CRANFIELD UNIVERSITY

DAVID FERNÁNDEZ LÓPEZ-REY

EFFECTIVENESS OF H2O2/UV AND O3/H2O2/UV FOR METALDEHYDE REMOVAL IN DRINKING WATER AND FULL-SCALE COSTING ANALYSIS

SCHOOL OF WATER, ENERGY AND ENVIRONMENT

MASTER OF SCIENCE

MSc by Research in Water Science
Academic Year: 2016 - 2017

Supervisor: Dr Francis Hassard and Prof Bruce Jefferson
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DECLARATION

Chapter 1 compromises a pilot-scale experimental work carried out by Marine Diana and David Fernandez Lopez-Rey as part of two MRes partnership projects between Cranfield University and Severn Trent Water. Despite producing two separate theses, the results reported on that chapter have thus similarities with Diana's research as sample collection and DBPFP laboratory analysis were undertaken by both students. However, data interpretation and analysis, as well as the writing up, were solely done by David Fernandez Lopez-Rey.

ABSTRACT

Metaldehyde is a widely used pesticide in the UK and has been reported to produce drinking water quality failures across the national water utilities. Advanced Oxidation Processes (AOPs) are effective in the removal of recalcitrant organic constituents but pose (i) high energy and chemical costs and (ii) by-products formation upon disinfection stage. In this context, UV/H_2O_2 and O_3/H_2O_2 + H_2O_2/UV were tested at pilot-scale concurrently at Draycote water treatment work (WTW) (UK) for metaldehyde degradation and disinfection by products formation potential (DBPFP) at different energy demands (E_D), H_2O_2 and O_3 doses; and pesticide concentrations. Whole-life costing analysis (WLCA) was undertaken to assess which AOP was most economic for metaldehyde removal at a Draycote sized WTW. Sensitivity analysis considered potential costs of each AOP. Metaldehyde was removed up to 98% (UV/H_2O_2) and 97% (O_3/H_2O_2 + H_2O_2/UV) successfully fulfilling European Directive 98/83/EC below both 1.0 kWh m^{-3} and 2.14 µg L^{-1} pesticide inlet water level. Net DBPFP contribution ranged -283 µg L^{-1} to +255 µg L^{-1} for trihalomethanes formation potential (THMFP), which are UK regulated. DBPFP was related to organic background characteristics rather than the operating conditions tested in both AOPs. Cost estimating the AOPs for a 0.72-log metaldehyde removal enabled the total expenditures to be determined indicating that energy consumption accounted for 50% (UV/H_2O_2), 49 % (O_3/H_2O_2 + H_2O_2/UV) and 31% (O_3/H_2O_2) of their operating costs. Similar £14.7 million capital costs were appraised for O_3/H_2O_2 and UV/H_2O_2. Overall, O_3/H_2O_2 sub process outperformed the rest of AOPs when considering both metaldehyde degradation (≤96%) and net DBPFP contribution (≤51 µg L^{-1} THMFP) at the most economically operating costs for 5-month yearly treatment (£0.07 m^{-3}). Sensitivity analysis showed the O_3/H_2O_2 more efficient process requiring less inputs than UV/H_2O_2 for the same metaldehyde removal. However, the O_3/H_2O_2 was cost effective at an ideal stoichiometric mass ratio of 0.7 H_2O_2:O_3. Therefore, this would require validation at full-scale. The AOPs were robust for metaldehyde degradation with reasonable costs.

Keywords: Advanced oxidation process, AOP, DBP, THM, HAA, Whole-life costing analysis

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"…Sólo dos legados duraderos podemos dejar a nuestros hijos: uno, raíces; otro, alas" (Hodding Carter)

Gracias por apoyarnos a volar cada vez más lejos sin ningún miedo. Os quiero mucho, pese a no soler decirlo. Hemos superado, superamos y superaremos todas las dificultades que se nos presenten juntos, aunque físicamente separados por miles de km. Contad siempre conmigo, aunque esté lejos...

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LIST OF ABBREVIATIONS

2,4-D	2,4-dichlorophenoxyacetic acid
AOP	Advanced Oxidation Process
BCAA	Bromochloroacetic acid
BDCAA	Bromodichloroacetic acid
CAPEX	CAPital EXpenditures
CDBAA	Chlorodibromoacetic acid
DBAA	Dibromoacetic acid
DBP	Disinfection by-product
DBPFP	DBP formation potential
DCAA	Dichloroacetic acid
DistLM	Distance-based linear model
DOC	Dissolved Organic Carbon
DrWPA	Drinking Water Protected Areas
DW	Drinking water
DWI	Drinking Water Inspectorate
E_D	Energy demand
EE_O	Electrical energy per order
EPA	USA Environmental Protection Agency
EU	European Union
FBBR	Fluidised bed bioreactors
GAC	Granular activated carbon
H_2O_2	Hydrogen peroxide
HA	Humic acid
HAA	Haloacetic acid
HAAFP	HAA formation potential
LOX	Liquid oxygen
LPHO	Low-pressure high-output
MBAA	Monobromoacetic acid
MCAA	Monochloroacetic acid
MIC	Metaldehyde inlet concentration
Na_2SO_3	Sodium sulphite
NOM	Natural Organic Matter
NTU	Nephelometric Turbidity Units
O_3	Ozone

$^{\bullet}OH$	Hydroxyl radical
OPEX	OPerating Expenses
PCV	Permitted concentration value
RGF	Rapid gravity filter
TCM	Turbidity causing material
TBAA	Tribromoacetic acid
TCAA	Trichloroacetic acid
THM	Trihalomethane
THMFP	THM formation potential
TOC	Total Organic Carbon
TOTEX	TOtal EXpenditures
UP	Ultrapure
UV	Ultra Violet
UV254 nm	UV absorbance at 254 nm
WLCA	Whole-Life Costing Analysis
WTW	Water treatment work

1 INTRODUCTION

1.1 Background

The wholesome supply of drinking water (DW) is threatened from anthropogenic influences such as the application of pesticides to farmland. These pesticides or their degradation products can result in a public health risk and adverse environmental consequences, even at µg per litre range concentrations (PMEP, 1993; James, Germain and Judd, 2014). One such example is the pesticide metaldehyde, which is considered a pollutant of concern in the UK water sector (Cooper, 2011). Recent investigations showed that 20% of Drinking Water Protected Areas (DrWPA) in England and Wales were at risk due to metaldehyde (Pesticides Forum, 2015). Water suppliers are responsible for providing potable water meeting the Regulations under Section 68(1)(a) of the Water Industry Act 1991 and the requirement set in regulation 4(2)(c) of The Water Supply (Water Quality) Regulations 2000 (DWI, 2000). However, the majority of failures for DW non-compliance in the UK water sector are linked to metaldehyde concentrations (DWI, 2014). In addition, the compliance with the residual UK/EU statutory permitted concentration value (PCV) of 0.1 µg L^{-1} and 0.5 µg L^{-1} for individual and total pesticides, respectively (European Parliament, 1998) is often not achievable with metaldehyde levels regularly reaching >0.1 µg L^{-1} in source waters (Kay and Grayson, 2014). These high concentrations are due to the low organic carbon sorption coefficient of metaldehyde, resulting in not only high mobility in the environment, but also reported persistency half-life up to 223 days (Kay and Grayson, 2014). Therefore, metaldehyde peak concentrations are found around the time of their application. In the UK, metaldehyde is typically applied in October-December, extending to September-February (Kay and Grayson, 2014). The magnitude of this seasonal issue is exacerbated since this molluscicide bait, used to control gastropods for a wide variety of crops, is non-readily removed by the current water treatment technologies, such as granular activated carbon (GAC) beds (Autin *et al.*, 2012; Tang *et al*., 2016) and ozone (Comninellis *et al*., 2008). GAC is the most common treatment applied for removing other pesticides from raw water (Westerhoff *et al.*, 2005) due to the wide-scale applicability,

effectiveness and relatively low cost (Tang *et al*., 2016). However, GAC processes are ineffective at removing polar pesticides such as metaldehyde over long time scales (Semitsoglou-Tsiapou *et al*., 2016). Metaldehyde has low adsorption capacity onto GAC (IPCS, 1999; UKWIR, 2011) and was found to by-pass GAC systems which limited the removal efficiency to 30-50%, with an estimated bed life of <44 days if the media was not regenerated (Tao and Fletcher, 2016). Therefore, regeneration costs associated to maintain performance for metaldehyde removal using GAC treatment are currently unfeasible (Autin *et al.*, 2012; Castle *et al*., 2017).

Under this challenging landscape, chemical oxidation processes by means of different technologies, *e.g.* ozonation, UV-based, electrolysis, Fenton-related, solar visible irradiation or ultrasound irradiation (Comninellis *et al*., 2008), have been studied with the aim of effectively removing recalcitrant pollutants such as metaldehyde from source waters (Roche and Prados, 1995; Özcan *et al.,* 2010; Tizaoui *et al.*, 2011; Despotović *et al.*, 2012; Jefferson *et al.*, 2016; Semitsoglou-Tsiapou *et al*., 2016; Martinez, Delgado and Jarvis, 2016). Some water companies have alternatively decided to embrace catchment measures to reduce the risk of supply water polluted by pesticides (DWI, 2016). Catchment management is a potential option to address metaldehyde contamination problem. Nevertheless, it is unlikely to provide a stand-alone solution. This is because of the variable efficacy of catchment management operations subjected to uncertainties caused by such factors as rainfall patterns, ineffective understanding of the contaminant pathways from the source to waters, resistance of pests to alternative pesticides and human error (Reichenberger, 2007). Moreover, these practices are beyond water suppliers' control since they often do not have ownership of the land or decision making for that land to which pesticides are applied (Dolan, 2013). Also, regulating metaldehyde application would likely create pollution swapping derived from the alternative active substances (Dolan *et al*., 2014). Therefore, 'end-of-pipe' treatments for metaldehyde removal are likely to represent the ultimate barrier to prevent consumption of waters laden with metaldehyde concentration >0.1 µg L^{-1}. However, the implementation of promising advanced oxidation processes (AOPs)

for metaldehyde degradation present two main limitations: the high energy and chemical demand, and the formation of unwanted treatment by-products (Autin *et al.,* 2012; James, Germain and Judd, 2014; Kim and Zoh, 2016; Collins and Bolton, 2016). In this study, a pilot trial was undertaken to investigate UV/H_2O_2 and O_3/H_2O_2 + H_2O_2/UV performance (collectively AOPs) to reliably advise full-scale implementation costs based on the optimisation of the key performance parameters: UV, H_2O_2 and O_3. This allows an overall benchmarking between treatments through AOPs.

This thesis consequently is formatted in two chapters as papers for publication. Chapter 1 focuses on the pilot, lab-scale experimental work and the results for the removal of metaldehyde and disinfection by-products (DBPs) formation potential (DBPFP). Chapter 2 explores the economic viability of AOPs for metaldehyde removal and compares the costs of the treatments assessed in this project (H_2O_2/UV, O_3/H_2O_2 and O_3/H_2O_2 + H_2O_2/UV) which are currently commercially available technologies.

1.2 Aims and objectives

This research aimed to determine the effectiveness and cost of H_2O_2/UV and O_3/H_2O_2 + H_2O_2/UV AOPs for the removal of the recalcitrant pesticide metaldehyde to levels that are deemed acceptable. Moreover, the economic evaluation considered a trade-off between the optimum operating conditions to remove metaldehyde, to limit DBPFP levels from the inlet and to minimise the whole-life costs using real surface waters. To explore potential matrix effects on treatment performance, a bench scale experiment was intended to investigate the influence of turbidity causing materials (TCMs) such as kaolin and humic acid (HA) on the removal of metaldehyde within the H_2O_2/UV treatment.

In order to achieve this aim, the objectives were developed:

- To test and evaluate the technologies for metaldehyde removal under different reagents doses and UV fluences, sampling from commercially available H_2O_2/UV and O_3/H_2O_2 + H_2O_2/UV pilot-scale reactors
- To assess the influence of TCMs on the removal of metaldehyde
- To compare the metaldehyde removal efficiency of both AOPs according to the cost per m^3 treated
- To determine the optimum energy demand (E_D) (kWh m^{-3}), H_2O_2 (mg L^{-1}) and O_3 (mg L^{-1}) doses for each technology to respectively achieve the statutory limits of metaldehyde in DW and to attain the lowest DBPFP. The cost of these processes is considered with respect to CAPital EXpenditures (CAPEX) and OPerating Expenses (OPEX) using a Whole-Life Costing Analysis (WLCA)

2 SUCCEEDING METALDEHYDE AND DISINFECTION BY-PRODUCTS COMPLIANCE LEVELS IN SURFACE DRINKING WATER BODIES BY O_3/H_2O_2 + H_2O_2/UV AND UV/H_2O_2

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Abstract

The efficacy of UV, H_2O_2 and O_3 for the removal of metaldehyde and disinfection by products formation potential (DBPFP) was investigated at pilot-scale using UV/H_2O_2 and O_3/H_2O_2 + H_2O_2/UV advanced oxidation processes (AOPs) concurrently. Both AOPs degraded up to 98% metaldehyde from inlet metaldehyde concentrations of ≤2.14 µg L^{-1} and <1.0 kWh m^{-3} to meet the stringent European Directive 98/83/EC. The highest oxidants and energy demands (E_D) yielded the greatest metaldehyde removals in both technologies. O_3/H_2O_2 removed the majority of the metaldehyde in the UV/H_2O_2 and O_3/H_2O_2 system, up to 96%, depending on the operating conditions. However, the treated water from the O_3/H_2O_2 was above the 0.1 µg L^{-1} benchmark concentration adopted from the European Directive 98/83/EC for metaldehyde inlet concentration (MIC) >0.14 µg L^{-1}. A bench-scale study revealed UV/H_2O_2 effectiveness for metaldehyde removal was reduced in organic-enriched water matrices which had a turbidity >1.0 Nephelometric Turbidity Units (NTU). This was due to competition between organic compounds and metaldehyde for hydroxyl radicals (•OH). The AOPs also produced trihalomethanes (THMs) compliant water yielding net THM formation potential (THMFP) between -283 µg L^{-1} to +255 µg L^{-1}. Net haloacetic acid (HAA) formation potential (HAAFP) after the AOP varied from -164 µg L^{-1} to +131 µg L^{-1}. Natural organic matter (NOM) characteristics were found to be more important for DBPFP than the operating conditions tested in this study and metaldehyde concentrations in the inlet water.

Keywords: advanced oxidation process, DBP, haloacetic acid, pesticide, trihalomethane

2.1 Introduction

Advanced oxidation processes (AOPs) are characterised by the generation of highly reactive, non-selective hydroxyl radicals ($^{\bullet}OH$) able to oxidise and degrade organic compounds treating simultaneously a variety of contaminants (Oturan and Aaron, 2014; Collins and Bolton, 2016) such as antibiotics (Lester *et al.*, 2011) and pesticides, *e.g.* metaldehyde, clopyralid or mecoprop (Autin *et al.*, 2012; Martinez, Delgado and Jarvis, 2016). Extensive research has also been undertaken to evaluate the performance of AOPs for the reduction of persistent organic constituents from waters, including disinfection by-products (DBPs) precursors, not achievable through conventional technologies such as coagulation (Chin and Bérubé, 2005; Toor and Mohseni, 2007; Sarathy and Mohseni, 2010; Bond *et al.*, 2011). The molluscicide metaldehyde is widely used across the UK-residential and agricultural sector, being recognised one of the major causes for failing to achieve pesticide water-quality standards set in European Directive 98/83/EC (DWI, 2014). A number of pilot-scale and bench-scale experiments have been conducted, at different oxidant doses and/or UV fluences, to assess the effectiveness of AOPs to reduce metaldehyde concentration in water (Table 1). Anglian Water treated filtered water through the O_3/H_2O_2 process using a pilot-scale reactor and achieved a 0.7-log reduction of metaldehyde. In this peroxone trial, an initial concentration of 10 mg L^{-1} O_3 was typically applied (Collins and Bolton, 2016). The variety of combined radiation and oxidant doses suggest the importance of correct chemical and energy dosing to target metaldehyde. Moreover, some authors have stated that an excess of oxidants over the optimal concentration affect the AOP removal performance through hydroxyl scavenging (Lucas, Peres and Li Puma, 2010; Autin *et al*., 2012). In contrast, deficient UV and/or oxidant doses led to greater production of DBPs (Sarathy *et al*. 2011), which is one of the main limitations of AOP full-scale implementation (Collins and Bolton, 2016). DBPs are formed through the reaction between natural organic matter (NOM), iodide, anthropogenic contaminants, and

bromide with disinfectants, such as chlorine. Among the different DBPs, haloacetic acids (HAAs) are regulated in the USA whilst trihalomethanes (THMs) are regulated in the EU and the USA. In the EU, total THMs should not exceed 100 µg L^{-1} in tap water (European Parliament, 1998; DWI, 2000) and a risk assessment to control DBPs when exceeding 50 µg L^{-1} THMs (Jefferson *et al.*, 2016) was outlined in Regulation 26.1(a) of The Water Supply Regulations 2010 (DWI, 2010). The USA has established more stringent treated water standards of 80 µg L^{-1} for total THMs and 60 µg L^{-1} for HAAs (EPA, 2017).

Table 1 Treatability studies on metaldehyde removal

MIC (µg L^{-1})	Removal rate	Experimental conditions	UV fluences (mJ cm^{-2})	H_2O_2 (mg L^{-1})	O_3 (mg L^{-1})	Reference
1000	95%	Laboratory scale	600	272	N/A	Autin *et al.*(2012)
0.2	>90%		>2000	>2		James, Germain and Judd (2014)
300	97%		1000	15		Semitsoglou-Tsiapou *et al.* (2016)
0.5	72%	Pilot plant	N/A	16-22	8	Tang *et al.* (2016)
	90%		1200	16-22	8	

MIC: metaldehyde inlet concentration

The presence of background organic constituents, *e.g.* humic substances, proteins, carboxylic acids, carbonate and bicarbonate ions (Chin and Bérubé, 2005; Kim and Yu, 2005; Baghoth, Sharma and Amy, 2011) in water play a key role not only on the formation of DBPs (Richardson, 2007) but in the pollutant removal success of AOPs (Autin *et al.*, 2013a, Carra *et al.* 2016). NOM interferes with the degradation of metaldehyde using AOPs through •OH scavenging (Crittenden *et al.*, 2012; Autin *et al.*, 2013a). Hence, elevated UV fluences are required to attain necessary pesticide removal (Jefferson *et al*. 2016). NOM in conjunction with other suspended particles in water, *e.g.* clay, fine inorganic colloids, influences water quality parameters such as turbidity, an optical property related with light scattering and light absorption (Wang and Hsieh, 2001; Parsons and Jefferson, 2006). Humic acids (HA) represent a significant fraction of the

NOM chemical composition (Croue, Korshin and Benjamin, 2000; Carra *et al.* 2016), up to one-half of the dissolved organic carbon (DOC) (Kim and Yu, 2005), and pollutants are able to bind strongly in such a way that adversely affect their degradation in AOPs (Hollrigl-Rosta *et al.*, 2003). The negative effect of pesticides degradation via photo-Fenton process as a result of the •OH quenching process and UV light screening by increasing HA concentration has been reported (Farré *et al*., 2007; Carra *et al.* 2016). However, it is important to elucidate whether inorganic matter also weighs when degrading a target compound. The influence of kaolin clay on the photocatalytic oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) has been investigated (Giri *et al*., 2010). The authors concluded that UV shielding from kaolin concentration did not influence 2,4-D removal. Similarly, photocatalytic degradation efficiency of HA in kaolin-turbid water has been tested (Sen Kavurmaci and Bekbolet, 2014), reporting an insignificant effect of the clay mineral in the process.

The robustness of AOPs to decrease organic compounds in water has been discussed (Chin and Bérubé, 2005; Murray *et al*., 2007; Toor and Mohseni, 2007; Sarathy and Mohseni, 2010; Lamsal *et al.*, 2011; Jefferson *et al*., 2016) Therefore, the reduction in the formation of DBPs and the removal of metaldehyde is expected provided that adequate oxidants doses and UV fluences are applied (Sarathy *et al*. 2011). For those DBPs generated after AOPs, granular activated carbon (GAC) can subsequently be applied to adsorb them (Kawamura, 2000).

