or not, possibly because the natural burial ground was annexed to an existing, older, cemetery.

Policies on embalming

The recent development of natural burial grounds means they are unlikely to present a risk to groundwater from heavy metals employed in outdated embalming products, as these have been banned in England and Wales since 1951 [21]. Nevertheless, current practice is sometimes to embalm using formaldehyde to arrest decay until after burial. The issue of accepting embalmed bodies for burial had not arisen at three grounds, and no policy had been fixed. Fourteen of the 49 respondents replied that they do not accept embalmed bodies. Twenty-two sites responded without qualification that embalmed bodies are accepted, while 8 sites stated that although they preferred bodies not to be embalmed, they are flexible in practice.

Coffin types

Our study has adopted a premise that coffins adopted at natural burial grounds offer less containment for the contents than conventional coffins, many of which have plastic liners. In the survey, 33 responded that some form of discrimination was enforced. These sites described the types of coffin they accepted as 'biodegradable', 'environmentally-friendly', 'natural' or 'ecological'. Fourteen respondents listed the materials they accepted and these included bamboo, willow, cardboard, wicker and natural fibres. Sixteen respondents were prepared to accept any type of coffin, although 2 stated that the use of biodegradable coffins was encouraged.

Tree cover and the iterment of ashes

Burial site managers were asked to provide an estimation of the tree cover over the site to compare with the Agency model for water infiltration and evapotranspiration [7]. Three of the sites had no tree cover, being meadows or pasture. Another 3 had no trees amongst the graves, but trees surrounded burials at the edge of the site. Twelve grounds estimated that 70-100% of the area of the site was covered by trees, and 8 stated that one tree was planted per grave. Fourteen sites estimated 2-40% tree cover. Six grounds made no estimate, but stated that tree cover would increase over time.

Space is not always planned for interring ashes. When asked about the provision of ashes plots on the site, 31 of the 49 respondents had planned the potential number of plots on the site and 11 replied that their site was capable of accepting the same number of ashes plots as graves; both types of internments being treated the same. Eighteen sites had no dedicated space for burying ashes, although some sites commented that families were welcome to scatter ashes at the site.

Feasibility Trial of the Groundwater Vulnerability Tool

We recognise at the outset the challenge of making risk-informed decisions with incomplete data sets. This said, regulators face the challenge of offering a sound rationale for their advice whilst operating within these constraints.

Screening tool output

Of the 180 sites in England and Wales listed as members of the ANBG, 131 were identified and scored using the screening tool. Fewer locations than the listed 180 were identified because either no specific location existed for some planned sites, or because plans for the sites had been abandoned. Site scores were aggregated across seven risk attributes: (i) superficial deposit type; (ii) superficial deposit thickness; (iii) HOST classification; (iv) SPZ class; (v) aquifer type; (vi) flow mechanism; and (vii) distance to river. The scoring of these attributes was normalised, each attribute having a maximum score of 10 (9-10; Table 2). A maximum aggregate score of 66.5 (mean of the highest class score of 9.5 x 7) is achievable. The minimum vulnerability score theoretically achievable is 1.5 x 7, that is 9.5.

For the total set of sites investigated, of particular note was the high incidence of high scores (9-10) for deposit type and thickness, which results from the absence of superficial deposits. This was the case in 74 (54%) of the sites screened. Deposit type is mapped throughout the country, although it occurs as discontinuous patches. Each site is mapped onto a deposit type, although over half of the sites have no underlying deposits. For example, one site (Headington, Oxford) was mapped to an area of peat deposits, although superficial deposits were absent at that location. Wherever borehole data is unavailable, the model provides a thickness of 1.5m. The data for 26 sites (19%) gave a thickness of 1.5m, suggesting that accurate data may have been missing for as many as 26 sites.

Ninety sites scored 1-2 for HOST type. Only 8 burial grounds fell into the very high vulnerability class. One site (Entwhistle) was of HOST model K, which has raw peaty topsoil. The superficial deposits at this site, according to the BGS data, were diamicton, defined as "clay and silty clay, commonly pebbly and sandy, stiff, possibly interbedded with sand and gravel-rich lenses and rare peat" [22]. Prior to this

study, we anticipated that no sites would be located in Class I because the source water protection policy prohibits this type of land use within zone I. This appears to be accurate. Twenty-one sites are located in source protection zones II and III, the remainder lay outside the zones. There are no underlying aquifers at 30 sites; 80 sites occur over minor aquifers and 26 occur over major aquifers.

Determining the significance of risk in risk scoring systems is not straightforward, particularly for multiattribute systems such as the one described here. In all such systems there are the potential dangers of double counting and of assuming linear scales for individual attributes. We adopted a pragmatic approach to the analysis of the data here, being primarily interested in the relative banding of vulnerability scores than the absolute values obtained which are necessarily relative. Using the system developed a, 'moderate' score for each attribute would produce an aggregate vulnerability score of 35, whilst a 'high' score would produce an aggregate score of 63 and above (Table 2). In this feasibility assessment, we observed a concentration of aggregate scores around the mid range. For illustrative purposes, the aggregate scores for the highest scoring 30 sites (n = 131) are provided in Figure 4, which summarises the distribution of vulnerability scores by site identifier and attribute (note that all sites have a score >40). The distance to river, flow mechanism and aquifer type appear to be critical risk factors. Table 3 provides the raw data for the lowest eight scoring of these thirty sites as an illustration. We consider Figure 4 represents a series of 'medium risk' sites that, subject to review, may warrant further investigation on an individual site basis, initially by desk-based scrutiny of the full data set and supporting assumptions in light of the fact that we are not able yet to validate the feasibility trial.

DISCUSSION

Natural burials are on the increase in the UK and their impacts on the environment is less well understood than those from crematoria or conventional cemeteries. When consulted on new development proposals, the Environment Agency advises local authorities on such sites. However, the science of natural burial grounds and, in particular, the extent and nature of the potential risks posed by bodies is not well understood. The vulnerability assessment tool designed and trialled in this study did not suggest any high-risk sites; a reassuring and positive outcome because these sites are either operational or in the later stages of the planning process. This said, the study has highlighted the incomplete nature of several national data sets and demonstrated the critical importance of statutory consultation on siting decisions. By and large, those consultations that have taken place to date on the siting of natural burial grounds would appear to have been effective.

Methodological Limitations

All risk screening techniques, such as the one described in this study, have data limitations and simplifications embedded within them that demand scrutiny prior to their practical application. The regulator's challenge is to offer

