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Weathered hydrocarbon wastes: a risk management primer

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ABSTRACT: We provide a primer and critical review of the characterisation, 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.

There are several techniques by which petroleum hydrocarbons in soils can be characterised. Method development is often driven by the objectives of published risk assessment frameworks. Some frameworks stipulate analysis of a wide range of petroleum hydrocarbons *e.g.* 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 optimisation 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 towards compound-specific risk-based approaches for the assessment of hydrocarbon-contaminated land.

Keywords: weathered, hydrocarbons, environmental, risk, management, remediation.

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. Contaminated has become a subject of social, legal, environmental and economic concern within many of the world's industrialised countries[107]. .Land may be contaminated because of past industrial activity, historic disposal practices, or due to an adverse event such as a chemical spill[62]. 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 utilised resource throughout the world. Its use has resulted in the contamination through accidental spillage and leakage [71]. 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 sulphur[34]. The composition of petroleum hydrocarbon products can vary substantially depending on the nature, composition, and degree of processing of the source material[70]. Once released to the environment, petroleum products are subject to physical, chemical and biological processes that further change its composition, toxicity, availability and distribution (partitioning) within the environment (Figure 1). Such degradation processes include adsorption, volatilisation, dissolution, biotransformation, photolysis, oxidation, and hydrolysis[9,30,50,70,87]. The extent of weathering experienced is particularly important when characterising petroleum contamination prior to remediation[107]. Whilst 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 characterisation, 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 analysed 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 analysing 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)[107], methods can suffer from both positive and negative analytical bias[86]. Gas chromatography is a widely used technique for the analysis of petroleum hydrocabons[47,103,105]. 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 now is a well-established requirement for the management of contaminated land[4] and support tool for environmental management decisions. It is widely

used as a means of assessing and managing potential impacts to human- and ecosystem health[4,99]. 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 socio-economic 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, examples include Portugal and the UK[30,35]. Recent stakeholder consultations in the UK, 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. America[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[1,3,20,28,33,48,62,108,109]. Choice of approach depends on a number of environmental, economic and human health considerations[51]. The UK adopts the 'suitable for use' approach as the most appropriate strategy for the sustainable development of contaminated sites[23,43]. Within the land remediation sector, the EU Landfill Directive[80] is

now encouraging the development and implementation of alternative remediation techniques[62] and is expected to further increase the cost-effectiveness of bioremediation technologies[70,77]. This has resulted in increased interest 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, behaviour 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.

2. CHARACTERISATION OF WEATHERED HYDROCARBONS

2.1. Extraction and analysis

There are several techniques by which petroleum hydrocarbons in soils can be characterised. Method development is often driven by the objectives of published risk assessment frameworks (Table 1)[3,5,6,17,53,88]. 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)[3,17,53,87](Section 3). It is necessary to use analytical techniques capable of analysing specified aromatic and aliphatic 'fractions' as well as the specific indicator compounds selected by the different protocols (summarised in Table 1 and Section 3 of this review). These compounds are known carcinogens including benzene, toluene, ethylbenzene and xylene (BTEX) and the 16 EPA polynuclear aromatic hydrocarbons (PAHs) [1,17,30,53]. Some frameworks stipulate analysis of a

wide range of petroleum hydrocarbons *e.g.* 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, pressurised fluid extraction, microwave-assisted extraction and super-critical 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, e.g. TPHCWG, the Agency for Toxic Substances and Disease Registry (ATSDR) and the Texas Natural Resource Conservation Commission (TNRCC)[1,6,83,86]. This method involves shaking or vortexing 10g (typically) of soil with 10ml of an appropriate solvent (typically *n*-pentane) for 1 hour, after which an aliquot is drawn for analysis[1,59]. 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 United Sates Environmental Protection Agency (USEPA) methods for semi- and non-volatile organics in soil[19,91]. Soxhlet extraction is a highly exhaustive extraction technique and can handle both air dried and field moist samples, the latter being facilitated through the addition of chemical drying agents, such as anhydrous sodium sulphate, prior to extraction. A wide range of solvent types can be employed making

this technique versatile for different chromatographic end points. 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 minimised through the use of methods such as kuderna Danish.

The time taken to extract a sample using Soxhlet extraction and ultimately its cost has initiated investigations into alternative methods. Hawthorne *et al*. (2000)[41], 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[41]. Soxhlet and PLE yielded much darker and turbid extracts whereas subcritical water extracts were orange to dark orange in colour with moderate turbidity. SFE extracts were light yellow in colour and clear. Soxhlet and PLE yielded more artefact peaks in the gas chromatogram and, due to the extracts from these methods having a high soil matrix content, more frequent cleaning of GC injection ports was required in comparison to SFE extracts[41]. 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[41]. 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. Saifuddin and Chua (2003)[74] compared Soxhlet extraction to microwave-assisted extraction (MAE)[74]. Here, MAE was quicker (~33mins *vs*. 24hrs for Soxhlet extraction), used less solvent (4ml of solvent compared to 20ml for Soxhlet extraction) and 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 ($\alpha = 0.05$), thus the benefit of a slight increase in extraction efficiency is questionable[74].