The objective of this work was to critically assess the effectiveness of H_2O_2/UV and O_3/H_2O_2 + H_2O_2/UV for metaldehyde degradation under different reagents doses and UV fluences (E_D) in pilot-scale AOP reactors. It also addressed the influence of turbidity causing materials (TCMs) for metaldehyde removal under the UV/H_2O_2 process. Equally, the research evaluated the impact of the treatment conditions on the DBPs formation potential (DBPFP). Finally, the optimization of the AOPs, depending on MIC, was studied to comply the European Directive 98/83/EC in terms of both metaldehyde and DBPs.

2.2 Methodology

2.2.1 Pilot plant and operating conditions

Two pilot-scale AOP plants (Figure 1) were fed with post Rapid Gravity Filtration water (RGF), originally from Draycote water reservoir, and were installed in independent shipping containers at Draycote water treatment work (WTW) (Warwickshire, UK). The UV/H_2O_2 process comprised a flow-through UV stainless steel pressurized reactor (TrojanUVPhox™, Model 8AL20 oxidation system) providing nominal treatment to 1-5 $m^3 h^{-1}$ of water and equipped with 8 low-pressure high-output (LPHO) amalgam lamps (~12,000 h lifespan) and 3.38m L x 1.32m W x 1.93m H physical dimensions. The O_3/H_2O_2 + H_2O_2/UV process was from WEDECO, Xylem Water Solutions UK Ltd. and comprised an ozone generator (GSO3O) (0.80m L x 0.80m W x 0.3m H) supplied with liquid oxygen (LOX) 100 g h^{-1} nominal capacity production and 0.5 bar (g) operating pressure; an injection and reaction system (PRO$_3$MIX-MiPRO), and a flow-through UV system (LBX 10). The UV reactor (2.90m L x 0.95m W x 1.38m H) worked in the nominal range 0.5-4 $m^3 h^{-1}$ and was equipped with 3 Spektrotherm® LPHO (~12,000 h lifespan). As two pilot UV reactors from different suppliers were used in this research, from now on the UV/H_2O_2 process refers to the Trojan unit, so does H_2O_2/UV process to the Xylem model.

Post RGF water, hereinafter referred to as inlet water, was spiked with metaldehyde from a 100 mg L^{-1} stock solution contained in a tank with a motorised agitator. The stock solution was diluted in water to reach the concentration required, as different MICs were required at a number of operating conditions assessed (Table 2). All the operating conditions are displayed in Appendix A. H_2O_2 was dosed upstream of the UV reactor (UV/H_2O_2) and the O_3/H_2O_2 reactor system (O_3/H_2O_2 + H_2O_2/UV), respectively with static mixers. Outlets from both treatments were subsequently filtered by separate GAC contactors. Sodium sulphite (Na_2SO_3) was also used to quench the residual H_2O_2.

Table 2 Operating conditions

Treatment	Metaldehyde spiking dose (µg L^{-1})	Flow rate (m^3 h^{-1})	[H_2O_2] (mg L^{-1})	[O_3] (mg L^{-1})	Energy demand (E_D) (kWh m^{-3})
O_3/H_2O_2 + H_2O_2/UV	Raw water, 0.5 and 2	0.6-2.5	8-30	2-10	0-1.10
UV/H_2O_2		2.0-3.5	10-45	N/A	0.35-1.00

N/A: not applicable

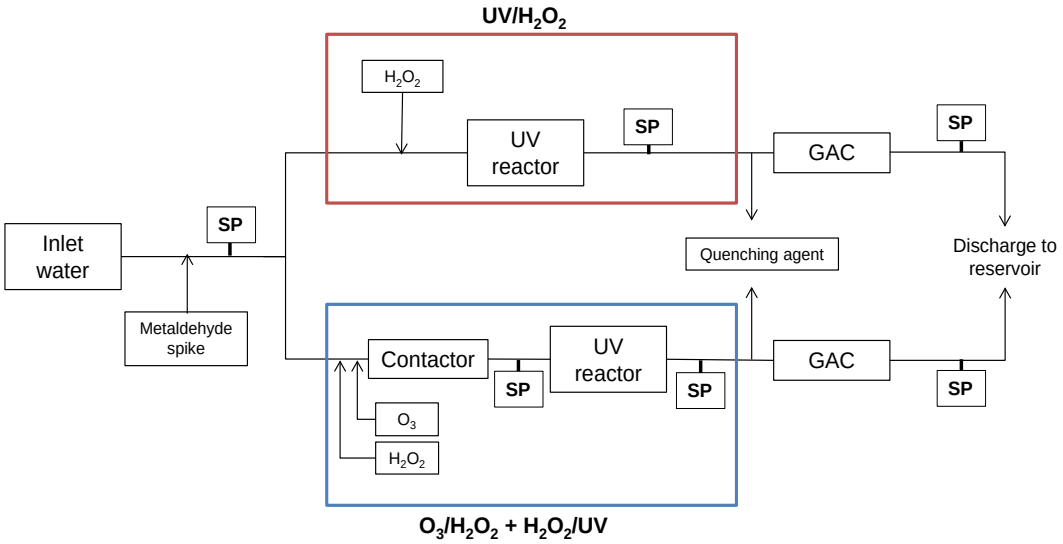

Figure 1 Flow diagram of UV/H_2O_2 and O_3/H_2O_2 + H_2O_2/UV pilots at Draycote WTW. SP: sample point

2.2.2 Chemical reagents

For pilot studies, 100 mg L^{-1} metaldehyde (99 wt. %) stock solution (CAS: 9002-91-9, Sigma-Aldrich, UK) was prepared in ultrapure (UP) water (resistivity 18.2 MΩ cm^{-1}, TOC <3 ppb, PURELAB®Ultra, UK) and stored at 5ºC until delivery to the pilot units. The concentration of metaldehyde was assessed by Liquid Chromatography - tandem Mass Spectrometry prior to operating experiments. H_2O_2 (35 wt. %) (CAS: 7722-84-1, Fisher Scientific, UK) and sodium sulphite anhydrous (CAS: 7757-83-7, Fisher, UK) were also purchased. For lab-scale

TCM experiments, Kaolin clay – light washed with acid (CAS: 1332-58-7, Fisher, UK) and Humic Acid sodium salt (H16752, Aldrich, UK) were used. For DBPs analysis, sodium hypochlorite (10-15%) active chlorine (CAS: 7681-52-9), sodium sulphate (99%) anhydrous (CAS: 7757-82-6), sodium phosphate dibasic (99%) (CAS: 7558-79-4), ammonium chloride (CAS: 12125-02-9) and potassium phosphate monobasic (99%) (CAS: 7778-77-0) were purchased from Fisher Scientific (UK).

2.2.3 Experimental procedure

2.2.3.1 Pilot-scale experiments

A number of relevant operating conditions were tested to evaluate the AOP pilot units for metaldehyde removal and DBPFP (Table 2, Appendix A). As the normal operating conditions involve steady state, operational parameters were regularly changed, but allowing to the AOPs respond to such adjustments. Therefore, samples were collected from each sample point (Figure 1) in 1-litre HDPE bottles 20 min after a flow rate change, and 10 min after the oxidant doses or UV fluences were changed. This decision was made upon operators' experience enabling a full evaluation of the impact caused by parameter changes. The DBPFP analysis involved chlorination.Therefore, Na_2SO_3 at a stoichiometric ratio of 3.7 (Na_2SO_3: H_2O_2) was added to exactly quench the peroxide residual present in samples after measure on-site by a 7100 Palintest photometer (Palintest Ltd., UK). Samples were placed into a cool box on ice. Inlet water was taken twice per day to verify the correct performance of the metaldehyde spiking pump.

2.2.3.2 Bench-scale experiment assessing the impact of TCMs on metaldehyde removal by UV/H_2O_2

Experiments were performed using 2 µg L^{-1} of target pesticide as representative of 'high' metaldehyde concentrations in surface waters, reported up to 2.7 µg L^{-1} (Kay and Grayson, 2014). Different concentrations of HA and kaolin to achieve 0, 0.1, 0.2, 0.4, 1, 2, 5 NTU were used to assess the resultant impact on metaldehyde removal via UV/H_2O_2 at 1800 mJ cm^{-2} UV fluences and 30 mg L^{-1} H_2O_2. The TCM concentrations selected are typically found in source and potable waters (Collins and Bolton, 2016),

The metaldehyde stock solution was prepared by adding the pesticide to UP water at a concentration of 1 mg L^{-1}. Two solutions at a nephelometric turbidity level (NTU) of 5.70 (5.80 mg) and 5.04 (24 mg) for kaolin and HA, respectively, were prepared in one-litre volumetric flasks of UP water. The rest of TCM solutions were obtained by two-fold dilution in UP water (1 part TCM, 1 part UP water) of the concentrated TCM stock solution. A total of five 2-fold serial dilutions were undertaken to cover the range 0.09-5.70 NTU and 0.09-5.04 NTU for kaolin and HA-TCM, respectively (Table 3, Table 4). The TCMs dilutions were subsequently spiked with the pesticide stock solution to attain a final metaldehyde concentration of 2 µg L^{-1}.

Appropriate control experiments were undertaken in addition to the H_2O_2/UV full exposure. All the samples were measured for metaldehyde residual concentration (µg L^{-1}), turbidity (NTU), UV absorbance at 254 nm (UV254 nm) and transmittance (%).Control test 1 entailed the analysis of 100 mL TCM solutionc spiked with metaldehyde, without adding H_2O_2 nor exposing it under UV light. Control test 2 involved adding 10 µL of H_2O_2 (35 wt. %) to 100 mL sample and, afterwards, analysing for the same parameters as in control 1. In the case of the complete H_2O_2/UV experiment, 10 µL of H_2O_2 (35 wt. %) to 100 mL sample was equally added as done in control 2. After that, 70 mL sample was poured into a glass Petri dish (9 mm diameter, 1.8 mm high). The 70 mL samples were subsequently irradiated with UV light (254 nm) at 1800 mJ cm^{-2} using a low pressure UV collimated beam device (Wedeco AG Water Technology, Germany). Before transferring the sample into the device, UV intensity was measured by VLX-3W radiometer (Vilber Lourmat, France). The UV intensity was 3.20-3.40 mW cm^{-2} resulting in an irradiation-time window of ~ 8'50'' to 9'20''. Over the irradiating time period, the solutions were mixed by a magnetic bar and stirrer located on the platform reactor. A 250 mm space was left between the UV lamps and the sample surface. Then, the irradiated solution was extracted by pipette. 'Control 2' and samples under H_2O_2/UV were quenched by adding 3.7 mg L^{-1} Na_2SO_3 per mg L^{-1} of H_2O_2.

Table 3 Range of kaolin concentrations assessed for metaldehyde removal at 2 µg L^{-1} metaldehyde initial concentration under UV/H_2O_2

Kaolin (mg L^{-1})	Metaldehyde (µg L^{-1})	H_2O_2 (mg L^{-1})	UV fluences (mJ cm^{-2})
5.80			
2.90			
1.45		0	0
0.58	2	and	and
0.29		30	1800
0.14			
0			

Table 4 Range of humic acid concentrations assessed for metaldehyde removal at 2 µg L^{-1} metaldehyde initial concentration under UV/H_2O_2

Humic acid (mg L^{-1})	Metaldehyde (µg L^{-1})	H_2O_2 (mg L^{-1})	UV fluences (mJ cm^{-2})
24			
12			
6		0	0
3	2	and	and
1.50		30	1800
0.75			
0			

2.2.4 Analytical methods

Measurements were carried out in duplicate. On filtered samples (Millex-HA filter, 0.45 µm, Aldrich, UK), UV254 nm absorbance was determined by means of a 6715 UV/Vis spectrophotometer (Jenway, UK) following standard method 5910. The non-purgeable organic carbon was measured by 5310 standard method with a TOC-V CSH TOC analyser (Shimadzu, UK). Turbidity was determined following 2130 method through a Hach 2100 turbidimeter (Hach Company, Loveland, CO) and a 4330 conductivity & pH meter was used for pH determinations (Jenway, UK). Metaldehyde residual concentration was analysed by gas chromatography-mass spectrometry using an Agilent Technologies 1260 HPLC with 6490 Triple

Quad LC/MS (Affinity Water, UK). A Poroshell 120 EC-C18 column was used (Capillary 2.7 m x 75 mm x 2.1 mm nominal).

The DBPs analytical method involved the chlorination of samples with total organic carbon (TOC) of < 1 mg L^{-1} from a chlorine stock solution of concentrated sodium hypochlorite diluted in UP water. In this research, each sample had a chlorine dose (mg L^{-1}) five times the TOC of the water. Seven days later, HAAs were quenched with ammonium chloride (100 mg L^{-1}) and THMs first buffered at pH 5 with a mix of sodium phosphate dibasic (1 g) and potassium phosphate monobasic (99 g) and then quenched with Na_2SO_3 (100 mg L^{-1}). HAAs and THMS were subsequently extracted by EPA Method 552.3 and 551.1, respectively. THM internal standard was 4-bromofluorobenzene (1 µg L^{-1}) and HAA internal standard was 1, 2, 3 - trichloropropane (300 µg L^{-1}). HAA_9 (MBAA, TCAA, MCAA, DCAA, bromochloroacetic acid (BCAA), (DBAA), bromodichloroacetic acid (BDCAA), tribromoacetic acid (TBAA) and chlorodibromoacetic acid (CDBAA)) and THM_4 (bromoform, chloroform, bromodichloromethane and dibromochloromethane) were analysed by transferring an autosampler vial to a gas chromatography with electron capture detection (ECD) (Agilent HP 6890, Agilent Technologies, USA).

2.2.5 Statistical methods

Metaldehyde and DBPFP variation was subject to crossed and interrelated factors (treatments and water quality) difficult to untangle: *e.g.* the response under O_3 doses differs with H_2O_2 concentration, UV fluences, DOC, etc. Therefore, standard normal linear models are limited for a multivariate and hierarchized set of factors, as the magnitude and direction of such interactions affect metaldehyde and DBPFP variation. A non-parametric multivariate multiple regression analysis through distance-based linear model (DistLM) analysis in PRIMER v6 software (Clarke and Gorley, 2006) was carried out to assess the AOP performance. The DistLM analysed and modelled the strength and significance of the relationship between a multivariate dataset (effectors) described by a resemblance matrix in Euclidean distance, and at least one predictor variable (Clarke and Gorley, 2006). The DistLM was used due to (i) it

takes into account possible interactions between the predictor variables (ii) multivariate data did not follow a normal distribution. The DistLM is constrained to find linear combinations of the predictors which best explain the greatest variation in the dataset (effector) response individually (marginal test). It also evaluates the cumulative effect of predictors, starting with such of the highest percentage influence and sequentially followed in ranking order by adding the rest, to improve the predictive power of the DistLM (sequential test). In doing so, the sequential test assesses whether the variation is better explained. The sequential routine is made until no further improvement to the model is attained. By using DistLM, the influence of an array of factors/predictors that can explain the change on the effectors before and after the AOP was achievable. In this study, the predictors were the process variables as well as the laboratory analysis results of turbidity, UV254 nm and DOC before such an AOP unit. Metaldehyde removal, net THM formation potential (THMFP) contribution and net HAA formation potential (HAAFP) contribution were the effectors of the model. All the measures were averaged, from each pair of duplicates, across the various operating conditions tested on the pilots.

Because predictors had different measurement scales, they were first square root transformed to equally distribute their weight. Those values were then standardised using the 'normalise' routine of the software (Clarke and Gorley, 2006). They were subsequently established in a resemblance Euclidean distance matrix, hence quantifying the between-normalised sample similarities. Effectors were excluded of square root transformation as the net DBPFP contribution provided with negative values (reduction of DBPFP after AOP). Stepwise permutation test (McArdle and Anderson, 2001) with the criterion of R^2 and 9999 permutations (Clarke and Gorley, 2006) was employed to obtain *P*-values for testing the null hypothesis of no significant differences in each effector change among the predictors tested. The null hypothesis was rejected if the significance level (P) was <0.05. A distance based Pseudo-*F* was calculated. The Pseudo-*F* represents the effect size and is analogous of *F* for multi-factorial univariate ANOVA models (McArdle and Anderson, 2001).

2.3 Results and discussion

2.3.1 Effectiveness of ozone and UV-based AOPs for metaldehyde removal

UV/H_2O_2 and the full O_3/H_2O_2 + H_2O_2/UV treatment reduced metaldehyde in the range of 38-98% and 55%-97%, respectively, which was dependent on the MIC and operating conditions (Figure 2). The virgin GAC system post AOP had an effluent metaldehyde concentration of less than 6% of the inlet. For both treatments, the maximum pesticide degradations were achieved at the highest chemical and energy inputs (Table 5). The O_3/H_2O_2 in isolation removed the majority of the metaldehyde (38%-96%) from the inlet. The subsequent H_2O_2/UV process achieved 79% peak metaldehyde removal of the O_3/H_2O_2 effluent. This more limited removal efficiency could be due to the requirement for greater UV fluences to degrade metaldehyde in the same order of magnitude as O_3/H_2O_2. The peroxone process acted as a pre-treatment for the pesticide of interest and could improve the treatability of the water prior to H_2O_2/UV. It is noticeable that the stand-alone UV/H_2O_2 unit and the O_3/H_2O_2 sub process equally removed 38% metaldehyde for the worst-case scenario. For the stand-alone UV/H_2O_2, it was at 0.53 µg L^{-1} MIC, 13 mg L^{-1} H_2O_2 and 0.41 kWh m^{-3}. In the case of the O_3/H_2O_2 sub process, the lowest metaldehyde removal was found at 0.14 µg L^{-1} MIC, 2.1 mg L^{-1} O_3 and 11 mg L^{-1} H_2O_2.

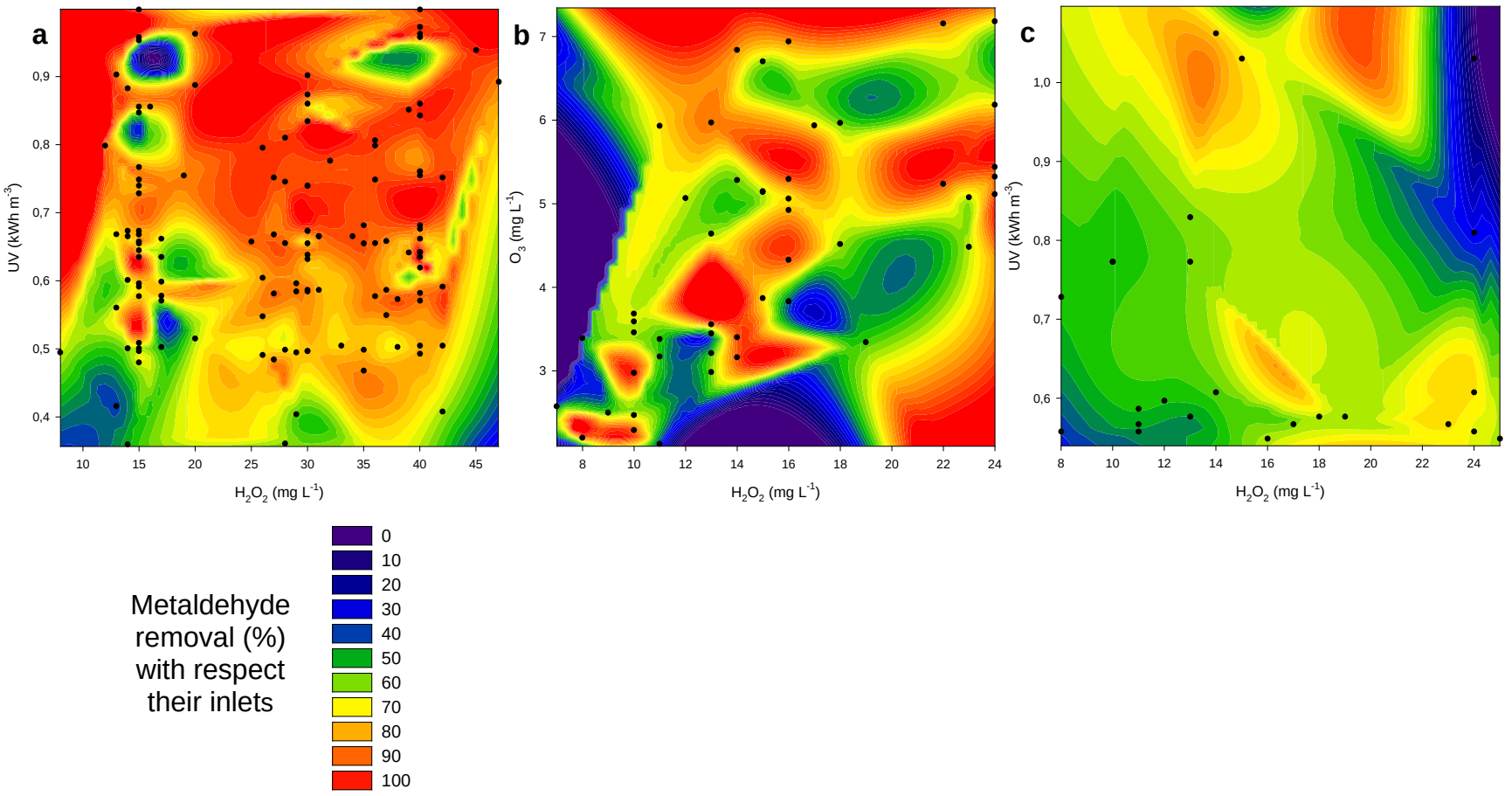

Figure 2 Net metaldehyde removal (%) contour plot regardless the initial concentration of pesticide and including all the operating conditions tested in the pilot-trial (n) by (a) UV/H_2O_2 (*n* = 127), (b) O_3/H_2O_2 (*n* = 50) and (c) H_2O_2/UV (*n* = 31). Black points represent sampled data. Contour represents interpolation of data between measured points according to *SigmaPlot 11.*

Similar maximum metaldehyde removals on the stand-alone UV/H_2O_2 process were observed in the literature (James, 2013; Semitsoglou-Tsiapou *et al.* 2016). However, their operating conditions and MICs differed to those herein required (Table 5). James (2013) achieved 98% metaldehyde degradation at 0.2 µg L^{-1} MIC, 3 mg L-1 H_2O_2 and 0.62 kWh m^{-3} E_D, while Semitsoglou-Tsiapou *et al.* (2016) achieved 97% removal applying 1000 mJ cm^{-2} UV fluences and 15 mg L^{-1} H_2O_2 for a 0.3 mg L^{-1} MIC. Similar 0.7 kWh m^{-3} E_D was required to degrade 90% metaldehyde as Lekkerkerker-Teunissen *et al*. (2013) found in 90% atrazine degradation of an initial concentration of 10 µg L^{-1}. However, they dosed 5 mg L^{-1} H_2O_2 whilst 28 mg L^{-1} and 40 mg L^{-1} were required in this study for metaldehyde inlets of 0.53 µg L^{-1} and 2.14 µg L^{-1}, respectively.