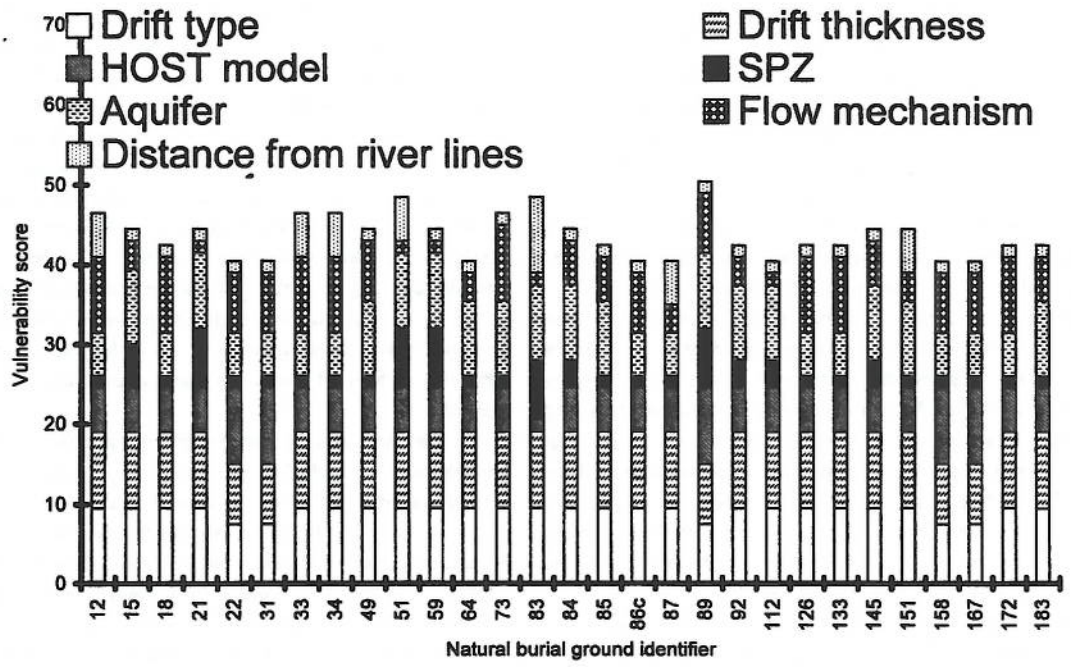


Figure 4. Aggregated vulnerability scores and within-score distribution for 30 top scoring natural burial grounds.

well-reasoned and proportionate advice, often in the face of a paucity of data or incomplete data sets and using assumptions that despite best intention, may not be able to be validated. Whilst adoption of a precautionary approach to siting decisions should err on the side of caution, seeking desk and site investigation data to support decisions, site investigation is not always practically possible and judgements have to be made using a well-reasoned rationale, hence the motivation for this study and feasibility trial.

Scores within ranking schemes represent surrogates for the true value of the attributes under study, and the aggregation of attributes across a complex system forces caution on interpretations of the output. This screening tool is no exception. Source protection zones are centred on approximately 2200 major abstraction sites, some of which are used for public water supplies. Individual site investigations are required to identify additional sites of abstraction when considering new developments. An absence of data on drains and field drains is also an important limitation. No national data on smaller or private abstractions are available for a desk-based assessment of groundwater vulnerability. However, the same methodology may be employed for a more detailed on-site groundwater vulnerability assessment for the later stages of risk assessment. An identical scoring method may be used where smaller abstractions are made from viable aquifers.

A slightly different approach may be required when considering the presence of small local wells, where water is abstracted from shallow depths. The location of such wells is also unavailable on a national scale. Suitable soil types include HOST classes (Figures 1 and 2) within those described by HOST models H-K, where there is no underlying groundwater body. For example, HOST model I has an impermeable layer within 1m and a gleyed layer between 0.4m-1m, and model J has a gleyed layer within 0.4m. This results in much of the infiltrating rain being confined to the upper levels of the soil and moving in a predominantly lateral direction, such that water is held at shallower depths. If an on-site assessment is conducted and local wells identified, an amended scoring system is required.

Flow mechanism scores were assigned to HOST models. Scores were assigned solely on the basis of the method that water travels through soil, with the exception of Models H – K. These models describe soils which do not overlie any significant groundwater or aquifer. While these soils are slowly permeable or impermeable and may display fissured flow (mechanisms 4 and 5), particularly during summer months of low rainfall, there is no underlying groundwater or aquifer, so assigning a high risk score to these soils does not appear to be informative. For this reason, only low vulnerability scores (1-2) were assigned to these models. If an on-site risk assessment was to be conducted and the presence of local wells detected in areas of HOST models H-K, higher vulnerability scores would need to be assigned for flow mechanisms (7-8 for slowly permeable substrates and 9-10 for impermeable substrates). While hydrological processes described in the HOST models may be disrupted where the soil is disturbed for a grave, the main physical settings of the model are constant. In addition, water also infiltrates some of the ground between graves through undisturbed soil (*e.g.* at boundaries and services areas) and the HOST models hold true for the rainfall response in this soil.

Assigning the distance from the river line is the most problematic parameter, as distances have been measured from a single point within the sites. For the largest sites (8 ha and larger) the accuracy of this method is poor. The area of the site needs to be plotted in order to accurately measure the distance to the nearest river from the edges of the burial ground. Also, the distance from river lines was measured from the site-co-ordinates to the nearest river. The shortest distance between the two points was measured without taking into account topography. This potential source of error may result in an increased estimated risk to underlying groundwater because short distances can exist between sites and rivers without there being a hydraulic link between the two.

The use of postcodes for the assessment does not provide the highest degree of precision for the location of sites, which may produce inaccurate scoring, particularly in rural areas. Also, point data were extracted from two-dimensional mapping information to perform the assessment. Mapped data consist of a series of polygons of varying sizes and shapes, each of which contain the values for that area. Analysis of sites at a higher level of sophistication is possible if the area of the site is used to conduct the assessment, rather than co-ordinates. Where site areas are used, the data from each polygon that intersects the site may be taken into account, providing a higher level of information about the site. If this methodology were used as part of the initial risk assessment in the planning process, the exact location and area of proposed sites would be submitted on an ordinance survey map as part of the planning application. This would permit a higher level of accuracy in the assessment.

Depth to water table was one of the original parameters assessed [7]. This is a key parameter to consider when assessing risks to groundwater and, because this information is not available for a desk-based study, the accuracy of our analysis remains somewhat impaired and constrained through application of the HOST scheme of water tables < or > 2m depth. One methodological improvement would be to consider water tables of at least 2.5 m bgl, allowing for a further 1 m beyond the 1.45m mean depth observed in the survey.

The standard of the modelled superficial deposits thickness data includes significant data gaps [22] and provides a simplified picture of superficial deposits.

To validate the initial approach presented here, we recommend that examples of natural burial grounds with the highest, median and lowest vulnerability scores be re-evaluated using data derived from site-specific measurements to determine if the results of the desk-based studies reflect field observations. With this level of validation, this method

Table 3. Attributes scores and aggregated total for eight sites.

Site ID	Superficial deposits type score	Mean superficial deposits score	Superficial deposits thickness score	Mean thickness score	HOST score	Mean HOST score	SPZ score	Mean SPZ score	Aquifer score	Mean aquifer score	Flow score	Mean flow score	Distance from river score	Mean distance from river score	Mean score
64	9-10	9.5	9-10	9.5	5-6	5.5	1-2	1.5	9-10	9.5	3-4	3.5	1-2	1.5	40.5
112	9-10	9.5	9-10	9.5	5-6	5.5	3-4	3.5	9-10	9.5	1-2	1.5	1-2	1.5	40.5
22	7-8	7.5	7-8	7.5	9-10	9.5	1-2	1.5	5-6	5.5	7-8	7.5	1-2	1.5	40.5
31	7-8	7.5	7-8	7.5	9-10	9.5	1-2	1.5	5-6	5.5	7-8	7.5	1-2	1.5	40.5
87	9-10	9.5	9-10	9.5	5-6	5.5	1-2	1.5	5-6	5.5	3-4	3.5	5-6	5.5	40.5
158	7-8	7.5	7-8	7.5	9-10	9.5	1-2	1.5	5-6	5.5	7-8	7.5	1-2	1.5	40.5
167	7-8	7.5	7-8	7.5	9-10	9.5	1-2	1.5	5-6	5.5	7-8	7.5	1-2	1.5	40.5

could be used to screen for high risk proposals early in the planning process. While this methodology was limited to the analysis of natural burial sites, it is equally applicable in principle to conventional cemeteries though the discrepancies with respect to burial depth are an important distinction between these classes of burial ground.