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[73]. It has been suggested that methods that only extract environmentally relevant pollutant molecules should be used[41,73]. 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 woodchip. 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 (USEPA methods 3611B and 3630C respectively), used by the TPHCWG, ATSDR, TNRCC, CCME and MaDEP risk assessment frameworks[1,19,30,53,83]. This cleanup method also facilitates fractionation into aliphatic and aromatic fractions, which is required by MaDEP, TPHCWG, ATSDR and the EA[6,30,32,53,85]. However it is likely that any moderately polar compounds will be retained in the silica matrix including any which increase in polarity as a

220 result of biotransformation. This may be an issue when analysing weathered hydrocarbon
221 wastes and those undergoing remediation. Attempts to automate the fractionation procedure
222 have resulted in incomplete resolution of the aliphatic and aromatic fractions. Whilst come
223 well resolved components could be eliminated by subtraction, incomplete separation does not
224 address any UCM present. The key fractions affected involve the mono- and di-aromatics.
225 Extracted samples often need to be concentrated prior to analysis, and before and/or after
226 cleanup steps where an unacceptable level of dilution may be introduced *e.g.* Soxhlet
227 extraction[34,86, 93] and class fractionation[34,86, 98]. There are several concentration methods that
228 can be used: Kuderna Danish concentration, nitrogen evaporation, and rotary evaporation. A
229 concentration step is further source of error. For example, identification errors may occur if
230 samples are evaporated too exhaustively during sample preparation using methods such as
231 rapid nitrogen evaporation, where volatile components are most likely to be lost[50]. The use of
232 a keeper solvent such as acetonitrile and methods such as Kurderna Danish, as specified by
233 the USEPA Soxhlet extraction protocol, are considered to minimise such losses[86].
234 Due to the wide carbon range covered by hydrocarbon products and the tiered nature of
235 some risk assessment frameworks, it is clear that no single analysis technique is likely to be
236 sufficient for analysing soil samples. It would seem sensible that if a tiered risk assessment is
237 used then a systematic tiered analysis strategy be matched to it, as progression to higher tiers
238 and thus higher levels of analytical complexity may not in all situations be necessary. The
239 use of tiered analytical approaches are increasingly being applied in oil spill
240 identification[102,103]. For example, Wang *et al.* (1997)[102] used a 5 tiered analytical approach
241 that enabled the identification of oil type, degree of weathering and biodegradation.
242 Many of the risk assessment frameworks for petroleum hydrocarbons specify preferred
243 extraction and analytical techniques; some having published their own recommended
244 methods (CCME, TNRCC, TPHCWG and MaDEP[19]; Table 1[1,56,57,83]). 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 [1,30,53,83]. 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 USEPA extraction method followed by silica cleanup and fractionation prior to analysis[56,57]. The CCME method specifies purge and trap for the fraction range C_6-C_{10}, or Soxhlet extraction followed by silica gel clean up 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 USEPA 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 ASTM specify 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[86]. There are also methods for the 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 upon 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 non-specific techniques[103]. These generate basic information that is a surrogate for contamination, *e.g.* a single TPH concentration. Such data are not suitable for risk assessment in isolation[34,86]. However, they are inexpensive, quick and easy and, as such, can offer a useful screening tool[34,86]. 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[86]. Gas chromatographic methods are the most preferred TPH measurement techniques as they offer relative sensitivity, selectivity, and can be used to identify risk critical compounds. As the compositions 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[103]. 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, high boiling temperatures and require high column operating temperatures. This can vary depending upon 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 [107]. 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, non-target analyte identification and can be used to separate hydrocarbon classes[47]. Even with ready benchtop availability, some jurisdictions have felt unable to recommend GC-MS analysis of petroleum hydrocarbons to inform risk assessments[47]. 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 specialised methods have been developed[107]. Whittaker *et al.*, 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 ionisation detection (TLC-FID), high-performance liquid chromatography (HPLC) and laser desorption laser photoionisation time-of-flight mass spectrometry (L^2TOFMS)[107].

The coupling of curie point pyrolysis to GC-MS (Py-GC-MS) is an alternative method to conventional techniques for the analysis of non-volatile compounds such as rubbers, paints and synthetic plastics and has been applied to several sample matrices including soil[15].

Recently, Buco *et al*. evaluated this technique for the analysis of the 16 PAHs included in the USEPA 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. 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"[65]. Where a 'pollutant linkage' between the source of a hazard and a receptor is present[3,70,103,105], 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, and 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 transission[3].

Different countries and organisations 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 use for exploration and production (E&P) sites are for ranch, agricultural or parkland land uses.