In the 'two-stage' AOP process (O_3/H_2O_2 + H_2O_2/UV), Tang *et al*. (2016) attained 90% metaldehyde removal from a MIC of 0.5 µg L^{-1} using 8 mg L^{-1} O_3 and 16-22 mg L^{-1} H_2O_2. However, similar doses (7.2 mg L^{-1} O_3 and 24 mg L^{-1} H_2O_2) achieved 97% metaldehyde degradation at 2.11 µg L^{-1} of initial pesticide level in this study. This was probably because 1800 mJ cm^{-2} UV fluences (1.03 kWh m^{-3} E_D) were used whilst Tang *et al*. (2016) irradiated 1200 mJ cm^{-2}.

Despite the higher removal efficiency of the peroxone sub stage than the H_2O_2/UV, only for a 0.14 µg L^{-1} MIC the O_3/H_2O_2 produced metaldehyde-compliant water according to the European Directive 98/83/EC (Figure 3). Otherwise, the presence of the H_2O_2/UV was crucial. This stresses that high removal does not imply achieving <0.1 µg L^{-1} metaldehyde permitted concentration value (PCV) as it is MIC dependant. Therefore, even a 90% removal is insufficient to produce metaldehyde-compliant water at 2.0 µg L^{-1} MIC, but it requires 95%.

Table 5 Optimum set of experimental conditions at pilot-scale achieved the best metaldehyde removal (%)

Treatment	Flow rate ($m^3 h^{-1}$)	[H_2O_2] (mg L^{-1})	[O_3] (mg L^{-1})	E_D (kWh m^{-3})	[pesticide]$_0$ (µg L^{-1})	Removal (%)
O_3/H_2O_2 + H_2O_2/UV	2.5	24	7.2	1.03	2.11	97
O_3/H_2O_2[a]	0.6	24	5.4	N/A	2.23	96
H_2O_2/UV[a]	2.5	18	6.0	1.10	0.53	79
UV/H_2O_2 stand-alone	2.0	45	N/A	0.94	2.11	98

N/A: not applicable; [a] Sub processes of the two-stage UV-based and peroxone AOPs

2.3.2 Impact of the operating conditions on metaldehyde removal

Statistical results over 127 samples indicated that H_2O_2 explained 13% of the variability in metaldehyde removal (*P*=0.0001) within the stand-alone UV/H_2O_2 process. Metaldehyde removal was improved when H_2O_2 dose was raised at equal MIC and E_D, *e.g.* at <0.5 µg L^{-1} MIC and 0.60 kWh m^{-3}, 68% removal dosing 14 mg L^{-1} H_2O_2 in contrast with the 83% removal at 29 mg L^{-1} H_2O_2. However, the UV/H_2O_2 process performance was not improved at >0.66 kWh m^{-3} E_D and 40 mg L^{-1} H_2O_2 dose regardless MIC, *e.g.* at 0.89 kWh m^{-3} and <0.5 µg L^{-1} MIC 93% removal dosing 30 mg L^{-1} H_2O_2, whilst 85% dosing 47 mg L^{-1} H_2O_2; or the same 93% metaldehyde removal for 32 mg L^{-1} and 40 mg L^{-1} H_2O_2 at 0.77 kWh m^{-3}. Negligible process optimisation was also detected for E_D above both 0.85 kWh m^{-3} and 30 mg L^{-1} H_2O_2 in >2.0 µg L^{-1} metaldehyde waters. At 0.5-0.8 µg L^{-1} metaldehyde inlet, there was a limited difference of pesticide removal either with 30 mg L^{-1} H_2O_2 and 0.86 kWh m^{-3} (91.4%) or 40 mg L^{-1} H_2O_2 and 0.97 kWh m^{-3} (96%). The DistLM revealed UV irradiation accounted for 32% of the variability in metaldehyde removal on its own (*P*=0.0001).

Regardless the inlet concentration of metaldehyde (µg L^{-1}) (0.14 / 0.53 / 2.2) and H_2O_2 doses (mg L^{-1}) (40 / 40 / 30), poorer metaldehyde removals (%) were observed at 0.66 kWh m^{-3} E_D and 2 m^{-3} flow rate (84.5 / 79.5 / 79.7) than that of 0.60 kWh m^{-3} E_D and 2.5 m^{-3} flow rate (86.6 / 83.1 / 83.8) which was in contrast to the positive trend previously stated up to 0.85 kWh m^{-3}. One possible

explanation was that of the better UV light distribution when irradiated at more turbulent regime of water (Koutchma *et al.*, 2004; Dobrović, Juretić and Ružinski, 2007). The AOP performance could be enhanced a maximum of 10% by increasing the flow rate from 2.5 $m^3\ h^{-1}$ to 3.5 $m^3\ h^{-1}$. The flow rate individually involved 13% of variability in metaldehyde removal (P=0.0001). The DistLM analysis showed that when UV and H_2O_2 were considered together, they influenced 43% of the variability in metaldehyde removal (P=0.0001). The DistLM over 64 samples indicated that H_2O_2 and O_3 influenced individually 34% and 45% of the variability in metaldehyde removal (P=0.0001) within the two-stages O_3/H_2O_2 + H_2O_2/UV process jointly evaluated. Greater metaldehyde removals (%) were found when adding more oxidants on equal H_2O_2:O_3 ratio, *e.g.* 47% (12 mg L^{-1} H_2O_2 and 4 mg L^{-1} O_3) versus 67% (24 mg L^{-1} H_2O_2 and 8 mg L^{-1} O_3) at 0.53 µg L^{-1} MIC. This was possibly explained due to greater •OH production by raising oxidants despite maintaining ratios. However, similar metaldehyde removal was attained when H_2O_2 was overdosed at the same ozone concentration, *e.g.* 46% vs 47% at a H_2O_2:O_3 ratio 2:1/3:1, respectively and 0.53 µg L^{-1} metaldehyde inlet. A 1:1 H_2O_2:O_3 mole ratio, 0.7:1 in terms of mass, has been reported to form $^{\bullet}$OH radicals (Lucas, Peres and Li Puma, 2010). Yet the specific ratio is also a function of the water quality parameters and pollutant concentration (Melin, 2000). Thus, it can be hypothesised that O_3 was the limiting factor for $^{\bullet}$OH production as H_2O_2 was of a dose two or three-fold higher than the O_3 concentration in the pilot-scale experiments. However, such H_2O_2 surplus was required to have H_2O_2 residual within the subsequent H_2O_2/UV process for $^{\bullet}$OH production. It can be inferred, therefore, that O_3 established the amount of •OH generated within the O_3/H_2O_2 stage and determined the H_2O_2 availability for $^{\bullet}$OH formation within the following UV-based AOP stage. UV fluences individually accounted 54% of the variability in metaldehyde removal (P=0.0001), improving the AOP performance with increased fluences. In the O_3/H_2O_2 + H_2O_2/UV process the UV power was fixed to 0.34 kW and the E_D (kWh m^{-3}) adjusted by flow rate variation ($m^3\ h^{-1}$). Through DistLM the UV and O_3 when considered together, accounted for 78% of the variability in metaldehyde removal (P=0.0001).

A separate assessment for each of the two sub processes revealed that for the O_3/H_2O_2, the inlet DOC influenced 35% of the variability in metaldehyde degradation (*P*=0.0001), whilst the absorbance accounted for 26% (*P*=0.0004), H_2O_2 12% (*P*=0.0128) and O_3 10% (*P*=0.0255). When considering the cumulative effect of the predictors, the DistLM indicated that 51% of the variation in metaldehyde removal was attributed to DOC and O_3. This was because (i) O_3 drove the production of $^{\bullet}OH$ and (ii) DOC is a •OH scavenger and thus an influential water quality parameter in determining metaldehyde removal (James, 2013). In the H_2O_2/UV sub process, all process variables were significant (*P*>0.05) for metaldehyde removal. A summary of the statistical data analysis is presented in Appendix B.

2.3.3 Optimum conditions to achieve the statutory limits for metaldehyde residual at the minimum supply of inputs

An optimal set of parameters that successfully achieved metaldehyde PCV in water with the minimum H_2O_2 concentration per energy supplied was identified (Figure 3b and Figure 4a). These operating conditions were dissimilar among MICs. As stated previously, the O_3/H_2O_2 exclusively complied with the legislation at metaldehyde inlets below 0.5 µg L^{-1} (0.14 µg L^{-1}) with a minimum 0.55 kWh m^{-3} E_D (Figure 3a). Unsurprisingly, the greater the metaldehyde inlet concentration, the greater the both UV and H_2O_2 doses which were required (Figure 3b). A ratio H_2O_2:O_3 of 3 was required for the minimum E_D (0.53 kWh m^{-3}) between 0.5-0.8 µg L^{-1} metaldehyde inlets. Equal oxidant ratio was demanded for the minimum E_D (0.79 kWh m^{-3}) between 2.0-2.14 µg L^{-1} metaldehyde inlets. The O_3/H_2O_2 + H_2O_2/UV process did not provide with metaldehyde-compliant water at >2.14 µg L^{-1} MICs. The costing analysis (Chapter 2) was used to understand the relative importance of capital and operational expenditures in the total expenditures for the economic viability of these AOPs. Electricity consumption was a paramount factor over the operational costs associated with chemicals for driving the decision-making of real-scale implementation towards O_3/H_2O_2 rather than O_3/H_2O_2 + H_2O_2/UV or UV/H_2O_2. Therefore, it is recommended that to fulfil the European Directive 98/83/EC, WTW operators should consider the lower E_D despite greater oxidants required when upscaling AOP pilot-trials (Table 6).

A set of optimal operating conditions were equally found for the stand-alone UV/H_2O_2 treatment (Figure 4). The lower limit of 15-20 mg L^{-1} H_2O_2 effectively attained metaldehyde residual UK/EU levels regardless the E_D (minimum 0.36 kWh m^{-3}) at <0.5 µg L^{-1} MIC. Between 0.5-0.8 µg L^{-1}, the compliance of European Directive 98/83/EC was achievable either by raising E_D and lowering H_2O_2 doses (0.67 kWh m^{-3} and 28 mg L^{-1}) or by lowering E_D and increasing H_2O_2 doses (0.55 kWh m^{-3} and 37 mg L^{-1}). Minimum 0.75 kWh m^{-3} E_D with 42 mg L^{-1} H_2O_2 were required to reduce metaldehyde <0.1 µg L^{-1} between 2.0-2.14 µg L^{-1} metaldehyde inlets. Similar findings to that of the O_3/H_2O_2 + H_2O_2/UV process were identified for metaldehyde inlets >2.14 µg L^{-1}. The virgin GAC contactor provided with metaldehyde-compliant water in all the samples analysed according to the benchmark concentration adopted from the European Directive 98/83/EC. However, it is unlikely these high metaldehyde removals would be achieved at full-scale with time due to loss adsorption capacity as the GAC in this pilot study was virgin media.

Table 6 Minimum E_D and their associated minimum oxidant doses tested producing metaldehyde-compliant water at dissimilar ranges of metaldehyde inlet concentrations (MICs)

Treatment	$[metaldehyde]_0$ (µg L^{-1})	$[H_2O_2]$ (mg L^{-1})	$[O_3]$ (mg L^{-1})	E_D (kWh m^{-3})
O_3/H_2O_2 + H_2O_2/UV	<0.5	8	2	0.55
	0.5-0.8	17	6	0.53
	2.0-2.14	22	7	0.79
UV/H_2O_2	<0.5	14	N/A	0.36
	0.5-0.8	37		0.55
	2.0-2.14	42		0.75

N/A: not applicable

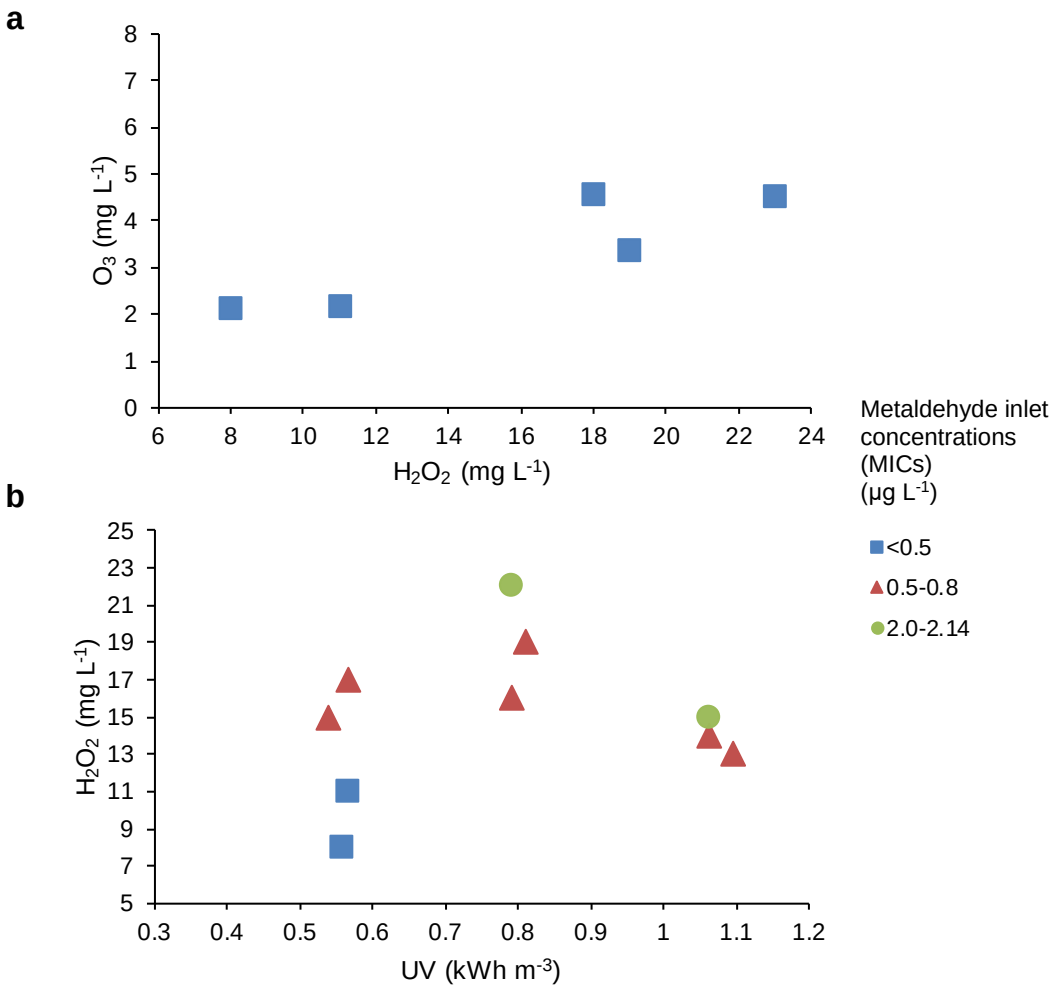

Figure 3 (a) Minimum O_3 concentration per H_2O_2 dose (O_3/H_2O_2) and (b) minimum H_2O_2 dose per UV energy demand (H_2O_2/UV) at <0.5 to 2.14 µg L^{-1} MICs based on benchmark concentration adopted from 0.1 µg L^{-1} PCV for individual pesticides (European Parliament, 1998) through the O_3/H_2O_2 + H_2O_2/UV process. Other conditions also achieved < 0.1 µg L^{-1} pesticide degradation, but required more chemical and are therefore excluded

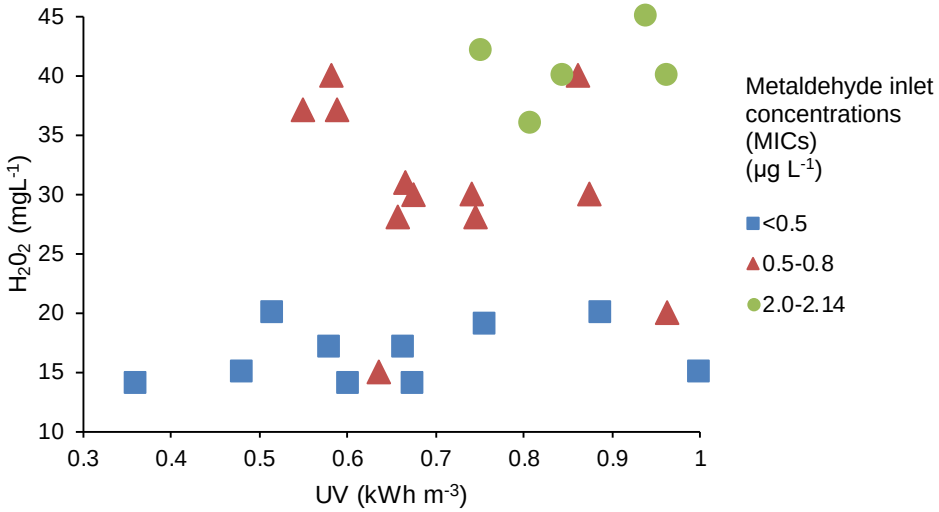

Figure 4 Minimum H_2O_2 dose per UV energy demand at <0.5-2.14 µg L^{-1} MICs based on benchmark concentration adopted from 0.1 µg L^{-1} PCV for individual pesticides (European Parliament, 1998) through the UV/H_2O_2 process Other conditions also achieved < 0.1 µg L^{-1} pesticide degradation, but required more H_2O_2 and are therefore excluded

2.3.4 Influence of TCMs on metaldehyde removal by UV/H_2O_2

The DistLM showed that turbidity contributed ~2% of the variability in metaldehyde removal within the stand-alone UV/H_2O_2 process (*P*=0.0186) when other parameters were already considered in the model (Appendix B). The lower influence, however, can be explained because turbidity was <0.2 NTU in all samples. Nevertheless, the transmittance of light including the penetration of UV photons into the water is reduced in turbid matrices (Melin, 2000; Yonar *et al*., 2006) negatively affecting UV system efficiency for the removal of compounds (Dotson *et al.*, 2010; Carra *et al.* 2016). Therefore, the bench-scale experiments assessed the impact of TCMs on metaldehyde removal by UV/H_2O_2. Kaolin clay and HA materials are typically found in surface water matrices (Wang and Hsieh, 2001; Templeton *et al*., 2007; Yang *et al*., 2016) and hence represent suitable test TCMs for experimentation. A strong inverse correlation (R^2=0.79) was identified between the turbidity caused by HA and metaldehyde removed by UV/H_2O_2 (Table 7).