CONCLUSIONS

This first operational survey of natural burial grounds in England and Wales provides a summary of current practices and allows a comparison with conventional cemeteries. The principal distinctions are between burial depth and the number of burials per plot, coffin type and by inference, the degree of containment offered by coffins used at natural burial grounds. This needs to be considered alongside the possible routine collapse of conventional coffins post-burial. The coordinates of 131 of 180 natural burial grounds have been used to extract nationally compiled data on seven physical parameters including superficial deposits type and thickness, distance to river, flow mechanism and HOST (hydrology of soil type) mechanism. These parameters were used to develop a groundwater vulnerability screening tool, the application of which was trialled scored for 131 sites and, in a first approximation, used to generate groundwater vulnerability scores. Finally, we have discussed in some depth the inherent limitations of the tool. These require additional attention prior to attempts to validate the tool's output with authentic site data from natural burial grounds.

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Exposure Assessment of Carcass Disposal Options in the Event of a Notifiable Exotic Animal Disease: Application to Avian Influenza Virus

SIMON J. T. POLLARD,[†] GORDON A. W. HICKMAN,*[,‡] PHIL IRVING,[§] RUPERT L. HOUGH,[†] DANIEL M. GAUNTLETT,[‡] SIMON F. HOWSON,[†] ALWYN HART,[∥] PAUL GAYFORD,[⊥] AND NICK GENT[#]

Cranfield University, Centre for Resource Management & Efficiency, School of Applied Sciences, Cranfield, Bedfordshire, U.K., MK43 0AL, Animal Health, Department for Environment, Food & Rural Affairs, Contingency Planning Division, Contingency Plans & Disposals Branch, 17 Smith Square, London, U.K., SW1P 3JR, Environment Agency, King's Meadow House, King's Meadow Road, Reading, Berkshire, U.K., RG1 8DQ, Environment Agency, Olton Court, 10 Warwick Road, Solihull, U.K., B92 7HX, Surveillance, Zoonoses & Emerging Issues Division, Department for Environment, Food & Rural Affairs, Nobel House, 17 Smith Square, London, U.K., SW1P 3JR, and Emergency Response Division, Health Protection Agency, Porton Down, Salisbury, Wiltshire, U.K., SP4 0JG

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We present a generalized exposure assessment of 28 disposal options for poultry carcasses in the event of a highly pathogenic avian influenza (HPAI) outbreak. The analysis supports a hereto unverified disposal hierarchy for animal carcasses, placing waste processing (e.g., incineration and rendering) above controlled disposal (e.g., landfill), above uncontrolled disposal (e.g., burial on-farm). We illustrate that early stages of the disposal chain (on-farm) pose greater opportunities for exposure to hazardous agents than later stages, where agents are generally contained, wastes are treated, and residues are managed by regulated processes. In selecting carcass disposal options, practitioners are advised to consider the full range of hazards rather than focusing solely on the HPAI agent, and to give preference to technologies that (i) offer high destruction efficiencies for target pathogens; (ii) do not give rise to significant releases of other pathogenic organisms; and (iii) do not release unacceptable concentrations of toxic chemicals. The approach offers an exposure assessment perspective for carcass disposal, thus providing a risk-informed basis for contingency planning and operational intervention. The authors recognize that relevant legislation, public perception, available capacity, and cost also need to be considered when selecting disposal options in the event of HPAI.

Introduction

Policy Context. Western governments are now managing outbreaks of the highly pathogenic, avian influenza (HPAI) A virus and its transmission to commercial poultry flocks (*1–3*). Of greatest concern is the HPAI H5N1 strain, since it causes serious disease in birds and can also infect humans who have been in close contact with infected birds. Contingency planning is essential and some governments are in a heightened state of alert and preparedness (*4, 5*). Policies are expected to be proportionate, risk-informed, evidence-based, and justified. Previous outbreaks of infectious animal disease have required the disposal of significant numbers of infected or culled stock (*6–11*) and, while the likelihood of humans acquiring HPAI in the United Kingdom (UK) is considered to be very small at present, carcass disposal cannot be performed without risks to people, animal health, and the environment (*11, 12*). Decisions on carcass disposal should help secure contingency plan objectives (biosecurity) and address issues of cost and regulatory compliance. Governments should not be concerned solely with either the cheapest or the safest disposal option at any cost; rather with developing a hierarchy of responses, topped by the optimal response. The development of a disposal hierarchy can be supported by (i) a general analysis of the exposures posed by a range of possible carcass disposal options, so that decisions on their suitability are risk-informed (this study); (ii) site-specific risk assessments, so that local environmental settings and exposures during planned or actual disposals are accounted for; and (iii) live, expert advice from health departments, health agencies, veterinary officials, environment agencies, emergency planners, researchers, and local operational partners, so that risk management is sensitive to conditions "on the ground". Critically, the range of hazards in these situations extends well beyond individual notifiable pathogens, to include all hazards associated with a carcass, its byproduct, and the associated infrastructure of disposal, including detergents, disinfectants, veterinary medicines, other animal-borne pathogens, and amenity hazards such as odor and noise.

The intensification of agriculture since the 1960s has demanded new strategies for contingency planning. Great Britain (GB) has a high human population density and carcass disposal is often in close proximity to communities and in the public view. We now have individual poultry units housing >1 million chickens on a single site. When culls are required, operational staff must kill animals quickly and humanely and have them disposed of safely and responsibly, without undue delay. The practical difficulties of maintaining biosecurity on the ground require that operational procedures are risk-informed. Calls for the adoption of historically acceptable practices, such as "on-farm" burial, become challenged by the sheer mass of culled stock and modern environmental legislation, which demands that greater consideration is given to the long-term environmental impacts of disposal.

International Context. Governments, companies, and individuals managing mass animal culls must make credible, evidence-based decisions in the face of intense political, media, and public scrutiny. The scale of carcass disposals in large outbreaks may represent a "shock load" to the waste management infrastructure of countries managing these events. Since 1997, in Asia alone, over 200 million chickens

* Corresponding author phone: +44 (0)20 7238 5111; fax: +44 (0)20 7238 1250; e-mail: gordon.hickman@animalhealth.gsi.gov.uk.
[†] Cranfield University.
[‡] Animal Health, Department for Environment, Food & Rural Affairs.
[§] Environment Agency King's Meadow House.
[∥] Environment Agency, Olton Court.
[⊥] Surveillance, Zoonoses & Emerging Issues Division, Department for Environment, Food & Rural Affairs.
[#] Health Protection Agency.

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and ducks have been killed by HPAI H5N1, or culled in efforts to contain the disease (*13*). In 2004, the Canadian Ministry of Agriculture, Food and Fisheries incinerated and composted *ca.* 17 million culled birds following an outbreak of the low pathogenic H7N3 AI virus in British Columbia (*14*). Similar disposals, adopting a range of waste technologies have been required (*15, 16*) in the United States (1983–1984; H5N2 strain; *ca.* 17 million birds culled), in Hong Kong (1997; H5N1; *ca.* 1.5 million chickens), in Italy (1999–2001; H7N1; *ca.* 13 million birds), in Virginia (2002; low pathogenic H7N2; 5 million birds), in The Netherlands, Belgium, and Germany (2003; highly pathogenic H7N7; *ca.* 28 million poultry rendered and landfilled), in Hungary (2006; highly pathogenic H5N1; *ca.* 13 000 geese buried) and most recently in the UK (2006; low pathogenic H7N3; *ca.* 49 000 poultry; incinerated and rendered; February 2007; highly pathogenic H5N1, *ca.* 159 000 turkeys rendered; May 2007; low pathogenic H7N2; *ca.* 60 backyard poultry incinerated (*17*)). The selection of carcass disposal options in these outbreaks, other than the recent 2007 H5N1 UK outbreak, appears to have been based on the scale of the requirement, the available waste technology capacity, and the logistics of local disposal, rather than on any examination of potential exposures to public and animal health and to the environment. Many responses in South East Asia have adopted uncontrolled disposal without apparent reference to the risks across the full process chain and, to our knowledge, no exposure assessment for carcass disposal in the event of an AI outbreak, addressing all the potential hazards, has been published.