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[53] as insufficient for characterising risks posed at a petroleum hydrocarbon release site and

370 fractions were introduced. The definitions of specific fractions are derived from either the
371 carbon number (C_n) or equivalent carbon (EC*n*) number. For example, MaDEP uses
372 fractions to evaluate the threshold contaminants and indicator compounds (or 'target
373 analytes') to evaluate non-threshold toxicity[5,30,53]. The MaDEP approach is one of the few
374 approaches that use carbon numbers. Here TPH fractions are based upon "chemical
375 structure, carbon number, and structure activity relationships"[54]. The majority of
376 frameworks use equivalent carbon numbers (EC_n), *e.g.* TPHCWG[30] because these are
377 considered more closely related to the mobility of a compound in environmental media[30]. As
378 such, EC*n* are based on "a range of physical-chemical properties and simple partitioning
379 models"[84]. In practice, the boiling point of the compound of interest on a non-polar GC
380 column is used to derive EC_n, assuming the relationship between boiling point and EC is the
381 same for both aromatics and aliphatics. In characterising the toxicity of a fraction, surrogate
382 compounds or mixtures that are well characterised and characteristic of a particular fraction
383 are often used [30,87].

384 The validity of the equivalent carbon number may be challenged. For example, the
385 TPHCWG derive EC_n using a simple empirical binomial model parameterised using data
386 describing the boiling point (T_B, °C) and carbon number of 75 key hydrocarbons; where K_1
387 and K_2 are empirical constants, and C is the intercept (Equation 1).

388 $$EC_n = K_1[T_B]^2 + K_2[T_B] + C \qquad (1)$$

389 At best, this provides only a rough estimate of EC_n (e.g. a measured EC value of 31.3 for
390 benzo[a]pyrene compared to the calculated value of 30.0 using Equation 1). Also, a T_B of 548
391 should relate to EC_{44}, however calculating this from Equation 1 provides a value of $EC_{34.6}$.
392 Clearly there is a disparity between the TPHCWG model and the empirical data. Different
393 parameterisations will have an effect on calculated EC_n. Figure 3 shows a series of fitted
394 binomial models based on four different parameterisation 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 $EC_{>20}$. Simple empirical models, such as Equation 1, do not hold true; and the theory that T_B can be used to calculate EC_n representative of normalisation 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[3,53,87] However, the 'New Zealand Approach'[60] 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 upon 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 $EC_5 - EC_{35}$ [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% $^{w}/_{w}$ 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 0.03mg/kg/day and 0.8mg/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[68]. 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 characterised with 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 behaviour 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 utilise naturally occurring biological processes to transform, decrease or eliminate polluting substances[13,28,33,40,62]. 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 idealised 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 re-used with little/no further modification[15]. 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[30], 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[48]. High concentrations of heavy metals and other highly toxic compounds can be prohibitive of microbial growth[48], 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

469 degradable or transformable[27,48]. Hence, biological remediation systems are more suited to
470 organic contaminants, including weathered petroleum hydrocarbons[48].
471
472 **4.1. Bioremediation techniques**
473 The choice of bioremediation technique can depend on a number of site specific factors,
474 including the type, mobility, concentration and volume of a contaminant, the soil structure,
475 surrounding geology, the proximity to structures and potential receptors, and intended end
476 use[13,20,28,33,62]. There is no single method for every situation and often combinations of
477 techniques are implemented at sites with multiple contamination sources. Bioremediation
478 processes can be divided into *in-situ* and *ex-situ*. *In-situ* methods include monitored natural
479 attenuation[12,13,28,43,48,58,62], biosparging[13,25,62] and bioventing[13,33,36,48,62]. They have the
480 advantage of not requiring the excavation or removal of soil[13,20,33,62]. They are able to deal
481 with deep contamination and enable remediation both under and around buildings[20]. These
482 techniques minimise problems with dust, and hence worker exposure may be reduced[20,33,62].
483 *In-situ* techniques can adapt, enhance and control bioremediation conditions. However, they
484 are limited by the degree of process control that can be used. In comparison, *ex-situ* methods
485 are contained and offer a higher degree of process control with greater control over time[27].
486 Techniques can be performed on or off site depending on the restrictions present at a
487 particular site[20]. Overall, *ex-situ* methods are considered to be more efficient than *in-situ*
488 techniques[13] and can deal with higher concentrations of contaminants[27]. *Ex-situ* techniques
489 include landfarming, composting, biopiling and bioreactor treatments[33].
490 'Landfarming' (also known as 'land treatment') is a simple technique used to treat large
491 areas of land. Land farming has been used for the remediation of many waste types, but
492 mainly for the remediation of hydrocarbon contaminated soils[13,20,46]. Landfarming involves
493 the excavation and spreading (to 0.3-0.5m thickness[28]) of contaminated soil over a bunded