Table 7 Summary of operating conditions and results of metaldehyde degradation bench-scale experiments applying UV/H_2O_2 process

TCM	Experimental conditions[a]	*k* value (NTU)	R^2
Humic acid	No treatment [b]	0.020	0.10
	10 µL H_2O_2 [b]	-0.045	0.04
	10 µL H_2O_2, 1800 mJ cm^{-2} UV fluence	0.103	0.79
Kaolin	No treatment [b]	0.009	0.11
	10 µL H_2O_2 [b]	-0.010	0.01
	10 µL H_2O_2, 1800 mJ cm^{-2} UV fluence	-0.018	0.17

[a] Initial metaldehyde concentration 2.03 µg L^{-1}; [b] Reaction volume 100 mL; The *k* value was calculated by division of the ratio C/C_0 (residual metaldehyde concentration divided by initial concentration) and the NTU values obtained for each sample. The coefficient of determination (R^2) was obtained by linear regression

Metaldehyde degradation kinetic by UV/H_2O_2 was significantly affected by the presence of HA (Figure 5) in line with other studies assessing the influence of organic matter on pollutant removals (Hollrigl-Rosta *et al.*, 2003; Carra *et al.* 2016). The greater HA concentration in the solution, hence the greater turbidity, the lower metaldehyde removal post AOP (Figure 5b). This was evidenced through analysis of the initial (2.03 µg L^{-1}) and residual metaldehyde concentrations, *e.g.* 41% and 89% metaldehyde removals at 4.71 and 0.68 NTU, respectively. Similarly, these outcomes suggested that greater UV irradiations would have been required to achieve similar >86% metaldehyde removals to those of <1 NTU (Figure 5b).

By contrast, the concentration of inorganic material did not interfere with metaldehyde removal. There was a poor correlation ($R^2 = 0.17$) between the amount of kaolin in water and the removal rate achieved which was 92% on average. Kaolin concentration did not interfere with the photolysis of metaldehyde (*k* = -0.018) with similar removals across the range of turbidity tested, *e.g.* equal

97% pesticide removals at 2.74 and 1.28 NTU. Therefore, a minimal effect of inorganic materials on UV-based AOP performance for metaldehyde removal can be inferred. The outcome of this experiment showed that kaolin does not have UV shielding effect as confirmed by others (Giri *et al*. 2010; Sen Kavurmaci and Bekbolet, 2014). Control 2 demonstrated the H_2O_2 negligible effect on metaldehyde removal (R^2=0.04 and R^2=0.01; Table 7). It can be equally assumed that H_2O_2 adsorbed a small fraction of the UV light irradiated, even using three-fold higher H_2O_2 concentration than the 0.29 mM H_2O_2 (~10 mg L^{-1}) dosed in some previous studies (*e.g.* Rosenfeldt *et al.*, 2006). The standard deviation of the metaldehyde residual (C/C_0) from the untreated samples revealed a 5% and 10% metaldehyde experimental error for kaolin and HA experiments, likely a pipetting error. Therefore, the greater metaldehyde concentration than the stock solution (2.03 µg L^{-1}, 0.09 NTU) found in some control samples, thus concentration ratios >1 theoretical top-end limit, could be explained (Figure 5). These findings, therefore, stressed the importance of (i) the type of TCM for the AOP performance and also (ii) the processes that remove DOC before a UV-based AOP treatment in organic-turbid waters, *e.g.* coagulation or activated carbon.

After assessing the efficiency of AOPs on the removal of metaldehyde, the generation of DBPFP was also evaluated. DBPs are considered to be a major limitation preventing the wide-scale application of AOPs. Therefore, this is discussed below.

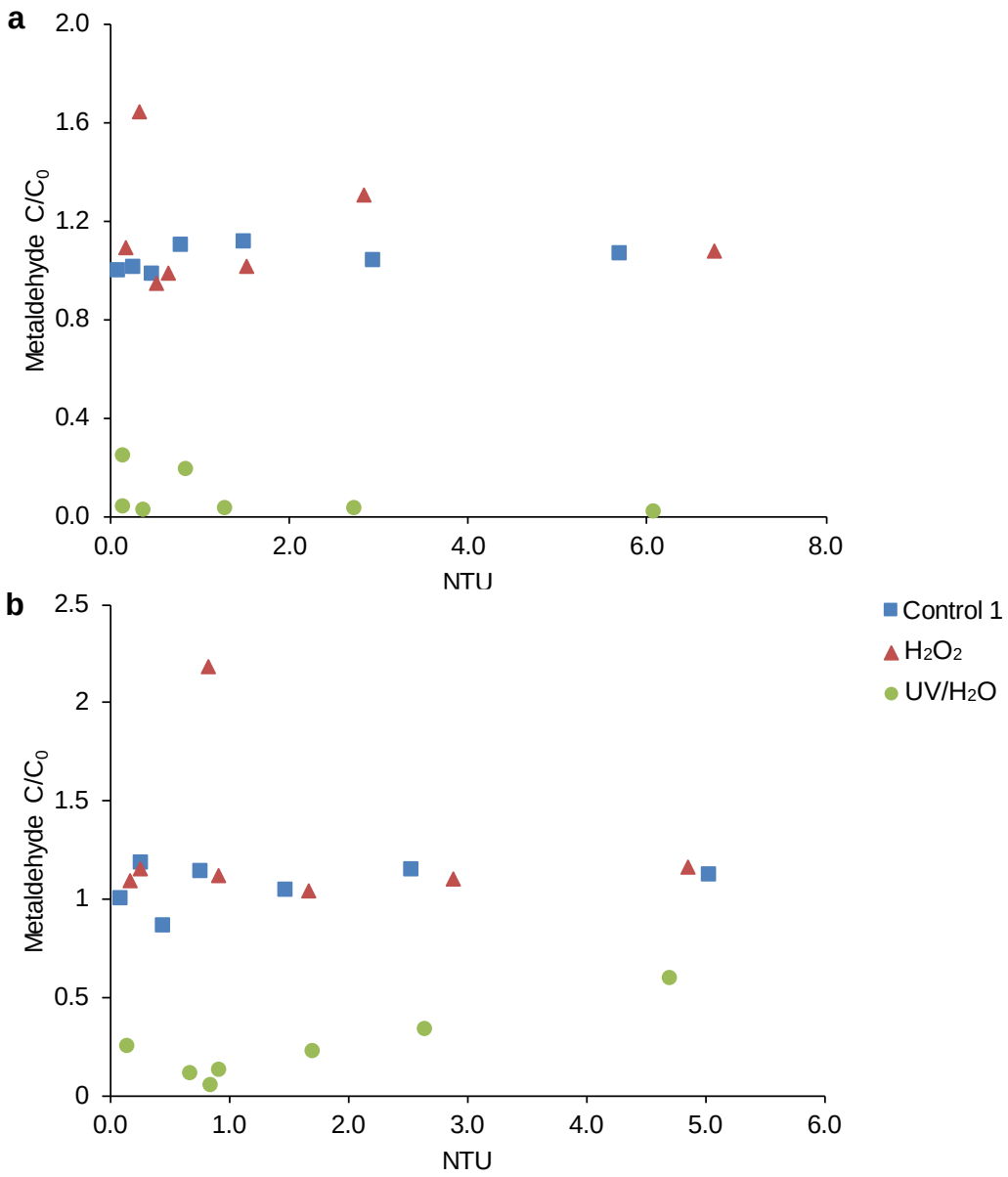

Figure 5 Normalized residual metaldehyde concentration profiles regarding control tests and UV/H_2O_2 full treatment in (a) kaolin-turbid UP water and (b) HA-turbid UP water at different concentrations of TCMs

2.3.5 Disinfection by-product formation potential (DBPFP) by ozone and UV-based advanced oxidation processes

Results of DBPFP after AOPs showed either production or reduction with respect to the DBPFP from the inlet water. Henceforth the difference between DBPs production/reduction after AOP and the DBPFP from the inlet is referred as net contribution. Inlet DBPFP results ranged 234-610 µg L^{-1} THMFP and 174-321

µg L^{-1} HAAFP. These results would theoretically be 47-121 µg L^{-1} THM_4 and 35-64 µg L^{-1} HAA_9 using a 0.199 conversion factor DBP:DBPFP (Hutton 1994 in Jefferson *et al*., 2016). Interestingly, the maximum inlet THMFP and HAAFP were found at one of the greatest metaldehyde spiking doses (2.14 µg L^{-1}), yet the lowest THMFP was at 2.04 µg L^{-1} metaldehyde inlet and similarly for the HAAFP at 2.11 µg L^{-1}. This suggested that metaldehyde concentration did not influence the formation of DBPs, but the water quality of samples, in terms of NOM, of the pilot-trial day (Figure 6). The DistLM also revealed the absence of UV fluences and reagent doses impacting on DBPFP (Appendix C). In the O_3/H_2O_2 + H_2O_2/UV, the H_2O_2 accounted for 14% (*P*=0.018) of the variability in net THMFP contribution, whilst for the O_3/H_2O_2 sub process, 11% (*P*=0.0375). The DistLM showed that H_2O_2 was not statistically significant (*P*>0.05) to explain the variability in net THMFP contribution under the UV/H_2O_2 treatment. Neither UV fluences nor O_3 influenced the variability in net THMFP contribution (*P*>0.05). Regarding HAAFP, the H_2O_2:O_3 ratio accounted for 37% (*P*=0.0018) of the variability in net HAAFP contribution through the O_3/H_2O_2 + H_2O_2/UV process whilst the UV explained 39% of the net HAAFP varaibility (*P*=0.0223) in the H_2O_2/UV sub process. Moreover, analogous operating conditions were applied and only metaldehyde spiking solution and water quality were dissimilar throughout the experimental plan. The water quality influence on DBPFP can also be seen in Table 8 and Appendix C. Under similar operating conditions (H_2O_2 and E_D), the UV*/*H_2O_2 achieved a net DBPFP reduction on day 2, whilst increased DBPFP on day 4. The results of this study suggested that such DBPFP can be ameliorated by removing DBPs precursors upstream an advanced oxidation process. A limitation of this study is the low number of inlet samples collected, 10 in total. Therefore, DistLM results need to be interpreted with caution.

O_3/H_2O_2 sub process contributed the lowest to the DBPFP after an AOP treatment with maximum 549 µg L^{-1} THMFP and 245 µg L^{-1} HAAFP. Either the stand-alone UV*/*H_2O_2, the O_3/H_2O_2 + H_2O_2/UV and the H_2O_2/UV sub process overcame 600 µg L^{-1} THMFP top end (638 µg L^{-1}; 616 µg L^{-1}, 616 µg L^{-1}, respectively) and 300 µg L^{-1} HAAFP top end (305 µg L^{-1}; 316 µg L^{-1}, 316 µg L^{-1} respectively). However, the net contribution of UV*/*H_2O_2 and O_3/H_2O_2 + H_2O_2/UV

varied in the range -283 µg L^{-1}, hence reducing the production, to +255 µg L^{-1} THMFP and -164 µg L^{-1} to +131 µg L^{-1} HAAFP. It was found a similar HAAFP maximum net reduction in all the AOPs and sub processes (~ -160 µg L^{-1}), but the lowest maximum net production was given by O_3/H_2O_2 sub process (+22 µg L^{-1}). The peroxone sub stage also achieved the THMFP maximum net reduction (-283 µg L^{-1}), yet attained the maximum net production (+269 µg L^{-1}). Nevertheless, these THMFP boundaries were obtained in a pilot-trial day (day 3) in which an ozone gas leak was reported. Therefore, the results should be approached with some caution due to power outages during clean-up (Figure 6). Over 39 total THMFP samples analysed within this sub process, the maximum net both THMFP reduction and production were -101 µg L^{-1} and +51 µg L^{-1}, respectively, if these extreme values are excluded. Surprisingly, the HAAFP data behaved in the same way as did it on other days of testing (Figure 6b). Even with the offset exclusions, the O_3/H_2O_2 sub-process typically formed less THMs than both UV-based pilots. This was confirmed when the net contribution of the UV and peroxone sub processes on DBPFP was assessed (Figure 7). Whilst O_3/H_2O_2 mostly attained a net DBPFP reduction, H_2O_2/UV enhanced the production. A likely reason can rely on Dotson's *et al*. (2010) conclusions highlighting the strong correlation between THMFP and •OH exposure. It was before discussed that the O_3/H_2O_2 removed the majority of the metaldehyde and •OH production was limited to O_3 dose (up to 10 mg L^{-1}), therefore hydroxyl radical scavenging by NOM could be constrained. However, the lower metaldehyde to remove on the subsequent H_2O_2/UV sub treatment might enable greater •OH to interact with NOM, thus increasing DBPFP.

In both global treatments, a positive correlation between THMFP and HAAFP was also found: the greater production of THM or HAA involved greater production of the other and conversely. Some of the DBPFP results showed clear differences between duplicates under the same treatment. If there was variability of greater than 15% between duplicates, then, the DBPFP analysis was repeated on them. The persistence of the difference involved the exclusion of the data (Figure 6b and Table 8).

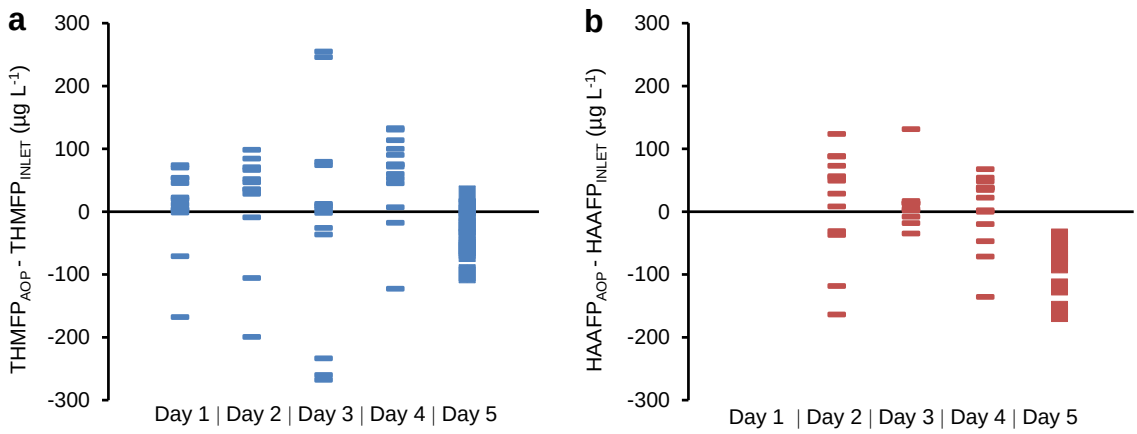

Figure 6 Net contribution of the stand-alone UV/ H_2O_2, and the O_3/ H_2O_2+ H_2O_2/UV on (a) THMFP (*n* = 66) and (b) HAAFP (*n* = 48) based on the day of pilot-scale work

Under optimum oxidant doses and E_D operating conditions for metaldehyde-compliant water production, a wide range of net DBPFP results were found (Table 8). However, potential THMs formed by an AOP would be <100 µg L^{-1} regulatory limit (European Parliament, 1998; DWI, 2000) when applied the Hutton's (1994) theoretical conversion factor to THMFP. Therefore, the effectiveness of both AOPs to comply the legislation in terms of metaldehyde as well as on THMs was demonstrated. The GAC contactor limited to a maximum 246 µg L^{-1} THMFP (49 µg L^{-1} THM) and 78 µg L^{-1} HAAFP (16 µg L^{-1} HAA).

Table 8 Net contribution of the AOPs on THMFP and HAAFP using minimum oxidant doses per UV (E_D) for metaldehyde-compliant water production at different metaldehyde (M) spiking doses

Treatment	Day	$[M]_0$[1]	$[H_2O_2]$[2]	$[O_3]$[2]	E_D[3]	THMFP[1]	HAAFP[1]
O_3/H_2O_2 + H_2O_2/UV	2	0.5-0.8	16	10.8	0.79	98	88
	3	2.0-2.14	22	7.2	0.79	-37	2
UV/H_2O_2	1	<0.5	20	N/A	0.52	45	N/D
			19		0.76	12	N/D
	2	0.5-0.8	28		0.75	-200	-164
	4		30		0.74	133	38
	3	2.0-2.14	42		0.75	-234	14

N/A: not applicable; N/D: no data; [1](µg L^{-1}); [2](mg L^{-1}); [3](kWh m^{-3})

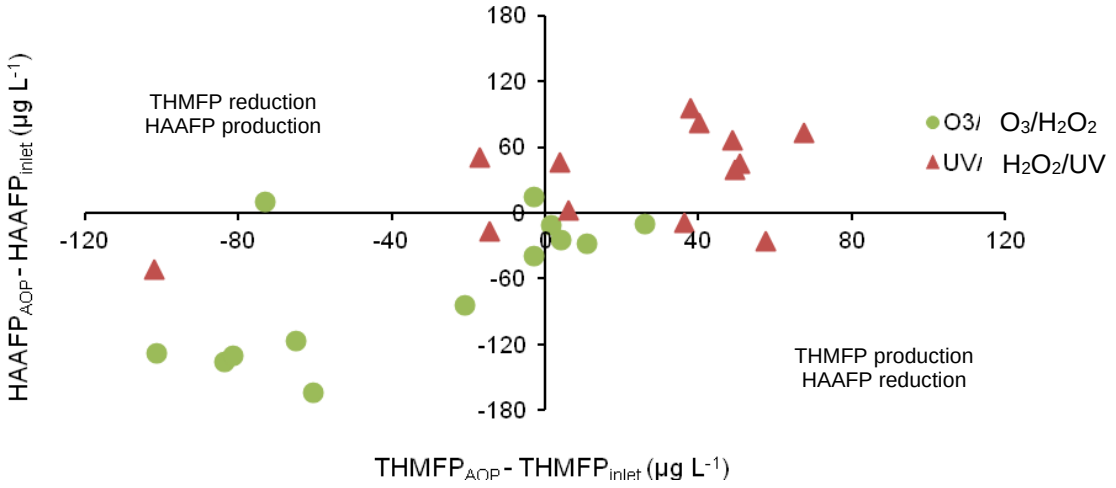

Figure 7 Net contribution of the O_3/H_2O_2 and H_2O_2/UV sub treatments on DBPFP

2.4 Conclusions

This study evaluated the removal of metaldehyde attributed to UV/H_2O_2, and O_3/H_2O_2 + H_2O_2/UV fed with the same post RGF water quality to comply the European Directive 98/83/EC for individual pesticides. Also, it addressed the changes in DBPFP due to both AOPs. UV/H_2O_2 degraded 38-98% pesticide whilst O_3/H_2O_2 + H_2O_2/UV 55%-97%. Within the two-stage process, the O_3/H_2O_2 removed 38%-96% compared to the 79% highest metaldehyde removal of H_2O_2/UV. The stand-alone UV-based AOP unit showed more significant removal by increasing flow rate, H_2O_2 dose and E_D up to 3.5 m^3 h, 30 mg L^{-1} and 0.85 kWh m^{-3}, respectively. UV/H_2O_2 process was also found to be negatively affected by HA-turbid waters over 1.0 NTU. O_3/H_2O_2 + H_2O_2/UV metaldehyde removal effectiveness was enhanced by (i) dosing more O_3 and H_2O_2, but maintaining the same ratio and by (ii) raising UV fluences. Ozone was a limiting factor on the success of O_3/H_2O_2 + H_2O_2/UV as it defined the H_2O_2 available for •OH production on the H_2O_2/UV sub treatment. The minimum E_D to fulfil metaldehyde PCV was <0.6 kWh m^{-3} for <0.8 µg L^{-1} metaldehyde inlets and close to 0.8 kWh m^{-3} for inlets between 2.0 and 2.14 µg L^{-1}. None of the operating conditions tested achieved <0.1 µg L^{-1} metaldehyde residual at 2.2 µg L^{-1} metaldehyde spiking dose. Similarly, the peroxone sub process provided with metaldehyde-compliant water only at MIC of 0.14 µg L^{-1}. The net contribution of the advanced oxidation

technologies on DBPFP was likely related to the NOM characteristics in the inlet water on each the day of the pilot-trial. The peroxone sub process contributed the lowest to the DBPFP in absolute terms. Equally, in net terms, O_3/H_2O_2 slightly increased by 22 µg L^{-1} HAAFP and 51 µg L^{-1} THMFP at most, significantly below to that of the rest of the processes. There was a positive trend between THMFP and HAAFP either decreasing or increasing commensurately. Among the optimum operating conditions that successfully achieved the 0.1 µg L^{-1} metaldehyde target, THMs were in all cases below 100 µg L^{-1} PCV. The virgin GAC contactor additionally assisted the AOPs limiting both metaldehyde residual and DBPFP. It is likely however that an acclimated GAC would not be as effective as the virgin media used in this study All these results evidenced the efficacy of AOPs to assist water companies on recalcitrant pollutant degradation in drinking water.