Carcass disposal raises a suite of logistical, legal, economic, and sustainability issues that are reviewed elsewhere. Ellis (*18*) provides a valuable critique of carcass disposal, particularly following natural disasters in the United States, in which a range of waste technologies have been applied. Morgan (*19*) reviews the U.S. Department of Agriculture's (USDA's) emergency planning system for AI. The National Agricultural Biosecurity Center's (Kansas State University) Carcass Disposal Working Group has published an authoritative review (*20*) of carcass disposal options and cross-cutting policy issues for those managing disposals. A high priority for contingency plans is to identify protective measures so that tested disposal strategies can be applied when outbreaks occur. Examples of the practical considerations required to maintain biosecurity include (i) securing derogations from existing legislation to allow the rapid development of storage, treatment, and disposal facilities, and (ii) the rapid development of operational procedures.

Study Rationale. The UK has experienced two overlapping and significant epidemics of animal disease in the last 12 years: bovine spongiform encalopathy (BSE; (*21*)) and foot and mouth disease (FMD; (*22*)). Both had substantive, long-lasting consequences for individuals, farming communities, animal health, the environment, and other stakeholders and receptors. In February 2007, the UK successfully managed an outbreak of HPAI (H5N1) in a flock of commercial turkeys, 159 000 of which were rendered more than 300 km from the site of infection in Eastern England. In preparation for threats of this kind, the Department for Environment, Food and Rural Affairs' (Defra) and its' executive agency, Animal Health, formerly the State Veterinary Service (SVS), prepared a generic contingency plan for exotic animal disease outbreaks covering FMD, AI, Newcastle disease, and classical swine fever (*4*). The version of the plan laid before Parliament in December 2006 (*23, 24*) proposes a disposal hierarchy (Figure 1) for animal carcasses informed by a qualitative analysis of risks to public health from FMD disposals undertaken in 2001 (*25*). There has since been a desire within Government to expose the hierarchy to greater scrutiny and test its robustness for application beyond FMD disposals. It may be tempting to suggest such an analysis is not required. However, given

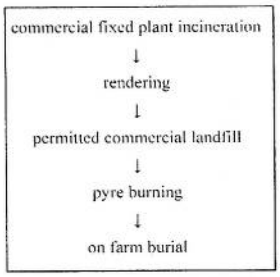


FIGURE 1. Disposal heirarchy presented in the exotic animal disease generic contingency plan, presented in decreasing order of preference (*4*).

the range of carcass disposal hazards, the differences in environmental fate posed by the sources of these hazards, and the substantive volume of stock culled during these outbreaks, GB has considered it prudent to review its disposal strategy by reference to the potential exposures that could occur. The objective of this research was to contribute to this test by undertaking an exposure assessment of disposal options for AI-infected bird carcasses. We have drawn on the following: Defra's guidelines on environmental risk assessment and management (*26–28*); a review of the prior work and critical analysis of good practice (*29*); prior work contained within Defra's generic contingency plan (2005; (*4*)); development of a methodology for reviewing disposal options in the event of an outbreak of a notifiable exotic animal disease that informed this study (2006); the methodology within the Department of Health's rapid qualitative assessment of possible risks to public health from current foot and mouth disposal options (2001; (*25*)); a series of meetings and workshops with 14 policy, academic and regulatory professionals, including a facilitated 2-day exposure analysis workshop (2006); internal consultation of study group members (2006); an independent peer review (November 2006); and consultations on the approach with a range of stakeholders (January 2007).

We were concerned with a generic assessment of exposures posed by the disposal of animal carcasses prior to their mitigation and, at the analysis stage, did not wish to be constrained by considerations of legislative compliance, costs, or public perception, though these important factors are discussed later. One reason for this is the ability of governments, should they desire, to request derogations from the current statute in emergencies; for example, on waste incineration and burial.

Methodology

Carcass Disposal in Great Britain. Carcass disposal is a multistage process (*4, 11, 12, 20*) initiated by the collection of fallen stock or the culling of live stock (e.g., birds), with subsequent disinfection of carcasses, their transport to localized collection points, and the potential off-site transport to waste processing (e.g., incineration, rendering) facilities. UK poultry farms have *ca.* 90 000 birds on average, though larger farms have up to 1 million birds and there are >258 million poultry in GB held at 23 762 premises (as of January 17, 2007; *30, 31*). Preventive measures for AI are prescribed by European statute and the domestic regulations that transpose European Directives (*32*). In the event of a need for off-site disposal, carcasses are loaded into specialist leak-proof vehicles whose movements are licensed by Animal Health (*4*). Vehicles are leak-tested and travel to a disposal facility by a predetermined route. Each load is covered and escorted to ensure the vehicle does not develop a leak. Transport of infected carcasses is also covered by the International Carriage of Dangerous Goods by Road (ADR) regulations. At the disposal facility, carcasses are disposed

of under Animal Health supervision. Following the initial removal of the carcasses from the site of discovery, all litter, equipment, and areas occupied by the affected poultry are sprayed down with an approved disinfectant and left to dry for 24 h, this being referred to as preliminary "cleansing and disinfection" (C&D). The owner/keeper of the poultry is then responsible for undertaking a thorough cleansing and disinfection of the premises (final C&D; under Animal Health supervision) and for the treatment and controlled disposal of waste litter. This involves removing the litter and other organic material and a full "wash down", followed by degreasing and application of an approved disinfectant at a recommended dilution. Restocking can commence a minimum of 21 days after final C&D is complete.

The characteristics of the early stages of this process are common to most disposal options. Differences arise later, mainly in the extent to which waste processing alters the containment of hazardous agents, their relative destruction, and the generation of post-treatment waste residues (e.g., ash, or meat and bone meal) requiring onward disposal. The carcass disposal "process chain" has five key stages: (1) disinfection and collection; (2) transport; (3) preprocessing; (4) processing; and (5) dealing with residues. A consideration of disposal options must recognize two critical factors: (i) the range and distribution of opportunities for exposure along the length of the process chain; and (ii) the available reductions in exposure, and thus risk, offered by individual technologies during waste processing. Both are important because the stages that pose the greatest opportunities for exposure may be those that precede waste processing. These exposures can be reduced, but not eliminated, by good operating practices and the proper use of protective measures (wearing personal protective equipment), so that exposures to front-line workers and the environment are minimized. These issues must be considered and risk management measures must be put in place as routine.

Exposure Assessment Overview. A methodology was developed and applied during an expert workshop facilitated by Cranfield University in March 2006. The intent was to focus on AI, as one example of an exotic animal disease, and test the methodology by undertaking an exposure assessment of disposal options for poultry carcasses. The research was desk-based and informed by a panel of fourteen cross-Government scientists, researchers, and policy specialists working within the Government guidelines on environmental risk management (*26–28*). Workshop attendees undertook six structured tasks: (i) hazard identification, screening, and prioritization; (ii) representation of the process chain for a series of disposal options and consideration of the efficacy of barriers for risk reduction along each process chain; (iii) review of a master list of exposure pathways for hazards from carcasses (*25*); (iv) development of conceptual exposure models for a series of process chains and a semiquantitative exposure assessment for each option; (v) development of a draft disposal hierarchy informed by (i)−(iv); and (vi) a preliminary screening of operating constraints acting on the disposal options.