494 area (incorporating a leachate collection system and impermeable liner material[13,28,62]) which
495 is tilled to aerate the soil at regular intervals[20,28,33]. Composting is an aerobic process using
496 systems that involve the construction of piles, often using bulking agents to increase porosity
497 and facilitate airflow[13,33]. Anaerobic conditions can also be used to compost wastes;
498 however, this can result in the synthesis of unpleasant odorous compounds such hydrogen
499 sulphide[20] and the generation of methane. Purpose built closed reactor composting systems
500 can be used to compost wastes, and have been used as the basis of soil treatment centres in
501 mainland Europe [13,20,62]. Here, the soil is combined with water to form a slurry which is
502 continuously mixed using mechanical agitators, giving rise to improved contact between the
503 pollutants and the microorganisms[33,62]. Closed systems provide a high degree of process
504 control over environmental conditions and allow for the control and treatment of volatile
505 compounds. However they are more expensive than open systems such as windrows[33].
506 Engineered biopiles are an intensive static pile version of composting that enable greater
507 control over important environmental factors that effect biotransformation rates (i.e. oxygen,
508 water and nutrient levels[13]) compared to other methods. This intensive method is especially
509 useful when space is limited[13]. Details regarding biopile design and operation can be found
510 elsewhere[11,13,20,28,40].
511 As highlighted by some of the responses to the EAs survey[27], the timescale in which
512 pollutants can be remediated is an important consideration when selecting the most
513 appropriate remedial treatment to use at a given site. Cost, guaranteed insurance, and risk
514 reduction were also cited as reasons for not using bioremediation methods. Engineered
515 biopiles offer a high degree of control, have a smaller footprint and are comparatively quick,
516 yet they are not as expensive as closed bioreactor systems (~£10-40 per m^3 vs. ~£30-150 per
517 m^3)[13]. This makes biopiling attractive to contaminated land remediation specialists,

518 especially as the high degree of control allows the processes to be optimised for
519 biotransformation of specific pollutants of interest.
520 Bioremediation works well for remediating soils contaminated with petroleum
521 hydrocarbons [36,49]. Most studies have reported biotransformation to be rapid in the initial
522 stages of bioremediation, with rates seen to asymptote as the weathered proportion is
523 biotransformed[26,37,111]. Weathered petroleum hydrocarbons have typically been present in the
524 soil for a long period of time, they display relatively low bioavailability, and thus are more
525 recalcitrant in the environment[40]. As a result, the optimisation of environmental conditions is
526 imperative for the remediation of land contaminated with weathered petroleum
527 hydrocarbons[40]. Giles *et al.* (2001) studied the bioremediation of weathered oil sludge (C_{20}-
528 C_{38}) in composting piles. A biotransformation of 97% % $^{w}/_{w}$ TPH was achieved after 10
529 weeks. This study showed that indigenous bacterial populations were more suited to
530 biotransforming the sludge[28]. Unexpectedly, the bulking agent used had a greater effect on
531 biodegradation than augmentation with a consortia of oil-degrading bacteria. The authors
532 suggested that the bulking agent achieved higher degradation rates (complete compost) due to
533 the presence of indigenous hydrocarbon-degrading microorganisms. However, this may have
534 been due in part to the increased adsorption capacity of the amended soil matrix. It was
535 suggested that this material was effective at modulating the temperature thus maintaining the
536 bacteria within their optimal range[38].
537
538 **4.2. Optimising bioremediation**
539 Contaminated soils usually contains a number of microbial species capable of degrading
540 the contaminants present[28]. The degradation process can be enhanced through biostimulation
541 and bioaugmentation. The former refers to the enhancement of the bioremediation process by
542 optimising specific environmental parameters such as temperature, pH, oxygen partial

543 pressure, moisture and nutrient levels[33,62]. The latter describes the augmentation of
544 bioremediation systems with commercially available microbial cultures which, in some cases,
545 perform specific functions[13,28,40,62]. Bioaugmentation may be required where native microbial
546 populations are insufficient to achieve effective biotransformation. For example
547 *Phanerochaete chrysosporium* (white rot fungus) can aid in the degradation of problematic
548 recalcitrant compounds[28]. However, it should be noted that resulting increased costs are
549 rarely justified by the benefits[28]. Additionally, it was shown by Trindade *et al.* (2005)[89] and
550 Giles *et al.* (2001)[38] that indigenous micororganisms can be better adapted and more resistant
551 to the contaminants present, with greater remediation potential than foreign organisms[28,38,89].
552 Typically, the addition of foreign organisms are not required when degrading hydrocarbons[11].
553 To grow, microorganisms require an electron donor (source of energy) and an electron
554 acceptor as a means of extracting energy from the electron donor. Thus, electron acceptors
555 play a key role in the biotransformation of a contaminant (the energy source – electron
556 donor). Potential electron acceptors for microbial activity are (in order of energy yield,
557 highest first): oxygen, nitrate, iron, manganease, sulphate, carbon dioxide and organic
558 carbon[49]. Clearly as oxygen yields the highest amount of energy it is the preferred electron
559 acceptor and is important to optimise its diffusion into- and concentration within the soil
560 matrix (typically need to keep oxygen in the soil gas >2%).
561 Different bacterial classes require different temperature ranges to achieve optimum
562 growth. For example, mesophiles grow from about 15° to 45°C[49] whereas thermophiles grow
563 best between 45° and 65°C[33,49]. Typically during bioremediation mesophilic temperatures
564 are common, with Giles *et al.* (2001)[38] having found optimum growth for the bacteria present
565 during the bioremediation of a weathered oil sludge to be less than 45°C[38].
566 The pH of the soil can inhibit microbial activity and also affect the solubility of
567 important nutrients such as phosphorus[33,49]. The typical optimum pH range for