Once evaluated UV/H_2O_2, and O_3/H_2O_2 + H_2O_2/UV efficiency on the removal of metaldehyde and control of DBPs, a cost evaluation was undertaken for decision making on the most appropriate AOP to implement using a full-scale case study with scenario analysis to project future costs.

2.5 Acknowledgments

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3 ECONOMIC EVALUATION OF UV/H_2O_2, O_3/H_2O_2, AND O_3/H_2O_2 + H_2O_2/UV PROCESSES THROUGH A WHOLE-LIFE COSTING ANALYSIS FOR FULL-SCALE APPLICATION

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Abstract

Metaldehyde is a pesticide which is poorly removed by conventional water treatments. UK water utilities consequently have plans to upscale AOP pilot-scale trials from commercial technologies aiming at metaldehyde removal due to its demonstrated effectiveness and technical feasibility. However, the high economic cost of real-scale implementation is still a matter of controversy. For decision making, this research presents a site-specific Whole-Life Costing Analysis (WLCA), comparing three AOP systems: O_3/H_2O_2 + H_2O_2/UV, O_3/H_2O_2 and UV/H_2O_2 to estimate their TOtal EXpenditures (TOTEX) for 5 months annually treatment within 25-year operational life. In doing so, it was possible to determine which technology was most viable for implementation. The costs were calculated for 25 MLD capacity treatment plant based upon the results of 0.72-log metaldehyde degradation from a treatability pilot-scale research. The AOP asset costs in terms of capital (CAPEX) and operation (OPEX) were covered while achieving the performance necessities, <0.1 μg L^{-1} metaldehyde residual. A sensitivity analysis to reflect variability in TOTEX from the price inflation and deflation of energy, hydrogen peroxide and liquid oxygen was also conducted. The cost assessment showed that the benchmark commercial O_3/H_2O_2 unit outperformed H_2O_2/UV owing to the operating costs related to energy demand (E_D), 84% cheaper. The O_3/H_2O_2 offered a unit cost of £0.07 m^{-3} water treated compared to £0.1 m^{-3} and £0.13 m^{-3} of UV/H_2O_2 and O_3/H_2O_2 + H_2O_2/UV, respectively. The O_3/H_2O_2 process was the most cost-effective treatment for metaldehyde removal and was the lowest sensitive to reagent and energy price changes.

Keywords: advanced oxidation process, metaldehyde, peroxone, pesticide

3.1 Introduction

Metaldehyde often reaches ten times greater concentrations than the European Directive 98/83/EC regulatory levels (0.1 μ L^{-1}) (Marshall, 2013; Castle *et al.* 2017) evidencing poor removal efficiency of the existing methods, *e.g.* granular activated carbon (GAC) (Autin *et al.*, 2012; Tang *et al*., 2016). The water industry, therefore, has resorted to different approaches to fulfil drinking water (DW) standards for metaldehyde. A popular initiative followed by a number of UK water suppliers, *e.g.* Severn Trent, Southern Water, Anglian Water, Affinity Water and Thames Water, involves stakeholder engagement in the upstream catchment areas of their rivers. Within this action plan, Southern Water provides with financial incentives (£1 kg^{-1}) for metaldehyde substitution aiming to widespread the use of ferric phosphate (Castle *et al.* 2017). However, the complex nature of catchment dynamics, the variable and limited removal efficiency, up to 60% (Castle *et al.* 2017) and the challenges associated to community commitment to undertake these practices, outside the remit of the water companies, lead to further invest in water treatment processes. Affinity Water, for instance, applied Powdered Activated Carbon (PAC) to diminish metaldehyde levels below the maximum allowable limit (Nabeerasool *et al*., 2015) Yet a major limitation of PAC is disposal costs. Another proposed option is that of the advanced oxidation processes (AOPs) (Autin *et al.*, 2012; James, Germain and Judd, 2014; Jefferson *et al.*, 2016). This modern 'end-of-pipe' technology achieved up to 97% metaldehyde removal (Semitsoglou-Tsiapou *et al.*, 2016). However, AOPs present high capital and operational costs, due to consumables and E_D impacting decision making on a wider implementation (Autin *et al.*, 2012). Anglian Water reported a £17 million $year^{-1}$ estimate to operate UV/H_2O_2+GAC system across their 27,500 km^2 supply region (Castle *et al.* 2017).

UV and ozone-based AOPs are the most frequently technologies used at full-scale due to their lower energy consumption than other AOPs (Collins and Bolton, 2016). This finding was previously highlighted after comparing the E_D required for organic constituents' removal in non-alkaline water using UV/H_2O_2 (5.45 kWh m^{-}

^{3}) and UV/TiO_2 (6.4 kWh m^{-3}) (Autin *et al.*, 2013b). Between the commonly used UV and ozone-based AOP alternatives at industrial scale, the O_3/H_2O_2 process was generally less energy intensive to form hydroxyl radicals (•OH) than UV/H_2O_2 in several water bodies (Rosenfeldt *et al.*, 2006). Tang *et al*. (2016) also reported 33% lower energy demanded by O_3/H_2O_2 than UV/H_2O_2 to degrade metaldehyde by 72%. By contrast, 0.54:1.05 kWh ratio (UV/H_2O_2:O_3/H_2O_2) was required to generate a mole of •OH under optimum conditions (Bolton and Cater, 1994). Nevertheless, the authors stated the UV process more energy consumptive than the O_3 process in waters with high UV absorbance. Other researchers also agreed with the greater electrical energy efficiency of O_3-based processes than the UV-based processes for organics mineralization (Crittenden *et al.*, 2012; Gassie and Englehardt, 2017).

The total costs* for degrading any pollutant from water relies on its particular physical and chemical characteristics (Nabeerasool *et al*., 2015). The UV/H_2O_2 treatment cost for different contaminant concentrations were: £0.12-0.58 m^{-3} (0.1 mg L^{-1}) £0.40-0.89 m^{-3} (1 mg L^{-1}) and £0.44-1.33 m^{-3} (10 mg L^{-1}) (Chemviron, 1997). Similarly, total costs were estimated at £1.78 m^{-3} for the treatment of 0.2 mg L^{-1} trichloroethylene-contaminated groundwater using UV/H_2O_2 (Hirvonen *et al.*, 1998). Recently, the UV/H_2O_2 process costed £0.24 m^{-3} using synthetic water with 50 mg L^{-1} of H_2O_2 and a spiked solution of five different micropollutants at 0.1 mg L^{-1} each (Miralles-Cuevas *et al.*, 2017). UV/H_2O_2/O_3 was found the cheapest option per gram of degraded phenol (£0.79 g^{-1}), in model wastewater, against £2.42 g^{-1} of the UV/H_2O_2 process (Kusic, Koprivanac and Bozic, 2006). Three-fold greater costs were also found in the UV/H_2O_2 treatment than that of O_3/H_2O_2, £2.58 m^{-3} and £0.90 m^{-3} respectively, treating MTBE-contaminated groundwater from 100 mg L^{-1} initial concentration and achieving 0.01 mg L^{-1} final concentration (Safarzadeh-Amiri, 2001). However, very few publications have appraised the costs incurred on UV-based AOPs for metaldehyde removal (Autin *et al.*, 2013c; James, Germain and Judd, 2014; Rolph, 2016). And, besides that,

* Prices herein presented were £ transformed from their original currencies by using location factors (LF). In section 3.2 the LF approach is explained

non-existent research is available on the costing of peroxone-based AOP processes for the same purposes. Therefore, an economic-assessment comparison of different AOPs (UV/H_2O_2, O_3/H_2O_2, and O_3/H_2O_2 + H_2O_2/UV) for addressing metaldehyde with the same water quality needs to be conducted to identify the most economically attractive option for real-scale implementation based on reliable data.

The reliability of AOPs to remove metaldehyde could be appealing for water suppliers, despite their reported high capital and annual operation and maintenance costs (James, Germain and Judd, 2014; Collins and Bolton, 2016). The partial treatment of AOPs throughout yearly cycle can also be coupled with other initiatives, *e.g.* catchment management, to reduce costs. Moreover, legal mechanisms are outlined in the Asset Management Plan 6 period to reduce metaldehyde levels in DW in the UK.

The objective of this study was, therefore, to present a practical and viable life cycle cost comparison between conventional AOPs. A detailed analysis on OPEX and CAPEX of each technology is displayed, as well as a sensitivity analysis of the most economically viable alternatives (UV/H_2O_2, and O_3/H_2O_2).

3.2 Cost estimation methodology

The methodology developed to arrive at the costs of a full-scale UV/H_2O_2, and O_3/H_2O_2 + H_2O_2/UV process mainly relied on the acquisition of a dataset from either operators, suppliers or research. The dataset was then updated using Location Factors (LF) (Table 9). LF relate costs of similar plants in two different places considering the currency exchange and time. It also captures other costs such as local labour, transport, local tariffs or other import duties, local construction and fabrication infrastructure (Gerrard, 2000; Towler and Sinnott, 2012). Table 9 only includes LF from few countries/world regions. Therefore, some assumptions were adopted when updating the prices:

1. The LF is chosen according to the country/area in which the research was primarily undertaken (correspondence address)

2. When such country is not outlined in Table 9, the LF of a listed country with similar economic/cultural situation in 2017 was chosen, *e.g.* Italy and Spain
3. The year of the research publication is used as baseline to update the LF by dividing the ratio 'local currency in 2003/$USA2003' and multiplying by the ratio 'GBP2017/$USA2017' (Towler and Sinnott, 2012)
4. Annual average exchange rates were taken from The Organisation for Economic Co-operation and Development (OECD) (2017)

All the cost-related assumptions are shown in Table 10. AOPs installation depend upon the water matrix being treated (Rosenfeldt *et al*., 2006). Therefore, a site-specific WLCA for Draycote sized WTW was undertaken. This WTW supplies 25 MLD (1,042 m^3 h^{-1}) and a five-months uninterrupted running was assumed for providing with metaldehyde <0.1 μg L^{-1} regulatory limit (European Parliament, 1998).

Under the array of metaldehyde inlet concentrations applied in the pilot-trial, a worst-case 0.53 μg L^{-1} pesticide level was selected for the AOP facility design. Metaldehyde is within the usual 0.4–0.6 μg L^{-1} range in surface waters (Kay and Grayson, 2014; Semitsoglou-Tsiapou *et al*., 2016). In order to provide with a safety factor to the WLCA, the electrical energy per order (E_{EO}) value, the H_2O_2 and O_3 demands corresponded to metaldehyde results <0.1 μg L^{-1} (0.075 μg L^{-1}) from the pilot-trial data.

The O_3/H_2O_2 sub process is also assessed as stand-alone unit. Because none of the conditions tested for such 0.53 μg L^{-1} initial concentration attained the European Union's statutory DW standard in Chapter 1, the O_3 concentration reported by Anglian Water to achieve 0.7-log reduction of metaldehyde was considered (Collins and Bolton, 2016). However, the authors did not mention H_2O_2 concentration, hence a H_2O_2:O_3 ratio of 0.7 was assumed. This decision was based upon the stoichiometric mass ratio for $^{\bullet}OH$ production (34 g mol^{-1} H_2O_2/ 48 g mol^{-1} O_3) according to (3-1) (Lucas, Peres and Li Puma, 2010). Moreover, a 0.5-1 H_2O_2:O_3 optimal range to remove compounds has been stated

(Ijpelaar *et al.*, 2002) and was previously observed on tetrachloroethylene destruction (Glaze *et al*., 1987).

$$O_3 + H_2O_2 \rightarrow {}^{\bullet}OH + HO_2{}^{\bullet} + O_2 \qquad (3\text{-}1)$$

As suggested by Ofwat (2013), the WLCA was calculated for 25-year asset life and based on (3-2) to minimise the bias towards CAPEX and to drive benefits for customers.

$$\text{TOTEX} = \text{CAPEX} + \text{NPV} \cdot \text{OPEX (NPV factor} = 14) \qquad (3\text{-}2)$$

Table 9 Location Factors of different countries relative to USA Gulf Coast for prices update based on 2003 data (Towler and Sinnott, 2012)

United States	Gulf Coast	1.00
	East Coast	1.04
	West Coast	1.07
	Midwest	1.02
Canada	Ontario	1.00
	Fort McMurray	1.60
Mexico		1.03
Brazil		1.14
China	imported	1.12
	indigenous	0.61
Japan		1.26
SE Asia		1.12
Australia		1.21
India		1.02
Middle East		1.07
France		1.13
Germany		1.11
Italy		1.14
Netherlands		1.19
Russia		1.53
United Kingdom		1.02

3.2.1 Procedure for OPerating Expenses (OPEX) calculation

Estimated oxidant usage (H_2O_2, O_3) costs, energy and equipment replacement costs, including the GAC media, accounted for the operational cost incurring on an annual basis in this evaluation. Other life-cycle costs, *e.g.* labour, chemical

delivery, analytical costs, DBPFP or site constraints (Collins and Bolton, 2016) were excluded.

3.2.1.1 Chemical costs

The two main consumables involved in the AOPs investigated were H_2O_2 and O_3. All calculations are based on oxidants dose is constant, assuming the reactor reaches steady-state operation. Therefore, the demand is only a function of the flow rate (1,042 $m^3\ h^{-1}$).

H_2O_2 35 wt. % commercial strength (20-40%) (American Water Works Association, 2005) was considered. The concentrations that successfully performed to achieve <0.1 µg L^{-1} in this study (Table 11) were multiplied by the flow rate at Draycote, adjusted by the oxidant purity, to estimate the volume.

Ozone production is carried out with on-site generators (American Water Works Association, 2005) owing to its short half-life (Melin, 2000). This fact involves costing the feeding source, liquid oxygen (LOX) herein. O_3 is a gas, hence the solubility of O_3 (0.34 mg L^{-1} in H_2O_2 per 1 mg L^{-1} of gas, 20ºC) (Stumm, 1958 in Roth and Sullivan, 1981) was used to determine the actual concentration required in the ozone generator. Select LOX over air was built upon a number of reasons. Energy requirements using dried compressed air for O_3 generation was quantified as 15 kWh kg^{-1} O_3 produced (Katsoyiannis *et al*. 2011) and 18-26 kWh kg^{-1} (Rosenfeldt *et al*., 2006; Wu and Englehardt; 2015). However, energy needs applying high purity oxygen fed system such as LOX are substantially lower (5-8 kWh kg^{-1}) (American Water Works Association, 2005; Smith, 2011). Furthermore, LOX is typically used since 1995 (Rakness, 2011). And besides, the use of an air fed generator requires dehumidification, which may be cost prohibitive in comparison to LOX (Melin, 2000). Finally, processing LOX by modern medium-frequency generators enables 8 to 12% by weight O_3 concentration production versus 1.5-2% using air (Kawamura, 2000). Therefore, 7 kWh kg^{-1} mid-way point for O_3 production was considered. A commercial ozone generator system producing at 1 $m^3\ h^{-1}$ (10 wt. % ozone in oxygen) (supplier data) was selected. Such percentage weight entailed ten-fold amount of LOX to produce the daily required amount of O_3. Moreover, O_3 production by high-voltage altering current

(6 to 20 kV) (Kawamura, 2000), 5.5 kV in the pilot trial, added to LOX chemical costs 4,118 kW day^{-1} (O_3/H_2O_2 + H_2O_2/UV) and 5,147 kW day^{-1} (O_3/H_2O_2).

3.2.1.2 Electrical efficiency per order of contaminant destruction

For UV systems, a measure of operating cost and accurate scale up system is the E_{EO} (Bolton *et al*., 2001; James, Germain and Judd, 2014). The E_{EO} is the energy (kWh) consumed to reduce an initial concentration of contaminant by one order of magnitude in a unit volume. By this way, the comparison of the efficiency between processes can be undertaken on the basis of the electrical use per amount of compound reduction. The E_{EO} is defined for flow-through reactors (3-3) (Collins and Bolton, 2016) as:

$$E_{EO} = \frac{P}{\dot{V} \log\left({C_i}/{C_f}\right)} \quad (3\text{-}3)$$

Where P is the electrical power (kW), $\dot{V}$ is the flow rate (m^3 h^{-1}), and C_i and C_f are the initial and final concentrations of a targeted pollutant. Given the E_{EO}, the power requirements were calculated for the processes (Table 11) and, thus the annual energy costs.

3.2.1.3 High-cost components replacement

For the three AOP case study, 58,915 kg year^{-1} GAC media needed to be regenerated off-site (EPA, 2014) assuming 10% loss of GAC per regeneration (James, Germain and Judd, 2014). With regards UV-based AOPs, lamp replacement was calculated according to (3-4). In the case of the peroxone AOP replacements, 1.5% of the O_3 generator and contactor capital cost was assumed (Melin, 2000; Mahamuni and Adewuyi, 2010).

$$\text{Replacement cost yr}^{-1} = \frac{24\ \text{h} \cdot 30\ \text{d} \cdot 5\ \text{months}}{9000\ \text{h (lifetime)}} \cdot \text{nº lamps} \cdot £300\ \text{lamp}^{-1} \quad (3\text{-}4)$$

Table 10 Assumptions for OPEX and CAPEX costing analysis from treatability studies and supplier information

Component	Cost	Reference	Country	LF-updated costs
H_2O_2 prices	\$0.295 L^{-1}	Ince and Apikyan (2000)	Turkey	£0.3 kg^{-1}
	\$0.51 kg^{-1}	Solmaz *et al*. (2009)	Turkey	
	€0.39 kg^{-1}	Rueda-Márquez *et al*. (2010)	Spain	
	€0.24 kg^{-1}	Lucas, Peres and Puma (2010)	Portugal	
	€0.55 kg^{-1}	Yalili, Yonar and Kestioğlu (2013)	Turkey	
	£270 m^{-3}	Autin *et al*. (2013b)	UK	
	€0.73 L^{-1}	Cédat *et al*. (2016) from Solvay S.A.	France	
Cost H_2O_2 tank	Large tank cost curve for preliminary estimates	Gerrard (2000)	UK	N/A
Electricity price	£0.1 kWh^{-1}	Energy EU (2017)	UK	£0.1 kWh^{-1}
GAC off-site regeneration	£0.31-0.44 kg^{-1}, assuming 5-10% loss of GAC per regeneration	James, Germain and Judd (2014)	UK	£0.51 kg^{-1}
UV reactor	£900,000 $unit^{-1}$	Supplier	UK	£900,000 $unit^{-1}$
Number of lamps per UV reactor	192 bulbs	Supplier	UK	192 bulbs
Power per lamp	1.00 kW	Supplier	UK	1.00 kW
Lamp price	£223 $lamp^{-1}$ (9,000h lifetime) LP-HO	James (2013)	UK	£300 $lamp^{-1}$
LOX price	\$0.04 lb^{-1}	Kawamura (2000)	USA	£0.07 kg^{-1}
Ozone generation unit (\$)	$31{,}015x^{0.6475}$; x=O_3 generation capacity (Lb d^{-1}, min. 10, max. 3,500). Including: LOX tanks, vaporizer and regulators, piping, valves, flow meters, filters and the O_3 generators	McGivney and Kawamura (2008)	USA	N/A
Ozone contact chamber (per unit) (\$)	$89.217x^{0.6442}$; x= Chamber volume (GAL; min. 1,060, max. 423,000). Including: piping, valves, diffusers and, air handling system, which collects and delivers the residual ozone to the destruct unit			

N/A: not applicable

3.2.2 Procedure for CAPital EXpenditures (CAPEX) calculation

The total plant cost was estimated by breaking down the total capital employed into different categories of expenditure. All these clusters are percentage-related to the total delivered cost of the main plant items (MPI) purchased for fluid-processing plants (Gerrard, 2000). However, Gerrard's (2000) percentages were adapted for an AOP facility (Melin, 2000; Mahamuni and Adewuyi, 2010).

Direct costs included controls and instrumentation (18% MPI cost), piping, valves and electrical (30% MPI cost), and buildings, including services, (18% MPI cost). The purchase of land, nor yard improvements were accounted. The sum of these categories provides the total direct plant cost (Gerrard, 2000). Indirect costs comprised engineering and supervision (33% MPI cost), construction expenses (41% MPI cost), the contractor's fee (21% MPI cost), contingency (20% MPI cost) and working capital (86% MPI cost). The total capital employed was obtained by adding the indirect costs to the total direct plant costs.