(i) Hazard Identification, Screening, and Prioritization. The approach first identified a set of hazardous agents using expert veterinary, environmental, and public health expertise. We applied a successive series of filters (Figure 2) to a pooled set of hazards to identify the most significant hazardous agents. The pooled set included the following biological and chemical agents and amenity issues associated with an avian influenza outbreak, a key aspect of the analysis being this review of all potential hazards associated with a HPAI outbreak and not just the HPAI agent: (i) avian influenza (H5N1), avian influenza (other strains), *Campylobacter* spp, *Salmonella* spp, *Yersinia* (*Yersinia enterocolitica, Yersinia fredriksenii, Yersinia pseudotuberculosis,* and *Yersinia kristensenii*), Q fever and bioaerosols (including fungal spores); (ii) ammonia, ammonium, disinfectants, veterinary medicines (pesticides, antibacterials, coccidiostats, barbiturates), methane, organic carbon, hydrogen sulfide, carbon monoxide, benzene, toluene, ethylbenzenes, and xylenes, wood resins, dioxins/furans and dioxin-like polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), oxides of nitrogen and sulfur (NO_x, SO_x) airborne particles (PM_{10}), heavy metals, hydrogen chloride, metal salts; and (iii) odor, smoke, and noise, as amenity impacts.

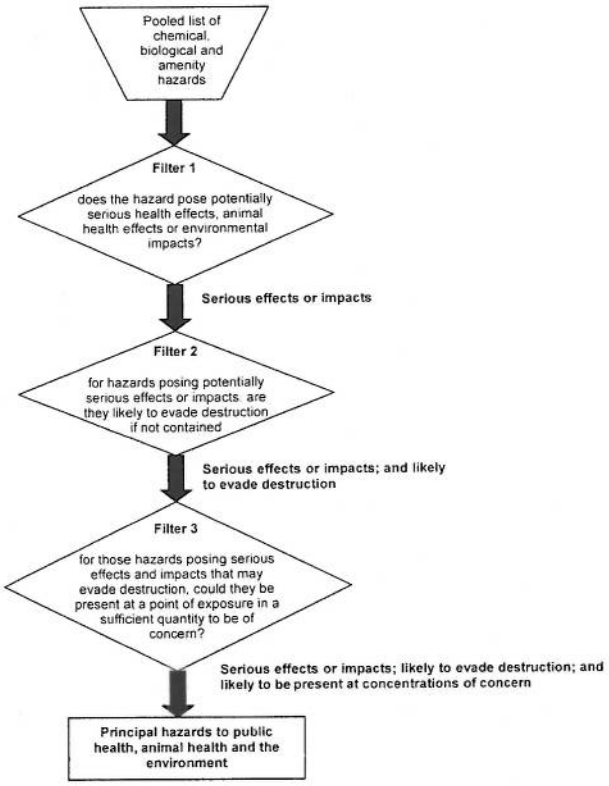


FIGURE 2. Approach to hazard screening. The application of three progressive filters to identify significant hazardous agents of concern (adapted from ref (*13*)).

Application of the filters (Figure 2) produced a subset of hazardous agents (Table 1) posing potentially significant human health, animal health, or environmental impacts; capable of evading destruction; and capable of presenting at sufficient doses to be of potential concern. We assumed those agents passing filter 3 could pose significant harm were exposure to occur within a typical (though generalized) setting.

(ii) Representation of the Process Chain. Having identified the key hazards, the likelihood of exposure to these agents for each process chain was evaluated, qualitatively in the first instance (Figure 3). The process chain for a series of disposal options was described by reference to five main stages, further broken down into twelve component stages (Figure 3): disinfection and collection: containment *in situ*, destruction at source, gather carcasses to local store, contained storage of gathered carcasses, containment during local processing, and destruction during local processing; transport: biosecure transport to facility; preprocessing: containment prior to processing; processing: containment during off-site processing and destruction during processing; dealing with residues: residuals containment and residuals destruction.

The length of the process chain is option-specific (Figure 3). Options may have very short process chains that terminate early (e.g., do nothing; leave carcass *in situ*), or longer chains

TABLE 1. Hazard Screening and Prioritization: Hazardous Agents Passing Filter 3

hazardous agent	qualifying comment on amount and/or timing of exposure to agent
avian influenza (H5N1)	for animal health (low dose exposure will cause disease in birds); a negligible public health risk
avian influenza (other strains)	for animal health (low dose exposure will cause disease in birds); a negligible public health risk for H5 and H7 strains
Campylobacter spp	prevalent pathogen; several potential pathways; low dose exposure will cause disease in animals and humans
Salmonella spp	present in UK pigs, cattle, and sheep; prevalence falling in recent years but still seen as an important pathogen (control of salmonella strains in poultry is very good)
veterinary medicines (in bird): pesticides, antibacterials, coccidiostats, barbiturates	if poultry are killed before they would normally have been, there is a possibility that veterinary products may be present in the body at elevated levels (within the normal withdrawal period); if killing is by lethal injection there may be barbiturates present, potential impact on the environment
ammoniacal nitrogen/ ammonia gas	present naturally and in high-strength leachate from decaying carcasses; significant potential impact on water bodies, especially groundwaters
disinfectants	used routinely on poultry units for biosecurity, but in the event of an outbreak of avian influenza usage will increase; carcasses will be sprayed with disinfectant prior to disposal; most disinfectants contain listed priority substances and should not be discharged to controlled waters
detergents	from cleansing and disinfection, potential impact on the aquatic environment through percolation and runoff
benzene, toluene, ethylbenzenes, xylenes	combustion byproducts, potential impact on air quality
wood resins and wood preservation products	poor combustion could release hazards, impact on air quality and ash quality
particulates	combustion products, nuisance and public health impact
odor	amenity and public health impact on local communities
smoke	amenity and public health impact on local communities
noise	amenity and public health impact on local communities

where carcasses are transported some distance to regional facilities, treated, and the residues then disposed of at some distance again from the treatment facility (e.g., incineration). The extent to which each stage in the process chain offers opportunities for the release of a hazardous agent, and thus exposure, was assessed qualitatively, by the expert panel considering the likely efficacy of existing barriers to exposure at each stage along the process chain. In general (Figure 3; red notation), early stages of a process chain offer more opportunities for the release of hazardous agents, thus more potential for exposure. Subsequent waste processing, where this is a component, offers differing degrees of effectiveness depending on whether destruction of the hazardous agent can be assured or not (amber, blue, green notation, Figure 3), and the degree of engineering process control. Exposures in the latter stages of the process chain are governed by the relative containment of process residues.

(iii) Semiquantitative Exposure Assessment. A semiquantitative exposure assessment was completed, first by reference to a master list of potential exposure pathways for hazards from carcasses developed during the 2001 FMD outbreak (*25*). The master list was developed through an understanding of the conceptual exposure models (Figure 4, for incineration) for different parts of the process chain. Having verified the suitability of this list to the case of AI, a series of exposure schematics was developed in Excel spreadsheet layers for a number of the process chains (not presented for brevity). This included exposure pathways associated with the transport of pathogens and chemicals through the environment and exposure routes such as the ingestion of water, inhalation of volatiles, direct contact with animals and people, human and animal consumption of fish or shellfish (raised in contaminated water), crop irrigation and consumption, the ingestion of irrigation water and the consumption of animals (Figure 4).