bioremediation is from pH 5.0 – 9.0, with a pH of 7.0 being preferable. Giles *et al.* (2001)[38] 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, phosphorous, and in lesser quantities potassium, sodium, magnesium, calcium, iron, chloride and sulphur[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 fertilisers containing appropriate quantities of the rate-limiting nutrients[11,40].

It is clear that successful bioremediation relies on the optimisation 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. Summarising this material is insightful in that it illustrates trends and approaches from a variety of perspectives. The view expressed

593 is that thirty years of research into petroleum microbiology and bioremediation have
594 bypassed an important observation - that many hydrocarbon-contaminated sites posing
595 potential risks to human health harbour weathered, 'mid-distillate' or heavy oils. These sites
596 present considerable challenges to remediation over and above those posed by fresh or more
597 refined petroleum distillates. Critically, there are important scientific components that drive
598 risk management for these wastes and specifically the partitioning of risk-critical compounds
599 within the oil/soil matrix.

600 Whilst early work suggested the recalcitrance of these wastes to microbial breakdown,
601 we now know that the risks from these wastes can be actively managed through optimising
602 treatment process parameters during bioremediation. This said, the 'in-field' verification of
603 *ex-situ* technologies such as biopiling, continues to be expressed in many countries in terms
604 of reductions in total petroleum hydrocarbon (TPH) load, or 'losses' from the soil being
605 treated, rather than by reference to reductions in risk. An observation from the UK is that the
606 absence of risk from the vocabulary of many remediation operators and remediation projects
607 reduces stakeholder (regulatory, investor, landowner and public) confidence in technology
608 performance, and in doing so, limits the market potential of these technologies.

609 For weathered hydrocarbon wastes, risk management decisions are complicated by the
610 gross complexity of the source term, the effects of weathering on the bioavailability of risk
611 critical contaminants and the variable performance of remedial technologies under authentic
612 site conditions. For heavy oils (the viscous (50-360 mPa s), high-boiling (ca. 300 - >600 °C)
613 products such as No. 6. fuel oil with carbon ranges in excess of C_{20}), their inherent
614 complexity is further compounded as they weather in the environment on account of biotic
615 and abiotic losses that shift their chemical composition towards recalcitrant, asphaltenic
616 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 behaviour 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)[78] first suggested the concentration of residual oil within a oil-soil matrix required for it to act as a discrete partition medium (*ca.* 1000 mg/kg) and suggested that this residual oil, as the original source of priority contaminants, could typically be ten 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)[113] showed that between 71-96%^{w}/w of PAH in weathered diesel-contaminated loam soils 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 (1999)[110] estimated oil - water partition coefficients (termed log K_{mw}) for a series of PAH to be between 4.5 - 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

642 estimating the fate of pollutants in complex environmental matrices, the application of
643 fugacity models [52] for predicting the relative phase distributions and concentrations of
644 contaminants and their metabolites during treatment[75,76] is now proving valuable for
645 informing exposure assessments and the optimisation of *in-situ* remediation. These
646 approaches have yet to be applied to the biopiling of weathered oils or to account for the
647 partitioning behaviour of PAH in weathered non-aqueous phase liquids (NAPL) within the
648 unsaturated zone. In short, the relationships between chemical presence, toxic response,
649 bioavailability and risk for weathered hydrocarbons have yet to be fully elucidated and
650 coupled into a meaningful risk management framework, though work is progressing[29-32,81].
651 One of the obvious research needs is to authenticate human exposures to oil/soil matrices in
652 the context of contaminated land and, in particular, to explore the bioavailability of risk-
653 critical compounds (benzene, benzo[*a*]pyrene) in light of these newly revealed partition
654 relationships.