3.2.2.1 Main plant items cost (MPIC)

From the manufacturer quotations with regards the number of lamps per UV reactor and their power (Table 10), the number of such standard commercial equipment to cover the electrical power demand was obtained (Table 11). Therefore, the number of lamps required was divided by the number of lamps per UV unit. The cost of the UV equipment and the lamps was then calculated by multiplying the requirements by their LF-updated prices (Table 10). UV commercial unit is equipped with low-pressure high-output (LPHO) lamps. This type of Hg discharge lamps is usual in AOTs (Collins and Bolton, 2016) which better facilitate $^{\bullet}OH$ formation in H_2O_2 presence and are electrically more efficient than medium pressure lamps (Melin, 2000; Lekkerkerker-Teunissen *et al*., 2013), which gave the formation of genotoxic activity (Lekkerkerker-Teunissen *et al*., 2013). However, LPHO lamps produce lower UV output per unit (1 kW) than medium pressure lamps (Melin, 2000; Van der Meer, van Lierop and LIT, 2015).

In the case of the ozone system, the ozone generation equipment and contactor accounted for the MPIC. Both costs were calculated using empirical formulae

(Table 10) (McGivney and Kawamura, 2008). The contact chamber equation requires the volume of ozone required, thus 2.0 kg m^{-3} O_3 density (20ºC, 1 atm) was utilised (Kawamura, 2000). The international units were subsequently transformed to those indicated by the authors. Two contact units were considered for system maintenance and redundancy (McGivney and Kawamura, 2008) as well as two O_3 generators operating at 75% of rated capacity (Kawamura, 2000).

When O_3 is diffused across the water, some gas inevitable reaches the top of the contact tank. Consequently, the O_3/H_2O_2 process requires of O_3 destructors to avoid the release of the residual gas to the atmosphere. Similarly, large amount of heat is generated when producing O_3 , so there is the nedd of a cooling system. The destructor and the cooling system, however, were not scoped in the WLCA due to lack of information, yet they have an energy-cost impact to consider within the O_3/H_2O_2 process.

For the hydrogen peroxide tank cost, a nomographical approach was followed (Gerrard, 2000). On the basis of the oxidant volume monthly required (Maher, personal communication, 2017), 15% headspace was added for gas expansion. A maximum 25 m^3 (up to 30 m^3) (Cefic, 2001) tank was considered. Therefore, if excess volume resulted in the calculations, this was divided by the minimum number of tanks covering the demand: 3 × 25 m^3 (65 m^3) (UV/H_2O_2), 2 × 20 m^3 (35 m^3) (O_3/H_2O_2 + H_2O_2/UV) and 1 × 15 m^3 (O_3/H_2O_2).

GAC capital costs were modelled using EPA (2014) upon the basis on GAC working as secondary filter, as it did in the pilot-trial. Therefore, 14-days interval between backwashes and recycling option for the spent backwashes was assumed (Kaur, personal communication, 2017). The input parameters were the design type (pressure), in parallel operation, 15 minutes theoretical empty bed contact time and regeneration off-site. These assumptions were founded on a similar AOP-based WTW cost exercise (Collins and Bolton, 2016). The design flow was input at MGD (6.604). H_2O_2 did not seem to affect GAC quenching performance neither in batch test nor after years of use at full-scale (Li, Zamyadi and Hofmann, 2016). However, Li, Zamyadi and Hofmann (2016) also reported fouling effects of natural organic matter (NOM) on GAC reducing its performance.

Therefore, carbon life span of 2 years was considered. Moreover, this assumption can be supported by the GAC-buffering contribution to minimise DBPs after AOPs, as concluded in Chapter 1. GAC capital cost included the GAC contactors, tanks, valves, pumps and instrumentation (propellers, alarms, pH meters, turbidity meters, temperature meters, carbon steel sampling port and head loss sensors), and initial GAC media charge (52,603 kg) (EPA, 2014). Other components such as the H_2O_2 injection system, supply and discharge pumps, and mixers were excluded since (i) these assets either make up a small component of the MPIC and/or (ii) the same assumption was made for the three AOPs. However, as in any WLCA, the quality of the cost estimate is the product of the input data quality and the approach taken.

3.3 Results and discussion

According to the pilot plant conditions studied, a benchmarking between the CAPEX, OPEX and TOtal EXpenditures (TOTEX) of each potential AOP treatment plant and the cost per cubic meter annually treated was calculated (Table 11 and Table 12). Over the 25-year project lifetime, the total cost (TOTEX) of the two-stage AOP was £30,406,141; considerably 41.5% (UV/H_2O_2) and 49.7% (O_3/H_2O_2) higher than that of the separated sub processes due to both capital and operational expenditures. Nevertheless, UV lamp replacement (£58,849) and ozone equipment replacement (£38,007) were cheaper in the O_3/H_2O_2 + H_2O_2/UV treatment. These two OPEX savings were attributed to lower UV power required than for UV/H_2O_2, hence fewer lamps to be replaced with time (Table 12), and lower O_3 doses than that of O_3/H_2O_2 (Table 11). For the UV/H_2O_2 process, Cédat *et al.* (2016) reported similar 0.155 € m^{-3} (£0.12 m^{-3} using LF) the total OPEX and 0.059 € m^{-3} (£0.047 m^{-3} using LF) the electricity costs, removing 80% estrogenic hormones at 30 mg L^{-1} H_2O_2 and 563 mJ cm^{-2} UV fluences.

Annual GAC regeneration for the three technologies was equally estimated at £33,051 as the same design flow is treated. The E_{EO} for the UV/H_2O_2 was lower than that of the O_3/H_2O_2 + H_2O_2/UV (Table 11). This indicated UV/H_2O_2 higher energy efficiency as greater levels of pesticide destruction resulted with less energy input. However, the H_2O_2/UV sub process only required 0.32-log

reduction to achieve <0.1 μg L^{-1} (0.72-log reduction for UV/H_2O_2). This was because 60% pesticide was previously removed by O_3/H_2O_2. This result explained the greater electrical power, thus E_D (kWh m^{-3}), of the stand-alone UV/H_2O_2 process (Table 11) than for the H_2O_2/UV.

Compared to the UV/H_2O_2, the O_3/H_2O_2 had a 40.2% lower OPEX and 0.9% greater CAPEX. Costly O_3 generators daily producing 735 kg O_3 explained the 0.9% difference between their CAPEX. A note of caution is due here since the capital cost of the generation system, as well as the contactors, is likely to be different since McGivney and Kawamura's (2008) empirical method was applied because of the lack of a suitable industrial quote. Equally, the WLCA of the O_3/H_2O_2 relied on a theoretical oxidant mass ratio. Further experimental work needs to examine more closely the optimum H_2O_2:O_3 ratio in order to validate these results.

As similar capital costs were found for both AOPs (Table 12), OPEX was the driving factor for suggesting to implement an O_3/H_2O_2 as the most economically feasible alternative for metaldehyde removal purposes. The use of energy was the principal component of the OPEX cost in all the systems (Figure 8). On average it represented 43% of the total OPEX cost. For the UV/H_2O_2 case the energy consumption was attributed to 50% of the OPEX, almost twice the cost of H_2O_2 (£96,429). This outcome is contrary to that of Rosenfeldt *et al.* (2006) where the UV portion of the OPEX accounted for less than 10%. However, James, Germain and Judd (2014) estimated 65% the energy consumption. For the O_3/H_2O_2, 31% OPEX costs were attributed to electricity consumption due to ozone production, whilst 39% were for oxidants (LOX + hydrogen peroxide) (£99,706) (Figure 8). Finally, the fact that O_3/H_2O_2 was 84% more cost-effective energy-saving than the UV/H_2O_2, in agreement with previous findings (Rosenfeldt *et al.*, 2006; Crittenden *et al.*, 2012), explained the higher operational costs of the UV-based technology, and thus greater TOTEX. Energy costs subtraction from TOTEX in both treatments rendered around only £400,000 difference between their TOTEX (£17.3 million for UV/H_2O_2 and £16.9 million for O_3/H_2O_2). Ways of reducing energy costs on-site throughout the development of UV technology, *e.g.*

LED (light-emitting diode) would boost the use of UV/H_2O_2 over O_3/H_2O_2. The peroxone process needs to be technically improved, in terms of the optimum oxidant ratio for metaldehyde-compliant water production regardless MIC. However, with the current state-of-art, it can thus be concluded that the UV/H_2O_2 technology is less economically attractive option for a potential full-scale plant installation at the given discount rate and project life.

The £19.96 million TOTEX costs estimated in this research for UV/H_2O_2 corroborated the £19-40 million whole life costs obtained by Rolph (2016). However, the advantages of this study were (i) the capital costs of the UV system considered the actual number of UV units required for the process, (ii) this approach also considered the number of lamps as well as (iii) the installation of a GAC system for H_2O_2 residual quenching not already in place and (iv) the H_2O_2 tank too. Similarly, the percentages of direct and indirect costs as piping, engineering and contingency differed between both research.

Table 11 AOP treatment conditions tested in the research achieving <0.1 μg L^{-1} metaldehyde and associated OPEX relating to such conditions

Process	O_3/H_2O_2 + H_2O_2/UV	UV/H_2O_2	O_3/H_2O_2
H_2O_2 (mg L^{-1})[a]	16	30	10
O_3 (mg L^{-1})	8	N/A	10
E_D (kWh m^{-3})	0.54	0.66	N/A
E_{EO} (kWh m^{-3} $order^{-1}$)	1.49	0.699	N/A
UV power (kW)	490.41	524.97	N/A
OPEX (£ m^{-3})[b]			
Energy	0.064	0.050	0.021
Chemicals	0.030	0.026	0.027
GAC	0.009	0.009	0.009
Lamp replacement	0.016	0.017	N/A
O_3 equipment replacement	0.010	N/A	0.012
TOTAL	0.128	0.102	0.068

N/A not applicable; [a] 1.135 g mL^{-1} density; [b] OPEX: yearly cost of each category divided by (25MLd^{-1} · 30 d · 5 months of treatment)

The WLCA of this research was normalised to Rolph's (2016) assumptions to be comparable. Therefore, the UV/H_2O_2 CAPEX herein calculated would drop to £1.7 million, slightly more costly than the range estimated by the author (£0.9-1.5

million). Nevertheless, this greater capital expenditure is globally balanced in the TOTEX by the likely overestimated OPEX range (£1.3-2.8 million), depending on the water quality, suggested by Rolph (2016). The length of the treatment was not equally mentioned in Rolph's (2016), thus a 12-month run can be inferred. Consequently, as per the author's criterion, the OPEX of this research would increase until £0.9 million. Overall, the UV/H_2O_2 TOTEX based on Rolph's (2016) assumptions would be £14.5 million, at least £4.5 million cheaper than that of the Rolph's (2016) estimates.

Other options for metaldehyde removal were also appraised. The WLCA of a 20MLD catchment management alternative was estimated at £11,000K (Rolph, 2016). Therefore, a 25 MLD catchment plan for metaldehyde removal would roughly cost £13.75 million, remaining only £0.75 million cheaper than a UV based AOP. Similarly, a biological treatment using fluidised bed bioreactors (FBBR) on a 20MLD WTW was estimated around £15 million TOTEX (Rolph, 2016), thus it is expected to be even more expensive for a 25MLD WTW. Despite of the FBBR lower environmental footprint and chemical costs than AOPs, this technology was 90% electricity dependent (Rolph, 2016). Hence, energy price inflation would increase metaldehyde treatment costs. The final option is to ignore any investment, thus metaldehyde standard could be breached. This unjustifiable decision would only lead to a negative impact on public perception and a number of potential penalties.

A sensitivity analysis was performed to predict the effects of input data variation on the TOTEX outcome (Figure 9). This analysis was restricted to three price inflation scenarios based on those operating costs that exhibited the greatest influence in each treatment (electricity consumption, H_2O_2 and LOX). The sensitivity of the life-cycle costs to each price was examined by allowing one such price to vary while holding constant the other two. The results showed that UV/H_2O_2 is more sensitive to changes in the energy price than O_3/H_2O_2 (Figure 9a). The steeper the slope of the curve, the greater the effect on the total expenditure in such AOP. The peroxone process remained cheaper than UV/H_2O_2 for a free energy bill by £86,017. However, the impacts of global

warming on energy consumption are estimated to raise the price rather than to cut it down. Similarly, a UV/H_2O_2 plant was more costly by £615,972 than an O_3/H_2O_2 full-scale installation even if H_2O_2 price was deflated to £0 kg^{-1} (Figure 9b). Moreover, TOTEX on the O_3/H_2O_2 process would only increase by 0.86% if H_2O_2 becomes 50% more expensive, whilst 3.38% greater TOTEX was found for the UV/H_2O_2.

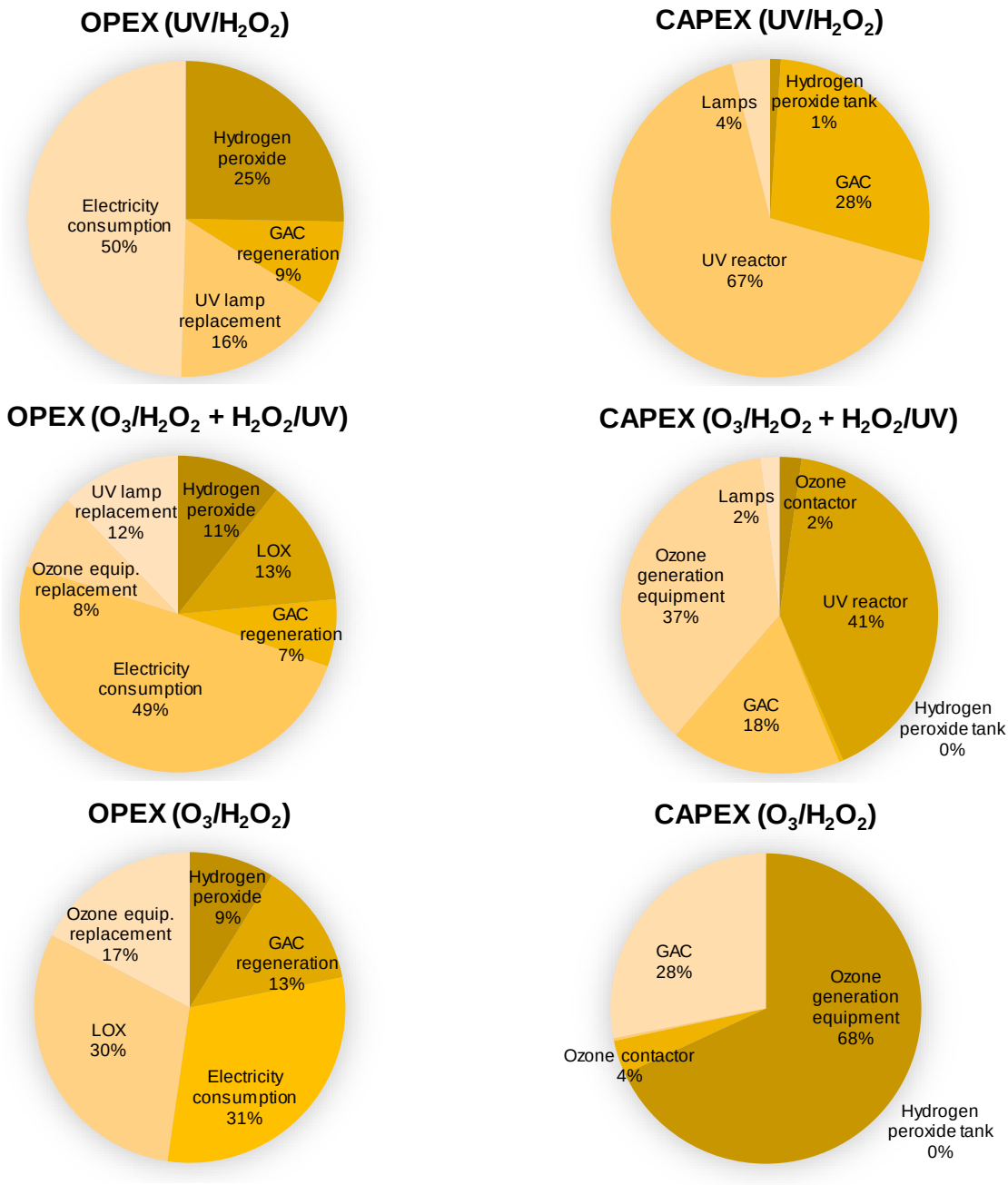

Figure 8 Breakdown of the operating expenses (OPEX) and capital expenses (CAPEX) for a UV/H_2O_2; O_3/H_2O_2 + H_2O_2/UV and O_3/H_2O_2 25 MLD DW treatment plant reducing metaldehyde levels <0.1 µg L^{-1}

Table 12 Estimated capital expenditures for metaldehyde treatment using commercial UV and O_3-based AOPs

Parameter	O_3/H_2O_2 + H_2O_2/UV	H_2O_2/UV	O_3/H_2O_2
Direct costs			
UV system			
UV Reactor			
Number of UV units	3	3	
Total cost	£ 2,700,000	£ 2,700,000	
LP-HO amalgam lamps			N/A
Number of bulbs	490	525	
Total cost	£ 147,124	£ 157,490	
Ozone system			
Ozone generation equipment	£ 2,407,606	N/A	£ 2,781,855
Ozone contactor	£ 126,174		£ 145,669
Peroxide tank	£ 28,000	£ 44,000	£ 11,500
GAC	£ 1,146,872	£ 1,146,872	£ 1,146,872
Main plant items cost	**£ 6,555,775**	**£ 4,048,426**	**£ 4,085,896**
Instrumentation and control	£ 1,180,039	£ 728,717	£ 735,461
Piping, valves and electrical	£ 1,966,732	£ 1,214,528	£ 1,225,769
Buildings (including services)	£ 1,180,039	£ 728,717	£ 735,461
Total direct plant cost	£ 10,882,586	£ 6,720,388	£ 6,782,588
Indirect costs			
Engineering and supervision	£ 2,163,406	£ 1,335,981	£ 1,348,346
Construction expenses	£ 2,687,868	£ 1,659,855	£ 1,675,217
Total direct and indirect plant cost	£ 15,733,860	£ 9,716,223	£ 9,806,151
Contractor's fee	£ 983,366	£ 607,264	£ 612,884
Contingency	£ 1,311,155	£ 809,685	£ 817,179
Total erected cost	£ 18,028,381	£ 11,133,172	£ 11,236,215
Working capital	£ 5,637,966	£ 3,481,647	£ 3,513,871
Total capital employed	**£ 23,666,347**	**£ 14,614,819**	**£ 14,750,085**

The O_3/H_2O_2 would only become less profitable if the LOX price was increased by more than 153% (£0.177 kg^{-1}) (Figure 9c) as UV/H_2O_2 is cost independent of such price. It can be concluded that UV/H_2O_2 is significantly more susceptible to price inflation than O_3/H_2O_2. All these outcomes are worth of consideration for industry decision makers.