Exposure pathways that are more available to hazardous agents are more likely to result in an exposure. Such exposures are of interest as they could be associated with significant levels of risk as only those hazards with the potential to cause serious health effects have been considered (see Figure 2 and Table 1). Potential pathways were ranked for human, animal, and environmental receptors using a linear scale by the expert panel, as being (nominal ranks in brackets): not available (0); of negligible availability (1); of low availability (2); of medium availability (3); or of high availability (4). Ranking was achieved by considering the environmental and microbiological characteristics of the key hazards, and applying expert knowledge of the principal environmental

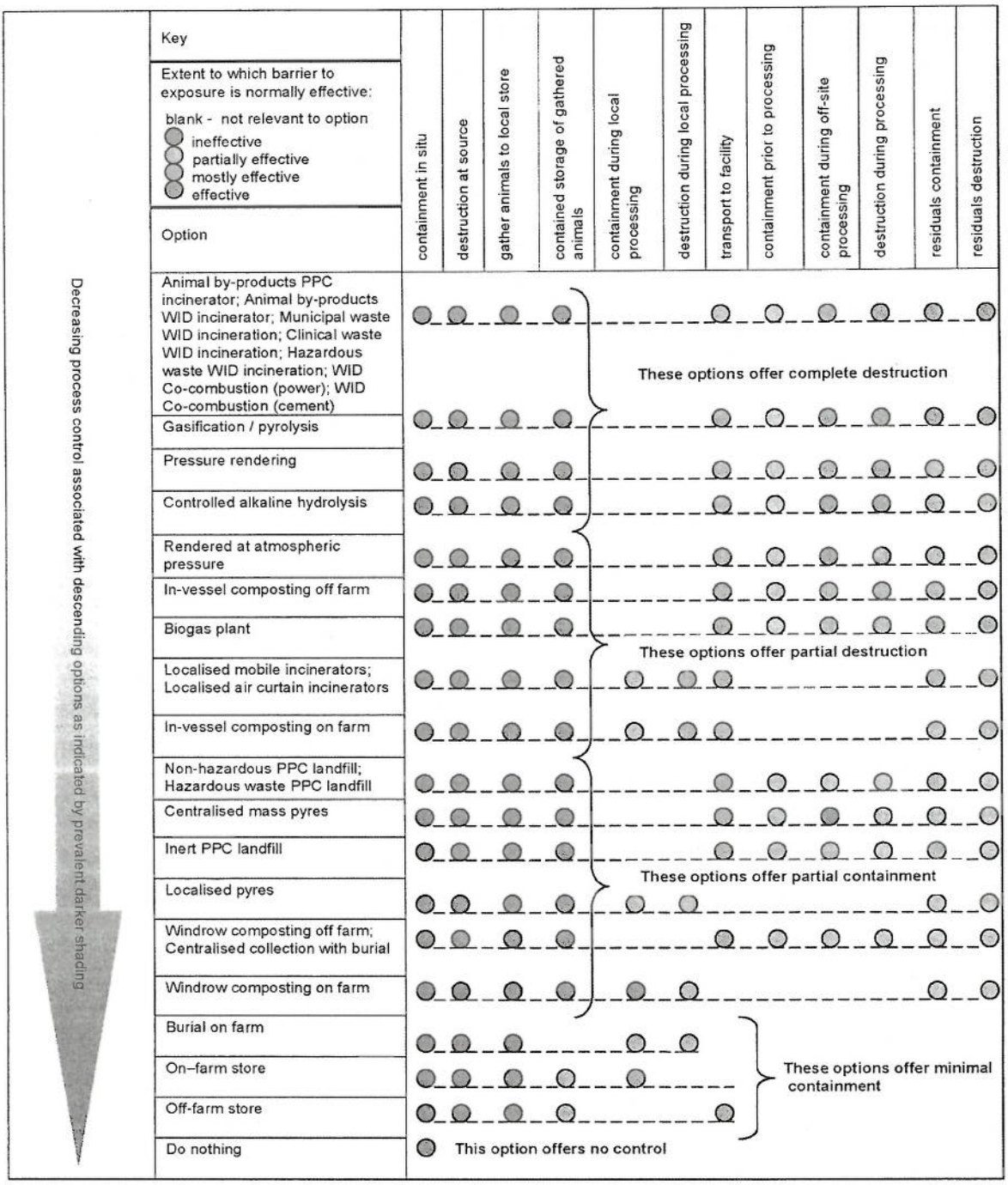


FIGURE 3. Qualitative assessment of process chains incorporating a range of waste processing technologies and categorization of carcass disposal options (WID = Waste Incineration Directive approved; PPC = Pollution Prevention and Control Directive approved).

pathways for these hazards. The consequences of impacts at the receptor were not considered in detail and were not weighted. For each disposal option, the exposure assessment represents an evaluation of the relative likelihood of exposure to the key hazards identified for humans, animals, and the environment across a multistage process chain. A number of metrics were developed for comparing exposure opportunities for carcass disposal options (Table 2): (i) the total number of available pathways, representing the number of opportunities for exposure to occur; (ii) the pathway score for human, animal, and environmental receptors, and then for all pathways; a surrogate for the overall likelihood of exposure, accounting for the relative likelihood of all pathways; (iii) the total number (n) of medium to high availability pathways, representing the number of opportunities for significant exposures to occur; and (iv) the percentage (%) of medium to high availability pathways across the full process chain, a surrogate for the likelihood of significant exposure.

At this level of analysis, it was not possible to infer a dose, nor identify the consequences of exposure, because individual receptors were not considered, as they would be in a site-specific analysis. Neither does this analysis take account of the additional measures that might be taken in the event of an outbreak to mitigate the risks of exposure. What it does provide is insight into the opportunities that exist for releases

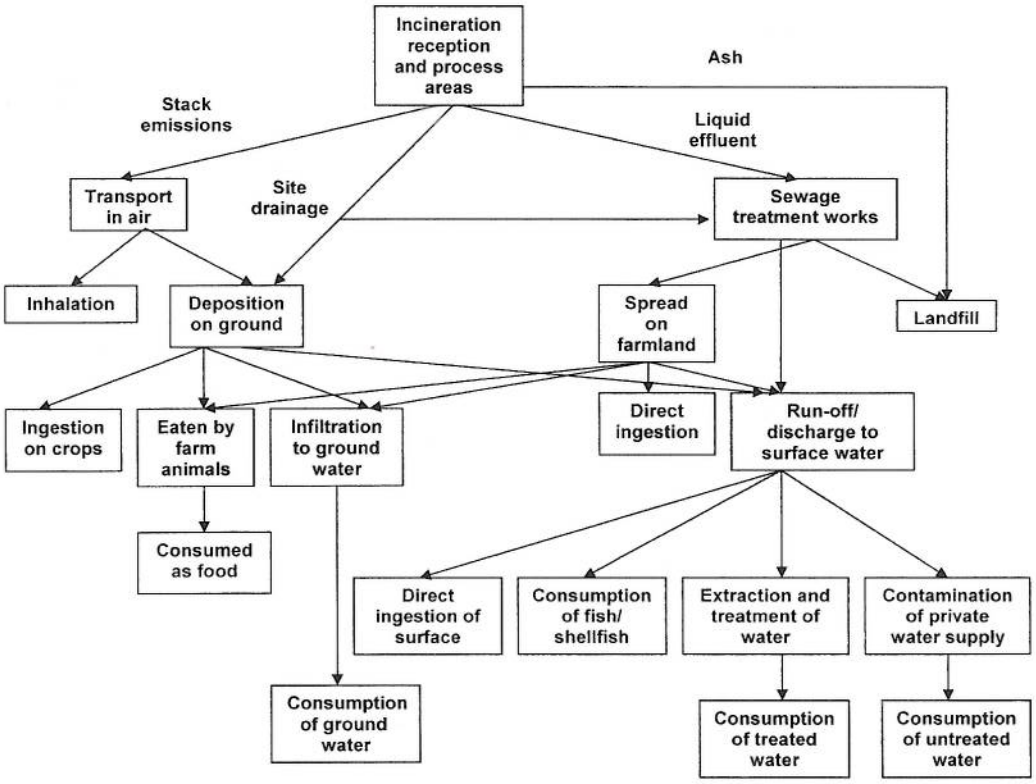


FIGURE 4. Generalized conceptual exposure model for incineration, used as a precursor for Excel spreadsheet layers.

of hazardous agents, and the distribution of potential exposures along a process chain. This is critical because risk management, in the form of sound contingency measures, needs to be targeted at critical control points; that is, at those points where the risk of exposure is greatest and where the opportunities for intervention are clear.