655 The regulation of site remediation now requires adoption of a risk-based approach and
656 this extends to technology verification[29]. Whereas the effectiveness of an environmental
657 technology in treating pollution has historically been expressed as a percentage reduction in
658 the pollutant concentration released to, or found in, a media of concern, regulators are
659 increasingly concerned with mass, toxicity and risk reductions within the multimedia,
660 multiphase environment. For petroleum hydrocarbons in soil, international regulatory
661 guidance on the management of risks from contaminated sites is now emerging. As shown in
662 this review, much of this guidance promotes the use of risk management frameworks to
663 guide decision-making, the application of reference analytical methodologies and the
664 derivation and use of acute, sub-chronic, and chronic toxicological criteria for these wastes.
665 These frameworks adopt a variety of approaches to the evaluation of risk-critical components
666 within the hydrocarbon waste-soil matrix.

667 In the US, a substantive research effort has focused on integrating hydrocarbon fate and
668 transport, petroleum microbiology and environmental diagnostics to inform regulatory
669 processes for site management under the Superfund Program. ThermoRetec (2000)[81] ,
670 reporting for the Petroleum Environmental Research Forum (PERF), provide an authoritative
671 account of the central importance of partitioning within soil-bound hydrocarbons in
672 developing environmentally acceptable endpoints (remedial objectives). Drawing on a
673 detailed understanding of NAPL and residual oil fate and behaviour, this work is now
674 influencing the development of remediation criteria for petroleum hydrocarbon in soils in the
675 US for human health, groundwater and ecological receptors, and a reappraisal of the level of
676 residual petroleum hydrocarbons that can be left at remediated sites without posing an
677 unacceptable risk. In contrast, weathered, mid-distillate and heavier oil sources are generally
678 given a narrow treatment by these reviews and frameworks. The Environment Agency
679 (2003)[30] have recognised this in their recent consultation on principles for evaluating the
680 human health risks from petroleum hydrocarbons in soils, and have called for views. One of
681 the few environmental exposure assessments explicitly to address heavy oils has been
682 discussed in a recent article relating to worker and visitor exposure following the wrecking of
683 the oil tanker 'Erika' in 65 km south of the Brittany coast[7]. Here, inhalation, dermal and oral
684 PAH exposures from beached No. 6 fuel oil were estimated and found to be negligible for
685 beach cleaners and tourists (occasional visitors) coming into to contact with heavy oil,
686 demonstrating the feasibility of this level of risk analysis for these problematical wastes.
687 The move towards risk-based corrective action (RBCA) has been slow in the UK and,
688 whilst some progress has been made in integrating the aspects of analysis, exposure
689 assessment and technology verification[29], there are gaps in the current knowledge base.
690 Specifically: (i) analytical strategies in the UK are not generally targeted at the
691 bioavailability of risk-critical components; (ii) risk assessments do not regularly account for

692 highly weathered residues encountered at many sites (API, 2001); and (iii) treatment
693 'success' is still supported by reductions in hydrocarbon load in isolation of combined
694 reductions in toxicity, chemical mass and risk. In a typical study, Al Awadhi *et al.* (1996)[2]
695 report an 80%^{w}/w reduction in oil from heavy oil-laden landfarming plots in Kuwait over a
696 15 month research period and Milne *et al.* (1998) between 30-50% ^{w}/w reductions in TPH
697 from heavy refinery sludge treated in amended composting plots over the treatment period.
698 Guerin (2000)[39] reports a 5 –year performance study of a land treatment facility for oil
699 wastes from heavy vehicle maintenance. Most of these studies and many of those since (e.g.
700 Tien *et al*., (1999)[82] and Owens and Bourgouin, (2003)[67]) follow a pattern of reporting
701 reductions in TPH load as a presumed surrogate for risk reduction.
702 A contributing factor to the over-reliance on TPH as an indicator of treatment
703 performance in isolation of other parameters, has been the cost of implementing more
704 sophisticated diagnostic techniques and their low uptake within the sector. This has been, in
705 part, as result of the absence of a regulatory framework. Nevertheless, researchers have been
706 concerned with improved diagnostics methods (the analysis of specific carbon number
707 ranges); the fingerprinting of hydrocarbon wastes for source identification (for liability
708 disputes) and in tracking biotransformation; and with biological techniques as indicators of
709 the impact of hydrocarbon contamination on soil function. Recent initiatives have included
710 the development of reference methods for the analysis of petroleum hydrocarbons from nC_6-
711 C_{50}[19,83], the application of biomarker analysis (*n*-alkane: substituted *n*-hopane indices) to
712 bioremediation verification[45,61,100] and the validation of microbial bioassays for petroleum
713 hydrocarbons in soil[24,68]. Our own work[69], building on that of Prince *et al.* (1994)[72]
714 demonstrated that the ratio of total alkanes ($\sum n$-alkanes) to 17α(H)21β(H)-hopane to be the
715 most sensitive of a series of biomarker ratios in reflecting oily waste depletion in a 256-day
716 soil microcosm study.

6. CONCLUSIONS

Risk assessment is a well-established paradigm for the management of contaminated land[4]. However, the move towards risk-based corrective action has been slow. Recent stakeholder consultations in the UK, 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 e.g. the level of remediation to be achieved. As shown, the use in some frameworks of deriving equivalent carbon numbers from empirical relationships representative of normalisation 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 analysed.