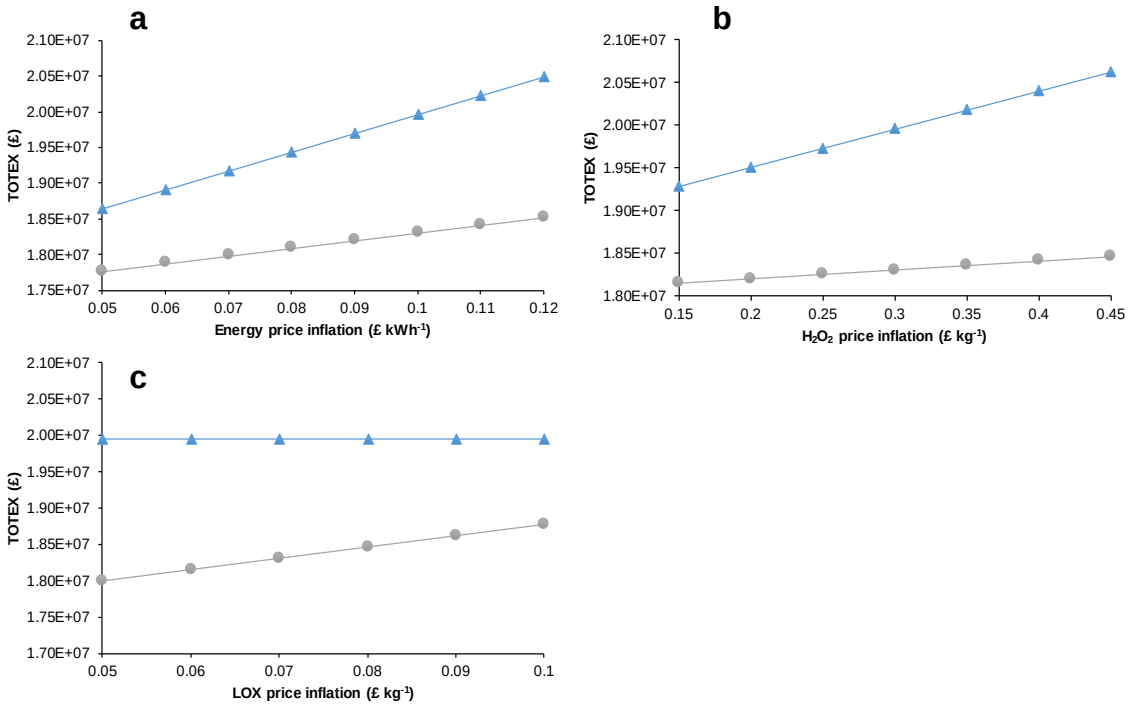

Figure 9 Influence of prices inflation in terms of (a) energy (b) H_2O_2 and (c) LOX on the TOTEX of UV/H_2O_2 (▲) and O_3/H_2O_2 (●) to reach the cost neutral point between both treatments

3.4 Conclusions

DW contamination by metaldehyde in treated waters, exceeding the permitted levels, challenges UK water supplier performance. AOPs have been studied at pilot and lab-scale to address metaldehyde removal not effectively achieved by conventional methods. However, AOPs are considered an expensive alternative with high running and infrastructure costs whose implementation would only be justified for significantly affected niche cases if effluent quality compliance is at risk. Nevertheless, to date, no published studies have indeed assessed the economic viability of two different AOPs fed with the same water quality through a WLCA after demonstrating their efficacy for pesticide removal. A site-specific

WLCA over 25-year period was undertaken from the UV/H_2O_2, and O_3/H_2O_2 + H_2O_2/UV results presented in Chapter 1 that achieved <0.1 µg L^{-1} metaldehyde residual for a conservative 0.72-log pesticide reduction. O_3/H_2O_2 became the benchmark for the treatment of metaldehyde at the most affordable total costs. Estimated O_3/H_2O_2 TOTEX was £18,304,347 saving £1.65 million regarding the UV/H_2O_2 and £12.1 million with respect to the O_3/H_2O_2 + H_2O_2/UV. The O_3/H_2O_2 process was 40.2% lower in OPEX (£0.07 m^{-3}) and similar in CAPEX than the UV/H_2O_2 for 5-months annual treatment. The O_3/H_2O_2 lower operating expenditure mainly resulted from its 84% lower energy costs. Therefore, electricity consumption was pivotal to the economic viability of both AOPs evaluated. However, O_3/H_2O_2 WLCA was based upon a 0.7 stoichiometric oxidant mass ratio assumption and a pilot-scale experience in the Anglian Water region that similarly achieved up to a 0.7-log pesticide removal. This decision was fundamentally made due to the limited performance of the sub process within the two-stage AOP (O_3/H_2O_2 + H_2O_2/UV) to meet regulatory levels in the pilot-scale study. Therefore, further research should carefully optimize H_2O_2:O_3 critical process mass ratio for metaldehyde removal to verify the cost estimates. UV/H_2O_2 showed greater sensitivity to energy and H_2O_2 price volatility than O_3/H_2O_2, hence greater risk associated if full-scale implemented. LED-based breakthrough technology would likely incline water utilities to use technically reliable UV/H_2O_2 over O_3/H_2O_2. Nevertheless, UV/H_2O_2 remained more affordable than alternative control methods for removing metaldehyde such as biological treatment when this research was normalised at equal assumptions to those of previous studies.

Notwithstanding the cost assumptions and modelling based approach to estimate the expenditures of some assets, this study offers an insight outline for preparing a good AOP cost estimate for a real water treatment plant. This work, therefore, has important implications for DW utilities as it suggests that O_3/H_2O_2 and UV/H_2O_2 are robust for metaldehyde removal and an economically viable alternative to source control interventions.

3.5 Acknowledgments

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4 CONCLUSIONS

An investigation of O_3/H_2O_2 + H_2O_2/UV and UV/H_2O_2 advanced oxidation technologies for metaldehyde removal and disinfection by-products formation potential throughout a pilot-scale study was carried out. A WLCA was undertaken based on data gathered in the pilot-scale study for industrial application and detailed literature search. From these analyses, a number of conclusions can be drawn:

- The results demonstrated AOPs effectiveness to degrade the pesticide below the legislative limits of 0.1 µg L^{-1} up to 2.14 µg L^{-1} initial levels with E_D <1.0 kWh m^{-3}. Worst-case 38% minimal removal was logged for O_3/H_2O_2 and the stand-alone UV/H_2O_2, yet up to 96% and 98% were equally yielded, respectively. The H_2O_2/UV sub process had conversely a more limited 79% top end removal efficiency. The O_3/H_2O_2 was exclusively successful at fulfilling the European Directive 98/83/EC for metaldehyde feed water concentration ≤0.14 µg L^{-1}. A surplus of H_2O_2 required for the H_2O_2/UV sub process might explain this technical limitation. Further studies should address the optimum H_2O_2:O_3 ratio, which is expected to be between 0.5 and 1, to achieve European Directive 98/83/EC limits for a wider metaldehyde inlet spectrum
- The assessment of metaldehyde degradation has also shown the need of greater oxidative chemical and energy doses to meet the stringent water quality standards when increasing MICs. Inhibitory effect of organic-turbid waters of greater than 1.0 NTU on UV/H_2O_2 metaldehyde performance was reported
- The AOPs had a different net DBPFP contribution for THMFP (-283 µg L^{-1} to +255 µg L^{-1}) to HAAFP (-164 µg L^{-1} to +131 µg L^{-1}). Overall, O_3/H_2O_2 sub process had a lower net production of DBPs than that of the rest of the processes. The impact of feed water quality in terms of NOM was critical for DBPFP, as no correlation was found with the process variables studied across the experimental work

- The practical implications of this work are that OPEX in terms of energy, 43% average, was the main driver for considering O_3/H_2O_2 a cost-efficiency contender for metaldehyde removal. Moreover, this AOP provided with a trade-off between metaldehyde and THM compliant water production at the minimum costs (£0.07 m^{-3}). However, reliable pilot data confirming the oxidants doses suggested on the O_3/H_2O_2 WLCA (10 mg L^{-1} and 7 mg L^{-1}, respectively) would validate this advanced technology as benchmark. The sensitive analysis showed greater influence of operational cost on the UV-based AOP than on the peroxone treatment. UV/H_2O_2 would even be £86,000 more expensive than O_3/H_2O_2 in a £0 kWh^{-1} hypothetical scenario. The UV/H_2O_2 remained an equivalent economic process comparable with catchment management and biological treatments for removing metaldehyde to trace levels. Do nothing should not be considered in any case. The WLCA undertaken in this study can be improved by using industrial prices from local manufacturers, thus avoiding updating prices from available research and empirical equations. LED-based breakthrough technology might incline water utilities to use technically reliable UV/H_2O_2 over O_3/H_2O_2 as evidenced metaldehyde efficiency for peaks of 2.0 µg L^{-1} were tackled

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APPENDICES

Appendix A Operating conditions evaluated

This Appendix gathers all the operating conditions under which the AOP pilot experiments were carried out.

Table A-1 UV/H_2O_2 process conditions, flow rate, metaldehyde inlet concentration (MIC) and metaldehyde removal after treatment

Flow rate ($m^3\ h^{-1}$)	UV (%)	Electrical power (kW)	UV fluence (KWh m^{-3})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post UV/H_2O_2 (µg L^{-1})
2.44	60	1.26	0.52	20	0.14	0.06
2.49	60	1.26	0.51	33	0.14	0.04
2.49	60	1.26	0.51	42	0.14	0.03
3.49	60	1.26	0.36	14	0.14	0.07
3.48	60	1.26	0.36	28	0.14	0.05
3.53	60	1.26	0.36	35	0.14	0.05
2.5	60	1.26	0.50	17	0.53	0.27
2.52	60	1.26	0.50	28	0.53	0.16
2.5	60	1.26	0.50	38	0.53	0.17
3.02	60	1.26	0.42	13	0.53	0.33
3.11	60	1.26	0.40	29	0.53	0.24
3.08	60	1.26	0.41	42	0.53	0.20
2.53	60	1.26	0.50	15	0.80	0.27
2.53	60	1.26	0.50	30	0.80	0.18
2.49	60	1.26	0.51	40	0.80	0.18
2.54	60	1.26	0.50	8	2.11	0.76
2.54	60	1.26	0.50	29	2.11	0.56
2.47	60	1.26	0.51	15	2.11	0.54
2.51	60	1.26	0.50	15	2.14	0.85
2.53	60	1.26	0.50	30	2.14	0.56
2.55	60	1.26	0.49	40	2.14	0.47
2.51	60	1.26	0.50	14	2.30	0.93
2.56	60	1.26	0.49	26	2.30	0.65

Flow rate (m^3 h^{-1})	UV (%)	Electrical power (kW)	UV fluence (KWh m^{-3})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post UV/H_2O_2 (µg L^{-1})
2.52	60	1.26	0.50	35	2.30	0.52
2.5	90	1.89	0.76	19	0.14	0.02
2.43	90	1.89	0.78	32	0.14	0.01
2.48	90	1.89	0.76	40	0.14	0.01
2.55	90	1.89	0.74	15	0.53	0.12
2.53	90	1.89	0.75	28	0.53	0.05
2.52	90	1.89	0.75	36	0.53	0.04
3.01	96	2.01	0.67	13	0.53	0.16
3.07	96	2.01	0.66	28	0.53	0.06
3.07	96	2.01	0.66	36	0.53	0.06
2.59	90	1.89	0.73	15	0.80	0.14
2.55	90	1.89	0.74	30	0.80	0.04
2.48	90	1.89	0.76	40	0.80	0.16
2.46	90	1.89	0.77	15	2.11	0.41
2.51	90	1.89	0.75	27	2.11	0.13
2.51	90	1.89	0.75	42	2.11	0.09
2.52	90	1.89	0.75	15	2.14	0.30
2.55	90	1.89	0.74	30	2.14	0.17
2.5	90	1.89	0.76	40	2.14	0.21
3.48	96	2.01	0.58	17	0.14	0.03
3.46	96	2.01	0.58	27	0.14	0.02
3.51	96	2.01	0.57	38	0.14	0.01
2.52	96	2.01	0.80	12	2.30	0.29
2.53	96	2.01	0.80	26	2.30	0.12
2.52	96	2.01	0.80	36	2.30	0.13
2.57	70	1.47	0.57	17	0.53	0.21
2.56	80	1.68	0.66	15	0.53	0.16
2.52	80	1.68	0.67	31	0.53	0.07

Flow rate (m^3 h^{-1})	UV (%)	Electrical power (kW)	UV fluence (KWh m^{-3})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post UV/H_2O_2 (µg L^{-1})
2.50	70	1.47	0.59	31	0.53	0.12
2.50	70	1.47	0.59	37	0.53	0.09
2.52	80	1.68	0.67	31	0.53	0.07
1.94	90	1.89	0.97	40	0.53	0.02
1.97	80	1.68	0.85	39	0.53	0.03
1.96	60	1.26	0.64	39	0.53	0.11
1.92	60	1.26	0.66	30	0.53	0.15
1.92	80	1.68	0.87	30	0.53	0.05
1.96	80	1.68	0.86	16	0.53	0.11
1.98	60	1.26	0.64	17	0.53	0.22
1.96	90	1.89	0.96	20	0.53	0.06
1.90	80	1.68	0.88	14	2.11	0.35
2.10	60	1.26	0.60	17	2.11	0.70
2.09	90	1.89	0.90	13	2.11	0.28
2.08	60	1.26	0.61	26	2.11	0.42
2.07	80	1.68	0.81	28	2.11	0.13
2.08	80	1.68	0.81	36	2.11	0.09
2.03	60	1.26	0.62	40	2.11	0.40
2.01	90	1.89	0.94	45	2.11	0.04
2.56	80	1.68	0.66	35	2.11	0.19
2.54	70	1.47	0.58	36	2.11	0.29
2.51	70	1.47	0.59	29	2.11	0.33
2.51	80	1.68	0.67	27	2.11	0.31
2.49	80	1.68	0.67	15	2.11	0.44
2.46	70	1.47	0.60	15	2.11	0.56
2.54	70	1.47	0.58	15	0.80	0.21
2.55	80	1.68	0.66	15	0.80	0.15
2.49	80	1.68	0.67	30	0.80	0.07

Flow rate (m^3 h^{-1})	UV (%)	Electrical power (kW)	UV fluence (KWh m^{-3})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post UV/H_2O_2 (µg L^{-1})
2.50	70	1.47	0.59	30	0.80	0.13
2.52	70	1.47	0.58	40	0.80	0.09
2.46	80	1.68	0.68	40	0.80	0.05
1.97	90	1.89	0.96	40	0.80	0.11
1.95	80	1.68	0.86	40	0.80	0.03
1.98	60	1.26	0.64	40	0.80	0.03
1.97	60	1.26	0.64	30	0.80	0.12
1.95	80	1.68	0.86	30	0.80	0.20
1.98	80	1.68	0.85	15	0.80	0.31
1.98	90	1.89	0.95	15	0.80	0.25
1.98	60	1.26	0.64	15	0.80	0.03
2.48	70	1.47	0.59	15	2.14	0.62
2.51	80	1.68	0.67	15	2.14	0.49
2.49	80	1.68	0.67	30	2.14	0.20
2.51	70	1.47	0.59	30	2.14	0.35
2.57	70	1.47	0.57	40	2.14	0.29
2.61	80	1.68	0.64	40	2.14	0.17
1.96	90	1.89	0.96	40	2.14	0.04
1.99	80	1.68	0.84	40	2.14	0.06
1.96	60	1.26	0.64	40	2.14	0.35
1.99	60	1.26	0.63	30	2.14	0.43
2.01	80	1.68	0.84	30	2.14	0.12
1.96	80	1.68	0.86	15	2.14	0.35
1.97	90	1.89	0.96	15	2.14	0.19
1.95	60	1.26	0.65	15	2.14	0.67
2.99	80	1.68	0.56	13	0.53	0.18
3.06	80	1.68	0.55	26	0.53	0.10
3.05	80	1.68	0.55	37	0.53	0.09

Flow rate (m^3 h^{-1})	UV (%)	Electrical power (kW)	UV fluence (KWh m^{-3})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post UV/H_2O_2 (µg L^{-1})
2.52	80	1.68	0.67	14	2.30	0.53
2.55	80	1.68	0.66	25	2.30	0.25
2.52	80	1.68	0.67	34	2.30	0.18
3.49	80	1.68	0.48	15	0.14	0.05
3.46	80	1.68	0.49	27	0.14	0.03
3.58	80	1.68	0.47	35	0.14	0.02
2.44	70	1.47	0.60	14	0.14	0.05
2.49	80	1.68	0.67	14	0.14	0.03
2.46	80	1.68	0.68	35	0.14	0.01
2.46	70	1.47	0.60	29	0.14	0.02
2.48	70	1.47	0.59	42	0.14	0.02
2.48	80	1.68	0.68	40	0.14	0.02
1.89	90	1.89	1.00	40	0.14	0.01
1.88	80	1.68	0.89	47	0.14	0.02
1.90	60	1.26	0.66	40	0.14	0.02
1.91	60	1.26	0.66	37	0.14	0.02
1.86	80	1.68	0.90	30	0.14	0.01
1.89	80	1.68	0.89	20	0.14	0.01
1.89	90	1.89	1.00	15	0.14	0.01
1.90	60	1.26	0.66	17	0.14	0.05

Table A-2 O_3/H_2O_2 process conditions, flow rate, metaldehyde inlet concentration (MIC) and metaldehyde removal after treatment

Flow rate ($m^3\ h^{-1}$)	O_3 ($mg\ L^{-1}$)	H_2O_2 ($mg\ L^{-1}$)	MIC ($\mu g\ L^{-1}$)	Metaldehyde residual post O_3/H_2O_2 ($\mu g\ L^{-1}$)
1.92	3.39	8	0.53	0.28
1.84	3.45	13	0.53	0.28
1.65	5.97	18	0.53	0.23
1.85	7.19	24	0.53	0.17
1.84	3.46	10	2.04	0.82
1.88	3.59	10	2.04	0.73
1.95	5.06	16	2.04	0.60
1.86	7.16	22	2.11	0.39
2.50	2.58	7	0.53	0.31
2.51	2.47	10	0.53	0.19
2.62	3.69	10	0.53	0.19
2.55	3.84	16	0.53	0.31
2.55	5.15	15	0.53	0.19
2.53	5.08	23	0.53	0.19
1.45	2.98	10	0.80	0.01
1.43	2.99	13	0.80	0.35
1.29	5.14	15	0.80	0.29
1.40	6.19	24	0.80	0.24
1.08	2.29	10	2.14	0.19
1.81	2.20	8	2.14	0.19
1.90	3.16	14	2.14	0.19
1.78	3.40	14	2.14	0.19

Flow rate ($m^3 h^{-1}$)	O_3 (mg L^{-1})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post O_3/H_2O_2 (µg L^{-1})
1.66	5.30	16	2.14	0.19
1.66	5.12	24	2.14	0.19
1.66	5.24	22	2.14	0.19
1.66	5.33	24	2.14	0.31
2.47	2.50	9	2.30	1.04
2.51	3.87	15	2.30	0.65
2.53	4.93	16	2.30	0.54
1.88	3.38	11	2.30	1.09
1.90	3.21	13	2.30	1.07
1.86	5.07	12	2.30	0.84
1.77	5.44	24	2.30	0.10
1.96	6.84	14	2.30	0.42
1.83	7.34	24	2.30	0.39
1.83	2.10	8	0.14	0.08
1.86	2.13	11	0.14	0.09
1.89	3.17	11	0.14	0.07
1.89	3.35	19	0.14	0.06
1.89	4.52	18	0.14	0.05
1.88	4.49	23	0.14	0.05
1.85	5.29	14	0.53	0.22
1.95	6.71	15	0.53	0.21
1.69	5.94	11	2.04	0.60
1.94	6.95	16	2.04	0.36
1.39	4.64	13	0.80	0.31
1.43	5.94	17	0.80	0.24
1.78	3.56	13	2.14	0.31

Flow rate ($m^3 h^{-1}$)	O_3 (mg L^{-1})	H_2O_2 (mg L^{-1})	MIC (µg L^{-1})	Metaldehyde residual post O_3/H_2O_2 (µg L^{-1})
1.47	5.98	13	2.14	0.31
2.05	4.33	16	2.14	0.19

Table A-3 H_2O_2/UV process conditions, metaldehyde inlet concentration (MIC), in this case the residual from the peroxone process, and metaldehyde removal after treatment

UV fluence (mJ cm^{-2})	Flow rate UV ($m^3 h^{-1}$)	Electrical power (kW)	UV fluence (KWh m^{-3})	H_2O_2 (mg L^{-1})	Metaldehyde residual post O_3/H_2O_2 (µg L^{-1})	Metaldehyde residual post H_2O_2/UV (µg L^{-1})
1400	0.47	0.34	0.73	8	0.28	0.14
1400	0.44	0.34	0.77	13	0.28	0.12
1800	0.31	0.34	1.10	18	0.23	0.05
1000	0.63	0.34	0.54	24	0.17	0.06
1400	0.44	0.34	0.77	10	0.82	0.38
1400	0.44	0.34	0.77	10	0.73	0.37
1800	0.31	0.34	1.10	16	0.60	0.13
1000	0.61	0.34	0.56	24	0.39	0.13
1400	0.41	0.34	0.83	13	0.35	0.14
1800	0.33	0.34	1.03	15	0.29	0.08
1000	0.62	0.34	0.55	25	0.24	0.09
1400	0.42	0.34	0.81	10	0.19	0.60
1400	0.42	0.34	0.81	8	0.19	0.54

1800	0.33	0.34	1.03	14	0.19	0.30
1000	0.61	0.34	0.56	14	0.19	0.49
1400	0.42	0.34	0.81	16	0.19	0.27
1800	0.33	0.34	1.03	24	0.19	0.18
1000	0.60	0.34	0.57	22	0.19	0.32
1400	0.42	0.34	0.81	24	0.31	0.22
1000	0.58	0.34	0.59	11	1.09	0.54
1000	0.59	0.34	0.58	13	1.07	0.57
1000	0.57	0.34	0.60	12	0.84	0.41
1000	0.58	0.34	0.59	24	0.10	0.41
1000	0.56	0.34	0.61	14	0.42	0.19
1000	0.56	0.34	0.61	24	0.39	0.11
1000	0.61	0.34	0.56	8	0.08	0.05
1000	0.61	0.34	0.56	11	0.09	0.05
1000	0.60	0.34	0.57	11	0.07	0.04
1000	0.59	0.34	0.58	19	0.06	0.03
1000	0.59	0.34	0.58	18	0.05	0.02
1000	0.60	0.34	0.57	23	0.05	0.02

Appendix B DistLM results on metaldehyde removal after AOPs

In this Appendix, the statistical tests undertaken in PRIMER v6 software are shown. This methodology was followed to evaluate the influence of the different predictors either process conditions tested (UV fluences, H_2O_2 doses, O_3 doses and flow rates) or water quality parameters analysed (DOC, turbidity and UV254 nm) on metaldehyde degradation after a given AOP. In each table, the predictors significantly explaining variation (P<0.05) and in noteworthy proportion ('Prop.') on metaldehyde removal (effector) appear in bold. For each AOP process and sub processes, the marginal test is first displayed and then the sequential test. In the sequential test, 'res.df' indicates the residual degrees of freedom after adding a new predictor to the DistLM while the 'Cumul.' value explains the predictive power of the model.