(iv) Development of a Risk-Informed Disposal Hierarchy. The results of the qualitative analysis (ii) and semiquantitative exposure assessment (iii) were critically reviewed and synthesized and used to derive a draft disposal hierarchy.

Results and Discussion

Application of the three filters (Figure 2) produced a subset of hazardous agents posing potentially significant human health effects, animal health effects, or environmental impacts, capable of evading destruction and presenting at sufficient doses to be of potential concern. Expert comments (Table 1) support the inclusion of these agents and offer qualifying statements as appropriate.

The qualitative analysis is an assessment, across the complete process chain, of the relative effectiveness of each disposal option to contain hazards (Figure 3). Process chains ending with stages that are effective (or mostly effective) at reducing exposures are preferred because these indicate minimal residual exposure. As one descends Figure 3, however, there are fewer options terminating with effective barriers for reducing exposure, hence a residual risk remains. All options will, if selected and used in practice, be subject to regulatory controls to ensure that risks are mitigated. Risk management measures adopted by operators need to focus on stages in the process chain where exposures could otherwise take place. We do, however, recognize the practicality that during the adoption of contingency measures, regulatory and operator controls may not be as completely effective as under normal conditions and so some aspects of the process chains (e.g., containment prior to destruction) account for this. The central insight is the incremental loss of process control on exposure, as one descends the list of options in Figure 3.

An example individual conceptual model is presented in Figure 4, from which Excel representations were constructed and pathways were ranked. Rankings were aggregated for each Excel layer and presented using the chosen metrics (Table 2). Disposal options (Table 2) with (i) a large proportion of highly available pathways ("leaky" process chains, irrespective of length); and/or (ii) large numbers of pathways (typically, longer process chains) are more likely to result in significant exposures. These options pose a greater potential risk to public health, animal health, and the environment but, while this is the case, it is important to note that regulatory frameworks are in place to mitigate these risks. The metrics (Table 2) allow a broad categorization of these options, which appear to group into four categories. We propose a distinction where the proportion of medium to high availability exposure pathways exceeds 1/6 of the total number of pathways across all receptors. For this screening analysis, undesirable options were judged to be those where the proportion of medium to high availability exposure pathways exceeded 1/3 of the total. The categorization is broadly consistent with the desirability of, first, waste process options, then controlled disposal, and finally uncontrolled disposal.

The semiquantitative exposure assessment allows consideration of the distribution of potential exposures along the process chains of the options considered. There is a tradeoff between process chain length and overall process control, which usually occurs off-site. A selective analysis of this for five options is presented in Tables 3 and 4, which illustrate that greater opportunities for exposure to hazardous agents occur in the early stages of the process chain, reinforcing the need for protective procedures throughout, but particularly at the outset of the management of carcasses. This disaggregation of exposure supports the qualitative analysis in Figure 2.

TABLE 2. Semiquantitative Exposure Assessment Metrics[a]

	option and process chain	metric	human	animal	environment	total	medium and high availability pathways across all receptors (*n*)	medium and high availability pathways across all receptors (%)
This is a preferred option	composting (in vessel)	no. of pathways	142	135	17	294	33	11
		pathway scores[b]	237	220	38	495		
	alkaline hydrolysis	no. of pathways	149	142	19	310	44	14
		pathway scores	244	235	44	523		
	gasification	no. of pathways	149	142	19	310	44	14
		pathway scores	245	235	44	524		
	biogas	no. of pathways	157	149	21	327	45	14
		pathway scores	252	242	50	544		
	atmospheric rendering	no. of pathways	157	149	21	327	45	14
		pathway scores	256	242	52	550		
	pressure rendering	no. of pathways	157	149	21	327	45	14
		pathway scores	256	242	52	550		
	incineration (generic)	no. of pathways	149	142	19	310	44	14
		pathway scores	246	235	45	526		
	co-combustion (cement)	no. of pathways	122	115	17	254	44	17
		pathway scores	210	202	44	456		
	mobile incinerator	no. of pathways	127	120	12	259	44	17
		pathway scores	198	186	28	412		
This is a secondary option	composting (windrow)	no. of pathways	163	156	17	336	62	18
		pathway scores	284	267	40	591		
	air curtain incineration	no. of pathways	163	154	18	335	62	19
		pathway scores	323	307	51	681		
	landfill	no. of pathways	109	103	12	224	46	21
		pathway scores	169	171	28	368		
	mass burial	no. of pathways	109	103	12	224	46	21
		pathway scores	190	192	30	412		
This is a possible option but not recommended	mass pyre	no. of pathways	164	154	18	336	90	27
		pathway scores	341	324	57	722		
	on-farm pyre	no. of pathways	164	154	18	336	96	29
		pathway scores	358	332	58	748		
This is a generally undesirable option	anaerobic digestion (pits)	no. of pathways	101	95	10	206	73	35
		pathway scores	214	203	30	447		
	on-farm burial	no. of pathways	101	95	10	206	73	35
		pathway scores	214	203	30	447		
	do nothing	no. of pathways	36	34	4	74	41	55
		pathway scores	90	92	14	196		

[a] The data presented herein should be interpreted to apply to the relative risks associated with each of the disposal options. They do not indicate that significant risks will actually be associated with these options should they be used in practice. Appropriate regulatory frameworks provide the means for assessing and managing site-specific risks. [b] Pathway scores were generated by summing the probability scores (0–4) assigned to each complete pathway for each disposal option.

TABLE 3. Distribution of Potential Exposure Pathways by Stage in the Process Chain

process stage	1		2		3		4		5	
description	disinfection/collection		transport		preprocessing		processing		residuals	
disposal option	no. of pathways		no. of pathways		no. of pathways		no. of pathways		no. of pathways	
	total	significant[a]	total	significant	total	significant	total	significant	total	significant
incineration	74	38	74	2	89	4	17	3	56	0
rendering	74	38	74	2	89	4	32	3	58	2
landfill	74	38	74	2	0	0	76	6	0	0
on-farm pyres	74	38	74	7	75	33	56	13	57	8
do nothing	74	41	0	0	0	0	0	0	0	0

[a] Pathways assessed to have a medium or high likelihood of being complete.