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 synthesised into regulatory tools. However, there is growing support for the move towards compound-specific risk-based approaches for the assessment of hydrocarbon-contaminated land.

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FIGURES & TABLES:

Figure 1: General petroleum hydrocarbon degradation pattern (modified after Kaplan *et al.*, (1996)[50])

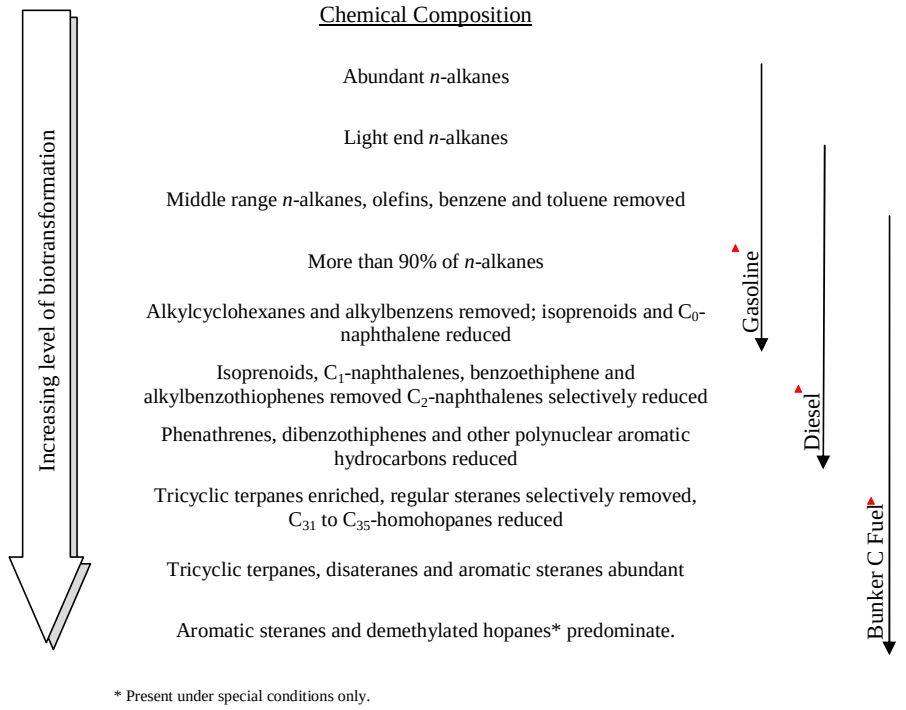

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Figure 2: Illustration of the interactions of the key elements involved in remediation of weathered petroleum hydrocarbon contaminated land.

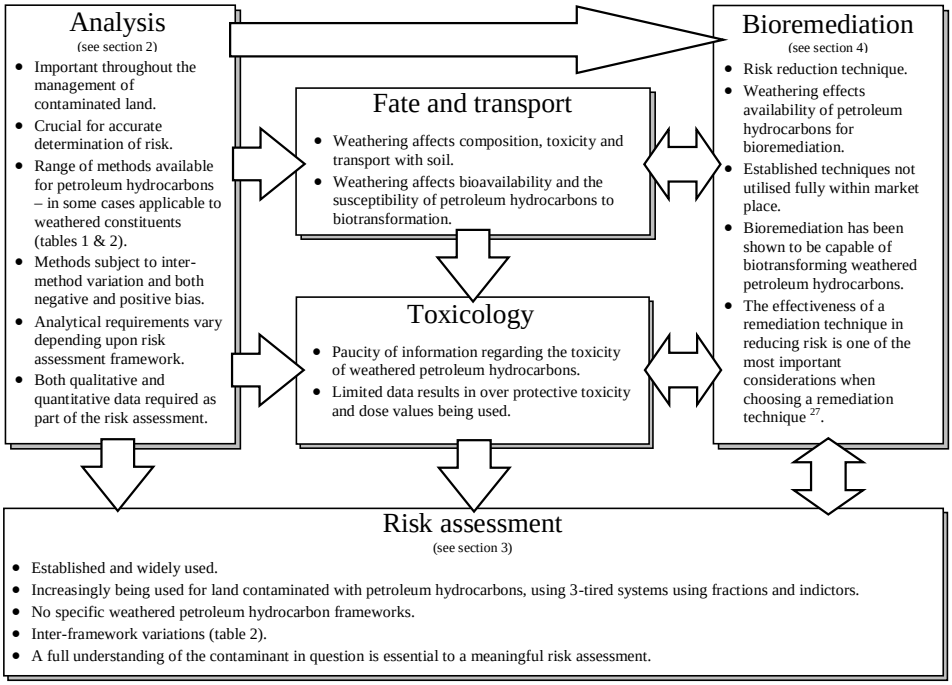
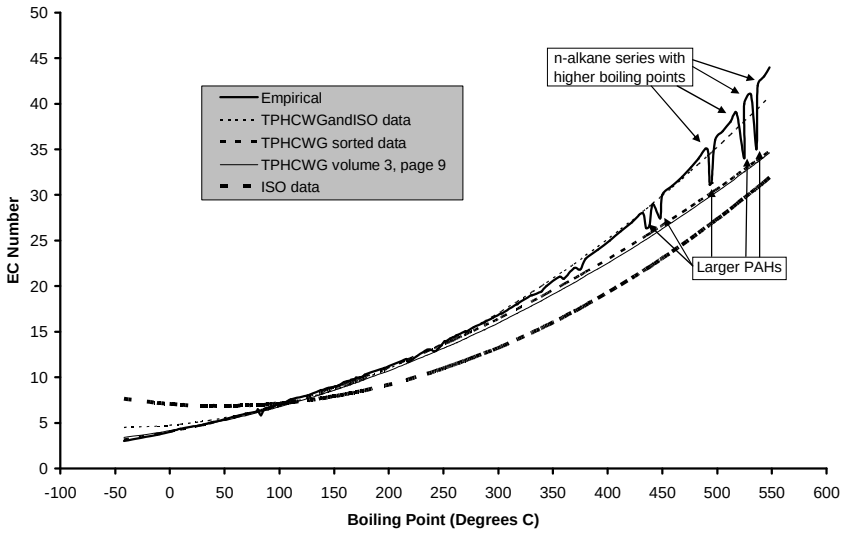