- UV/ H_2O_2

Table B-1 Individual influence of predictors on metaldehyde removal with n=125 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
Flow rate	16.101	18.313	**0.0001**	**0.12779**
H_2O_2	16.43	18.744	**0.0001**	**0.1304**
UV	39.827	57.771	**0.0001**	**0.31608**
Turbidity inlet	11.182	11.193	0.3022	0.0088746
UV254 Abs inlet	0.91015	0.90949	0.3471	0.0072234
DOC inlet	49.852	51.494	0.02	0.039565

Table B-2 Sequential DistLM test of the predictors explaining metaldehyde removal

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
UV	39.827	57.771	**0.0001**	**0.31608**	0.31608	125
H_2O_2	13.975	24.002	**0.0001**	**0.11091**	0.427	124
DOC inlet	3.6263	6.5046	0.0097	0.02878	0.45578	123
UV254 Abs inlet	2.2132	4.069	0.0473	0.017565	0.47334	122
Turbidity inlet	2.2173	4.1829	0.0382	0.017598	0.49094	121
Flow rate	0.10541	0.19753	0.6618	0.000837	0.49178	120

- O_3/H_2O_2 + H_2O_2/UV

Table B-3 Individual influence of predictors on metaldehyde removal with *n*=62 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
H_2O_2/O_3	1.969	2.0003	0.1561	0.031254
O_3	28.611	51.583	**0.0001**	**0.45415**
H_2O_2	21.155	31.345	**0.0001**	**0.3358**
UV	33.718	71.395	**0.0001**	**0.53521**
Turbidity inlet	0.057857	0.056991	0.8123	0.0009184
UV254 inlet Abs	0.35819	0.35452	0.5488	0.0056856
DOC inlet	0.16609	0.16388	0.6848	0.0026363

Table B-4 Sequential DistLM test of the predictors explaining metaldehyde removal

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
UV	33.718	71.395	**0.0001**	**0.53521**	0.53521	62
O_3	15.681	70.333	**0.0001**	**0.24891**	0.78412	61
H_2O_2	1.7669	8.9589	0.0031	0.028046	0.81217	60
DOC inlet	0.46052	2.3891	0.1289	0.00731	0.81948	59
UV254 Abs inlet	0.012533	0.063987	0.8056	0.000199	0.81968	58
Turbidity inlet	0.017697	0.088934	0.7708	0.000281	0.81996	57
H_2O_2/O_3	0.000103	0.00051	0.9799	1.64E-06	0.81996	56

- O_3/H_2O_2 sub process

Table B-5 Individual influence of predictors on metaldehyde removal with *n*=48 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
Flow rate	3.7589	3.9882	0.0528	0.076713
H_2O_2/O_3	0.021648	0.021215	0.8806	0.0004418
O_3	5.0298	5.4907	**0.0255**	**0.10265**
H_2O_2	5.988	6.6825	**0.0128**	**0.1222**
Turbidity inlet	7.2763	8.3709	**0.0052**	**0.1485**
UV254 Abs inlet	12.609	16.632	**0.0004**	**0.25733**
DOC inlet	16.964	25.417	**0.0001**	**0.3462**

Table B-6 Sequential DistLM test of the predictors explaining metaldehyde removal

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
DOC inlet	16.964	25.417	**0.0001**	**0.3462**	0.3462	48
O_3	8.1653	16.077	**0.0004**	**0.16664**	0.51284	47
Turbidity inlet	4.137	9.6433	**0.0023**	**0.084428**	0.59726	46
UV254 Abs inlet	1.3285	3.2481	0.0794	0.027113	0.62438	45
Flow rate	2.4893	6.8816	0.0107	0.050802	0.67518	44
H_2O_2/O_3	0.24518	0.67275	0.4169	0.005004	0.68018	43
H_2O_2	0.000224	0.000599	0.9822	4.56E-06	0.68019	42

- H_2O_2/UV sub process

Table B-7 Individual influence of predictors on metaldehyde removal with *n*=29 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
O_3	16.762	17.162	0.2032	0.055872
H_2O_2	0.0847	0.082109	0.786	0.0028233
H_2O_2/O_3	20.257	2.1	0.155	0.067524
UV	0.00098747	0.00095459	0.9766	0.32916
Turbidity post O_3/H_2O_2	0.010373	0.010031	0.9243	0.00034576
UV254 Abs post O_3/H_2O_2	0.021981	0.021264	0.8742	0.00073269
DOC post O_3/H_2O_2	23.633	24.799	0.1227	0.078776

Table B-8 Sequential DistLM test of the predictors explaining metaldehyde removal

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
DOC post O_3/H_2O_2	2.3633	2.4799	0.1228	0.078776	0.07877	29
H_2O_2/O_3	1.502	1.6092	0.2179	0.050066	0.12884	28
UV254 Abs post O_3/H_2O_2	0.51378	0.54144	0.4732	0.017126	0.14597	27
O_3	1.5379	1.6603	0.2052	0.051263	0.19723	26
H_2O_2	0.53655	0.56968	0.4394	0.017885	0.21512	25
Turbidity post O_3/H_2O_2	0.36311	0.3759	0.5468	0.012104	0.22722	24
UV	0.027798	0.027612	0.8656	0.000927	0.22815	23

Appendix C DistLM results on DBPFP after AOPs

In this Appendix, the statistical tests undertaken in PRIMER v6 software are shown. This methodology was followed to evaluate the influence of the different predictors either process conditions tested (UV fluences, H_2O_2 doses, O_3 doses and flow rates) or water quality parameters analysed (DOC, turbidity and UV254 nm) on the net DBPFP contribution after a given AOP. In each table, the predictors significantly explaining variation (P<0.05) and in noteworthy proportion ('Prop.') on DBPFP (THMFP/HAAFP) change (effector) appear in bold. For each AOP process and sub processes, the marginal test is first displayed and then the sequential test. In the sequential test, 'res.df' indicates the residual degrees of freedom after adding a new predictor to the DistLM while the 'Cumul.' value explains the predictive power of the model.

C.1 Net THMFP contribution after AOP

- UV/ H_2O_2

Table C-1 Individual influence of predictors on net THMFP contribution with n=25 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
Flow rate	0.1686	0.16317	0.6906	0.0064846
H_2O_2	28.397	30.653	0.0905	0.10922
Metaldehyde inlet	0.067532	0.065104	0.8118	0.0025974
UV	0.088542	0.085428	0.7719	0.0034055
Turbidity inlet	1.782	18.395	0.1882	0.068537
UV254 Abs inlet	16.086	16.487	0.211	0.06187
DOC inlet	0.67867	0.67005	0.4195	0.026103
UV254 Abs post AOP	0.70618	0.69798	0.4159	0.027161
DOC post AOP	22.785	24.013	0.1311	0.087635

Table C-2 Sequential DistLM test of the predictors explaining net THMFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
H_2O_2	2.8397	3.0653	0.0934	0.10922	0.10922	25
UV254 Abs inlet	1.5354	1.7041	0.214	0.059055	0.16827	24
Turbidity inlet	2.0217	2.372	0.1328	0.077759	0.24603	23
Metaldehyde inlet	1.5822	1.9315	0.189	0.060853	0.30689	22
DOC inlet	2.4141	3.2483	0.081	0.09285	0.39974	21
Flow rate	0.90527	1.2315	0.2826	0.034818	0.43455	20
UV254 Abs post AOP	0.31209	0.41209	0.536	0.012004	0.44656	19
DOC post AOP	0.5191	0.67365	0.4052	0.019965	0.46652	18
UV	0.003139	0.003848	0.9481	0.000121	0.46664	17

- O_3/H_2O_2 + H_2O_2/UV

Table C-3 Individual influence of predictors on net THMFP contribution with *n*=37 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
H_2O_2/O_3	2.8109	2.9555	0.0928	0.073971
O_3	0.61309	0.60675	0.4366	0.016134
H_2O_2	5.254	5.9366	**0.018**	**0.13826**
Metaldehyde inlet	0.054779	0.053414	0.8195	0.001442
UV	0.14927	0.14592	0.7157	0.003928
Turbidity inlet	0.43585	0.4293	0.5305	0.01147
UV254 Abs inlet	2.1783	2.2499	0.1409	0.057323
DOC inlet	5.2079	5.8762	**0.0145**	**0.13705**
UV254 Abs post AOP	0.75867	0.75375	0.3985	0.019965
DOC post AOP	0.54838	0.54177	0.4732	0.014431

Table C-4 Sequential DistLM test of the predictors explaining net THMFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
H_2O_2	5.254	5.9366	**0.015**	**0.13826**	0.1382	37
DOC inlet	4.9746	6.4486	**0.011**	**0.13091**	0.2691	36
DOC post AOP	1.4233	1.8906	0.182	0.03745	0.3066	35
UV254 Abs post AOP	1.5678	2.1512	0.150	0.04125	0.3478	34
UV254 Abs inlet	0.8825	1.2186	0.291	0.02322	0.3711	33
H_2O_2/O_3	0.39096	0.53222	0.454	0.01028	0.3814	32
Turbidity inlet	0.33613	0.44971	0.521	0.00884	0.3902	31
Metaldehyde inlet	0.82962	1.114	0.305	0.02183	0.4120	30
O_3	0.17178	0.2247	0.626	0.00452	0.4166	29
UV	0.032606	0.041242	0.835	0.00085	0.4174	28

- O_3/H_2O sub process

Table C-5 Individual influence of predictors on net THMFP contribution with *n*=37 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
Flow rate	1.7337	1.7688	0.1905	0.045625
H_2O_2/O_3	0.42498	0.41847	0.4987	0.011184
O_3	1.9574	2.0094	0.1707	0.051511
H_2O_2	4.0561	4.4213	**0.0375**	**0.10674**
Metaldehyde inlet	0.39409	0.38774	0.5551	0.010371
Turbidity inlet	0.24599	0.24108	0.6243	0.006474
UV254 Abs inlet	1.6058	1.6325	0.2074	0.042258
DOC inlet	3.2348	3.4428	0.0725	0.085127
UV254 Abs post AOP	0.000397	0.000387	0.9834	1.05E-05
DOC post AOP	2.0101	2.0666	0.159	0.052899

Table C-6 Sequential DistLM test of the predictors explaining net THMFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
H_2O_2	4.0561	4.4213	0.0396	0.10674	0.10674	37
DOC inlet	3.3022	3.8796	0.0532	0.0869	0.19364	36
UV254 Abs post AOP	2.8949	3.6516	0.061	0.076181	0.26982	35
O_3	3.4747	4.8673	0.0428	0.091439	0.36126	34
DOC post AOP	2.0314	3.0141	0.0886	0.053457	0.41472	33
Turbidity inlet	1.0844	1.6403	0.2086	0.028538	0.44326	32
H_2O_2/O_3	0.20694	0.30622	0.5716	0.005446	0.4487	31
UV254 Abs inlet	0.1559	0.22493	0.6406	0.004103	0.4528	30
Metaldehyde inlet	2.5829	4.1133	0.0542	0.067972	0.52078	29
Flow rate	2.1179	3.6849	0.061	0.055734	0.57651	28

- H_2O_2/UV sub process

Table C-7 Individual influence of predictors on net THMFP contribution with *n*=18 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
O_3	0.23358	0.22404	0.6554	0.012294
H_2O_2	0.0030564	0.002896	0.9598	0.00016086
H_2O_2/O_3	0.45059	0.43724	0.5323	0.023715
Metaldehyde inlet	38.762	46.134	**0.0362**	**0.20401**
UV	0.25148	0.24144	0.64	0.013236
Turbidity post O_3/H_2O_2	44.093	54.396	**0.0368**	**0.23207**
UV254 Abs post O_3/H_2O_2	0.42277	0.40963	0.5293	0.022251
DOC post O_3/H_2O_2	0.27709	0.26639	0.624	0.014584

Table C-8 Sequential DistLM test of the predictors explaining net THMFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
Turbidity post O_3/H_2O_2	4.4093	5.4396	**0.0353**	**0.2320**	0.23207	18
Metaldehyde inlet	1.3105	1.6775	0.2197	0.0689	0.30104	17
DOC post O_3/H_2O_2	2.162	3.1113	0.1009	0.1137	0.41483	16
O_3	1.5435	2.4181	0.138	0.0812	0.49607	15
UV	0.64499	1.0112	0.3297	0.0339	0.53001	14
H_2O_2/O_3	0.25793	0.38667	0.5515	0.0135	0.54359	13
UV254 Abs post O_3/H_2O_2	0.002396	0.003317	0.955	0.0001	0.54372	12
H_2O_2	0.001114	0.001413	0.9694	5.9E-05	0.54377	11

C.2 Net HAAFP contribution after AOP

- UV/ H_2O_2

Table C-9 Individual influence of predictors on net HAAFP contribution with *n*=21 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
Flow rate	0.018638	0.017806	0.8973	0.00084718
H_2O_2	0.83323	0.82666	0.3683	0.037874
Metaldehyde inlet	0.27858	0.26933	0.6147	0.012663
UV	0.54305	0.53149	0.4892	0.024684
Turbidity inlet	2.004	21.046	0.1723	0.091089
UV254 Abs inlet	15.266	15.658	0.2253	0.06939
DOC inlet	0.074921	0.07176	0.788	0.0034055
UV254 Abs post AOP	0.091652	0.087852	0.7665	0.004166
DOC post AOP	0.27176	0.26265	0.6079	0.012353

Table C-10 Sequential DistLM test of the predictors explaining net HAAFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
Turbidity inlet	2.004	2.1046	0.1626	0.091089	0.091089	21
UV254 Abs inlet	2.938	3.4447	0.082	0.13355	0.22463	20
DOC post AOP	0.70629	0.82068	0.3809	0.032104	0.25674	19
H_2O_2	0.93103	1.0868	0.3152	0.042319	0.29906	18
UV254 Abs post AOP	0.25484	0.28567	0.6097	0.011584	0.31064	17
DOC inlet	0.16193	0.17268	0.6907	0.007361	0.318	16
Flow rate	0.041116	0.041218	0.848	0.001869	0.31987	15
UV	0.04036	0.037865	0.8313	0.001835	0.32171	14

- O_3/H_2O_2 + H_2O_2/UV

Table C-11 Individual influence of predictors on net HAAFP contribution with *n*=23 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
H_2O_2/O_3	8.9524	13.684	**0.0018**	**0.37302**
O_3	1.8137	1.8802	0.1827	0.075572
H_2O_2	1.4117	1.4375	0.2399	0.058822
Metaldehyde inlet	9.531	15.15	**0.0016**	**0.39712**
UV	0.43903	0.42858	0.5206	0.018293
Turbidity inlet	11.905	22.638	**0.0002**	**0.49603**
UV254 Abs inlet	4.2818	4.9945	**0.0357**	**0.17841**
DOC inlet	9.0261	13.864	**0.001**	**0.37609**
UV254 Abs post AOP	4.4615	5.2518	**0.0307**	**0.18589**
DOC post AOP	1.0626	1.0655	0.3067	0.044274

Table C-12 Sequential DistLM test of the predictors explaining net HAAFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
Turbidity inlet	11.905	22.638	**0.0001**	**0.49603**	0.49603	23
H_2O_2/O_3	2.8207	6.6909	**0.0159**	**0.11753**	0.61356	22
UV254 Abs post AOP	1.9552	5.6096	0.0299	0.081465	0.69503	21
UV	1.1713	3.8105	0.0711	0.048806	0.74383	20
O_3	0.56108	1.9081	0.1748	0.023379	0.76721	19
H_2O_2	0.38814	1.3439	0.2601	0.016172	0.78338	18
Metaldehyde inlet	0.3418	1.1963	0.2878	0.014242	0.79763	17
UV254 Abs inlet	0.3517	1.249	0.2789	0.014654	0.81228	16
DOC post AOP	0.99573	4.2558	0.0555	0.041489	0.85377	15

- O_3/H_2O sub process

Table C-13 Individual influence of predictors on net HAAFP contribution with *n*=21 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
Flow rate	0.097202	0.093196	0.7674	0.004418
H_2O_2/O_3	2.7875	3.0468	0.0974	0.1267
O_3	0.56366	0.55218	0.4633	0.025621
H_2O_2	0.69771	0.68781	0.4169	0.031714
Metaldehyde inlet	6.5287	8.8617	**0.0086**	**0.29676**
Turbidity inlet	4.5019	5.4029	**0.0307**	**0.20463**
UV254 Abs inlet	6.5901	8.9807	**0.0075**	**0.29955**
DOC inlet	8.3656	12.885	**0.0025**	**0.38026**
UV254 Abs post AOP	0.10197	0.097787	0.754	0.004635
DOC post AOP	7.3889	10.62	**0.0046**	**0.33586**

Table C-14 Sequential DistLM test of the predictors explaining net HAAFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
DOC inlet	8.3656	12.885	**0.0026**	**0.38026**	0.38026	21
DOC post AOP	2.4477	4.3761	**0.0488**	**0.11126**	0.49152	20
Turbidity inlet	2.0844	4.3511	0.0508	0.094747	0.58626	19
H_2O_2	1.2109	2.762	0.1104	0.05504	0.6413	18
UV254 Abs post AOP	1.5548	4.1713	0.0567	0.070672	0.71197	17
H_2O_2/O_3	1.4075	4.5688	0.0485	0.063977	0.77595	16
O_3	0.90754	3.3851	0.0805	0.041252	0.8172	15
UV254 Abs inlet	0.15024	0.54331	0.4753	0.006829	0.82403	14
Flow rate	0.036709	0.12445	0.7341	0.001669	0.8257	13

- H_2O_2/UV sub process

Table C-15 Individual influence of predictors on net HAAFP contribution with *n*=11 residual degrees of freedom according to the DistLM marginal test

Variable	SS (trace)	Pseudo-F	P	Prop.
O_3	0.32409	0.30533	0.5922	0.027008
H_2O_2	0.61259	0.59175	0.4493	0.051049
H_2O_2/O_3	0.1324	0.12272	0.7327	0.011033
Metaldehyde inlet	58.377	10.421	**0.0087**	**0.48648**
UV	46.241	68.962	**0.0223**	**0.38534**
Turbidity post O_3/H_2O_2	0.50499	0.48324	0.4979	0.042082
UV254 Abs post O_3/H_2O_2	32.975	4.168	0.0649	0.27479
DOC post O_3/H_2O_2	10.057	10.062	0.3316	0.083806

Table C-16 Sequential DistLM test of the predictors explaining net HAAFP contribution

Variable	SS (trace)	Pseudo-F	P	Prop.	Cumul.	res.df
Metaldehyde inlet	5.8377	10.421	**0.0082**	**0.48648**	0.4864	11
UV	3.3978	12.291	**0.0068**	**0.28315**	0.7696	10
O_3	0.30226	1.1048	0.3183	0.025188	0.7948	9
Turbidity post O_3/H_2O_2	0.19083	0.67212	0.4291	0.015902	0.8107	8
DOC post O_3/H_2O_2	0.22802	0.78114	0.4091	0.019002	0.8297	7
UV254 Abs post O_3/H_2O_2	0.16898	0.54091	0.4917	0.014082	0.8438	6
H_2O_2/O_3	0.61739	2.4559	0.1755	0.051449	0.8952	5
H_2O_2	0.34482	1.5121	0.2897	0.028735	0.9239	4