Care is required in interpreting these data and only generalized trends can be used to infer conclusions. Rankings used to assess the relative availability of exposure pathways were made using a linear scale (0, 1, 2, 3, 4) and elicited in the expert workshop. This said, the metrics for the semi-quantitative exposure assessment (Tables 2–4) appear to provide a sound basis for assessing process chains in support of decisions on disposal such as those promoted within the 2006 international Terrestrial Animal Health Code (*33*), for example. With respect to identifying key risk drivers, this

TABLE 4. Risk-Based Carcass Disposal Hierarchy in the Event of an Avian Influenza H5N1 Outbreak[a]

disposal option[a]	statement of preference
alkaline hydrolysis; atmospheric rendering; biogas; composting (in vessel); controlled incineration; co-combustion in cement kilns; gasification; mobile incineration; pressure rendering	these are preferred options
air curtain incinerator; composting (windrow); mass burial; permitted landfill	these are secondary options
mass pyre; on-farm pyre	these are possible options, but not recommended
anaerobic digestion (pits), on farm burial, do nothing	these are generally undesirable options

[a] Options listed within each of the four categories are not presented in any order of preference.

analysis reveals little difference between the risks arising from individual waste technologies when exposures from their full process chains are considered. For differences that do exist, waste management options that offer engineered process control, containment, and high levels of destruction are preferred over open, on-site treatment because they destroy hazardous agents (e.g., avian influenza viruses and other pathogens are sensitive to heat), contain hazards within engineered systems, and minimize residual risk.

The distribution of opportunities for exposure by process stage is more important (Table 3), as is the proportion of medium and high availability pathways across the process chain. Even where process chains are short, the observation that these options harbor a high proportion of pathways readily available to hazardous agents (Table 2; on-farm burial; do-nothing) means they pose significant opportunities for exposure. The greatest opportunities (Table 2) are where there is poor or no process control (Table 3). Where this is the case, exposures are not being actively managed. Therefore, the longer carcasses remain in this process stage unmanaged, the greater the likelihood for exposure and thus the greater the potential risk. Our analysis supports this implicit, but hereto unsubstantiated, conclusion providing important credence to the necessity and priority for early operational controls during outbreaks. The analysis is now informing (i) the annual review of the department's contingency plans; (ii) operational protocols on the disposal of carcasses and their associated waste streams during outbreaks (*34*); (iii) stakeholder perceptions of the basis for the GB disposal hierarchy; and (iv) future policy options.

It is valuable to compare this analysis with previous studies and risk assessments. Government bodies in the UK have commissioned generalized evaluations of risk during both the BSE and FMD crises. Quantitative risk assessments (*35*) have made use of generalized event trees with attending conditional probabilities to estimate the environmental fate of BSE prions in the environment; specifically with the aim of informing the targeted environmental regulation of industrial premises processing meat. These analyses have been powerful in providing detailed sensitivity analysis, but hugely resource intensive in terms of time and cost for a single hazardous agent to achieve these ends. Arguably, quantitative, probabilistic event-tree analysis for multiple public health and environmental agents is not supportable for effective decision-making in a rapidly developing policy climate. During the 2001 FMD crisis, a qualitative risk analysis of hazards to public health and the environment was undertaken to support an independent evaluation of disposal options. Here (*25*), qualitative reasoning using the familiar "source–pathway–receptor" approach to risk analysis (*36*), supported by scientific judgments on hazard potency, pathway availability, and receptor sensitivity, allowed the scrutiny of the existing disposal hierarchy. The analysis presented in this paper seeks to strike a middle ground between the two historic approaches, offering a supportable level of analysis suited to a generalized risk assessment of disposal options, a hazard screen for multiple agents, and a process-chain approach that presents a more complete conceptual model. Other researchers have also successfully tracked the distribution of risk along the length of process chains (as presented in Table 3), most notably along processing lines within the food manufacturing industry, so as to inform hazard analysis critical control point (HACCP) protocols for microbiological risk management (*37*). The pragmatism advanced here is not without uncertainty however, and key issues for further consideration remain the appropriateness of the linear ranking of pathway availability, the generalized representations of each process chain, and the formalization of elicited judgments of barrier effectiveness. Effective mechanisms for addressing these issues without resorting to complex, lengthy evaluations are being sought.

This analysis has not been constrained by the range of important considerations that biosecurity experts must also consider in devising contingency measures. We sought deliberately to free the exposure analysis of these factors in line with Government guidance (*26*) prior to their broader consideration. They do, however, merit discussion. Issues of practicality, economics, social implications, public acceptability, industrial capacity, and the legality of options all impact the workability of a contingency plan. Certain waste processing options are constrained because of legality or capacity, for example. The composting of carcasses killed for disease control purposes, for example, is currently not allowed under EU legislation. Similarly, irrespective of its potential utility, GB has very little biogas or alkaline hydrolysis capacity at present. Practitioners will also need to consider the distance of a disposal facility from a particular outbreak, and it is possible that although there may be "spare" capacity nationally, that the risks of transporting carcasses for several hundred kilometers may not be justified. The cost of certain technologies may be considered prohibitively expensive or disproportionate to the risk. Such issues will need to be considered by those responsible for carcass disposal policy when formulating their plans.

Animal Health have subsequently taken the results of this exposure analysis and applied these additional constraints to the list of 28 disposal options. This additional analysis has, as indicated above, ruled out all forms of composting (on the basis of legality) as well as mobile incineration, biogas, alkaline hydrolysis, gasification, and pyrolysis (on the basis of capacity) and also ruled out mass burning and "do nothing" on the basis of risk and public perception. These results are not presented here since they will only be relevant to the particular circumstances in GB at the time the analysis was undertaken.

To our knowledge, this is the first exposure assessment of this kind. This generic analysis provides credence to the existing GB disposal hierarchy (Figure 1) and the intuitive, though not previously justified, rationale placing waste processing (e.g., incineration and rendering) above controlled disposal (e.g., landfill), above uncontrolled disposal (e.g., burial on-farm or pyres). Beyond this are issues of practicality,

economics, social implications, public acceptability, industrial capacity, and legality of these options. We conclude the following:

(1) The disposal hierarchy presented in the Defra contingency plan is supported by the hierarchy generated in this assessment. The hierarchy places waste processing (e.g., incineration and rendering) above controlled disposal (e.g., landfill) which is above uncontrolled disposal (e.g., burial on-farm or pyres).

(2) A number of technologies not mentioned in the Defra contingency plan are potentially suitable on risk grounds for use in the event of an outbreak of avian influenza. Some of these (e.g., alkaline hydrolysis and gasification) are preferred over options in the existing hierarchy (even though they are currently ruled out due to lack of available capacity).

(3) Carcass disposal comprises a series of stages (a process chain), with each stage offering opportunities for exposure to hazards. Typically, the process chains for disposal options offer hundreds of individual exposure pathways for hazards, although the majority are not likely to be of concern.

(4) The range of hazards of concern extends well beyond the avian influenza H5N1 agent itself, because of the other pathogens that may be present, the chemicals used to disinfect carcasses, the veterinary products within birds, and the byproducts of carcass decomposition and waste processing. HPAI is not the only hazard of concern, neither is it the most significant hazard of concern in these disposals. Other pathogens, chemical agents, and carcass byproduct may dominate exposures.

(5) This analysis indicates that the early stages of the process chain, on-farm, pose more opportunities for exposure to hazards than the later stages where hazards are generally contained, wastes are being treated, and residues are managed within regulated processes (Tables 2 and 3). This is a key consideration and evidence for this assertion is provided by the semiquantitative analysis (Tables 2−4). The potential risks of onward infection through fomite spread (by front-line workers, on the feet of site visitors, vehicles, etc.) must be considered and risk management measures must be put in place as routine.

(6) For the process chains associated with disposal options, risks are reduced where hazards are contained rather than left in an open environment; technologies ensure the destruction of hazards rather than partial treatment; technologies have engineered process control rather than systems open to the environment; residues are minimized; and process chain are short rather then extended (in time or distance).

(7) The approach represents an important advance in perspective for carcass disposal, away from one historically concerned with which waste technologies should be adopted for disposal (process mindset), toward one driven by where exposures are likely to dominate (risk-management mindset), thus providing a risk-informed basis for contingency planning and operational intervention.

Acknowledgments

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