Figure 3: Estimated equivalent carbon number using Equation 1 parameterised with four different data sets. The measured data are also provided for comparison.



1140 *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[118]	New Zealand[61]	New South Wales[64]
Description	Use of two methods. Volatile petroleum hydrocarbon (VPH) method[57] and extractable petroleum hydrocarbon (EPH) method[56] developed by MaDEP. The EPH method refers to USEPA methods for sample extraction[57,98].	Use of 'The Direct method' (AEHS)[1] developed for the TPHCWG framework. Based upon USEPA SW-864 test methods[97] and MaDEP EPH method[5]	Recommends the use of benchmarked methods[19], however also allows the use of non-benchmarked 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 USEPA 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)[63]. Where no suitable analytical method is available it recommends the use of USEPA[97]., 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 14days 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 aluminium 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.	100ml (volatiles) and 250ml (semi-volatiles) Borosilicate jars with Teflon-lined cap and completely filled. Stored at 4˚C in the dark.	Use of USEPA[97] or equivalent methods

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	Massachusetts Department of Environmental Protection	Total Petroleum Hydrocarbon Criteria Working Group	Canadian Council of Ministers of the Environment[18]	New Zealand	New South Wales
Extraction technique	VPH method uses Purge and trap with methanol. EPH method uses DCM for extraction and solvent exchanges into hexane. Using USEPA methods 3540C[92] (Soxhlet), 3545A[93] (pressurised fluid extraction (PFE)), 3541[90] (Automated Soxhlet extraction), 3546[95] (Microwave extraction) and 3570[96] (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.	USEPA methods 3540B[97] or C[92] (Soxhlet extraction), 3550B[94] (sonication extraction) or sequential bath sonication and agitation described by NEPC[63].
Evaporation	The EPH method uses those specified by the USEPA. 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.	USEPA methods specified for extraction using Kurderna-Danish (K-D) evaporation.
Clean up /fractionation	Silica gel clean up 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 USEPA method 1664[64,97].
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 ionisation detection
[#]GC/PID refers to gas chromatography with photoionisation detection
[$]GC/MS refers to gas chromatography with mass spectroscopy detection

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 [53]	Total Petroleum Hydrocarbon Criteria Working Group [84-88]	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[60]	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&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&3.	RBCA 3 tiered look up tables for tier 1 and increasing use of site-specific into in tiers 2&3.	RBCA 3 tiered look up tables for tier 1 and increasing use of site specific information in tiers 2 &3.	Modified TPHCWG approach.	Modified TPHCWG approach within UK context.	Use of a 3-tired 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.

	American Society for testing and materials[5]	Massachusetts Department of Environmental Protection	Total Petroleum Hydrocarbon Criteria Working Group	Agency for Toxic Substances and Disease Registry	Canadian Council of Ministers of the Environment	American Petroleum Institute	Environment Agency	New Zealand	New South Wales	National Institute for Public Health and the Environment
Analysis	No recommended method of analysis	Use of two methods developed by MaDEP for volatile petroleum hydrocarbons (VPH) [57]and Extractable petroleum hydrocarbons (EPH)[56]	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[66].	Dependent on source of threshold concentration. Using NEPC methods[63].	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 end points 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		*n*C_5-*n*C_{36} Aliphatics, *n*C_9-*n*C_{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}

List 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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Weathered Hydrocarbon Wastes: A Risk Management Primer

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