

CRANFIELD UNIVERSITY

MARINE DIANA

COMPARISON OF ADVANCED OXIDATION PROCESSES FOR
METALDEHYDE REMOVAL AND DOWNSTREAM DISINFECTION
BY-PRODUCT FORMATION

SCHOOL OF WATER, ENERGY, ENVIRONMENT AND
AGRIFOOD
MSc by Research

MASTER OF SCIENCE
Academic Year: 2016 - 2017

Supervisors: Peter Jarvis, Francis Hassard
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the degree of Master of Science by Research

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ABSTRACT

Metolaldehyde is the pesticide that has been found to exceed the maximum regulatory concentration of 0.1 µg/L in drinking water the most in the UK in recent years. As a result of the pesticide not being removed by conventional water treatment processes, there has been an interest in alternative treatments including advanced oxidation processes (AOPs). The latter have been reported as promising technologies for the removal of recalcitrant micropollutants. A large scale pilot study was carried out to compare the performance of two different AOPs for removing metolaldehyde from sources used to produce drinking water: the UV/H₂O₂ AOP and O₃/H₂O₂ followed by UV/H₂O₂ AOP. Since AOPs can increase the formation of disinfection by-products (DBP) under certain oxidation conditions, it is important to assess their impact on DBP precursors. For this purpose, the trihalomethane formation potential (THM FP) and the haloacetic acid formation potential (HAA FP) were measured upon chlorination of samples collected at different stages of the treatment. Both AOPs were shown to remove metolaldehyde efficiently achieving removals of up to 98%. They were able to reduce metolaldehyde concentration below the regulatory level with UV doses lower than 1 kWh/m³ for initial metolaldehyde concentrations of up to 2.10 µg/L. Concentrations as high as this value can be found in sources used to produce drinking water. The O₃/H₂O₂ - UV/H₂O₂ AOP was up to 33% more efficient than the UV/H₂O₂ AOP when applied at UV doses lower than 0.60 kWh/m³. In this work, the electrical energy applied to the system was expressed in kWh/m³ to enable the comparison of both AOPs at similar operating conditions. Both AOPs either increased or decreased the THM FP and the HAA FP between -85% and +155% with respect to the inlet. However, the quality of the inlet water better explained these changes rather than the UV and oxidant doses applied.

Keywords:

Hydroxyl radicals, UV/H₂O₂, O₃/H₂O₂, micropollutant degradation, pilot study, trihalomethanes, haloacetic acids, natural organic matter, chlorination

DECLARATION

Two Masters students were involved in this project and as a result, two different theses were produced. The present thesis compared the performance of two AOPs for metaldehyde removal and focused on their impact on DBPs. This included an investigation of the changes in background OM that can lead to increases or decreases in THM FP and HAA FP. The other thesis assessed the efficiency of the two AOPs for metaldehyde removal and provided an economical study of these AOPs. It did not include DBP data. The two students together collected the same samples from the pilot-plants and analysed them in the laboratory of the university, therefore both theses used the same primary data for metaldehyde removal. However, I, Marine Diana confirm that the analysis and interpretation of the data presented in this thesis is my own as well as the experiments performed on DBP formation and on the transformation of background OM during AOPs.

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LIST OF ABBREVIATIONS

•OH	Hydroxyl radicals
AOP	Advanced Oxidation Process
BCAA	Bromochloroacetic Acid
BDCAA	Bromodichloroacetic Acid
CDBAA	Chlorodibromoacetic Acid
COD	Chemical Oxygen Demand
DBAA	Dibromoacetic Acid
DBP	Disinfection By-Product
DBP FP	Disinfection By-Product Formation Potential
DCAA	Dichloroacetic Acid
DISTLM	Distance based Linear Models
DOC	Dissolved Organic Carbon
DWI	Drinking Water Inspectorate
FEEM	Fluorescence Excitation-Emission Matrix
FTIR	Fourier-Transform Infrared Spectroscopy
GAC	Granular Activated Carbon
GC-ECD	Gas Chromatography with Electron Capture Detector
H ₂ O ₂	Hydrogen peroxide
HAA	Haloacetic acid
HAA FP	Haloacetic acid Formation Potential
HPSEC	High Performance Steric Exclusion Chromatography
HPSEC-OCD	High Performance Steric Exclusion Chromatography with Organic Carbon Detection
LC-MS-MS	Liquid Chromatography - tandem Mass Spectrometry
LC-QTOF	Liquid Chromatography – Quadrupole Time Of Flight
MBAA	Monobromoacetic Acid
MCAA	Monochloroacetic Acid
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
NPOC	Non Purgeable Organic Carbon
O ₃	Ozone
OM	Organic Matter

RGF	Rapid Gravity Filtration
SUVA	Specific Ultraviolet Absorbance at 254 nm
TBAA	Tribromoacetic Acid
TCAA	Trichloroacetic Acid
THM	Trihalomethane
THM FP	Trihalomethane Formation potential
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
WTWs	Water Treatment Works

1 Introduction

There has been an increasing need to remove micropollutants from drinking water sources in the recent years because of their potential impact on human health and the increase in their occurrence (DWI, 2016a, 2016b, 2016c, 2016d, 2016e, Farré *et al.*, 2008; Morasch *et al.*, 2010; Pal *et al.*, 2010; Stuart *et al.*, 2012; Richardson and Ternes, 2014). Pesticides are among the most frequently found micropollutants in drinking water sources. The allowable concentration of pesticides in drinking water has been regulated in many countries. In Europe, the pesticide concentration must not exceed 0.1 µg/L for all individual pesticides and the maximum allowable limit for the sum of all pesticides is 0.5 µg/L (EU directive 98/83/EC).

However, in some countries it is difficult to meet these regulations all of the time as a result of the presence of specific pesticides in water sources. For example, the water quality regulator in England and Wales, the Drinking Water Inspectorate (DWI), reported that the pesticide metaldehyde was responsible for 94% of the water quality failures associated with pesticides in 2015 across all of the water supply regions of England and Wales (DWI, 2016a, 2016b, 2016c, 2016d, 2016e). Metaldehyde is a molluscicide that can be found in most slug and snail pellets (Autin *et al.*, 2012; Semitsoglou-Tsiapou *et al.*, 2016). As this pesticide is not efficiently removed by conventional technologies such as ozonation oxidation and granular activated carbon (GAC) filtration, it passes straight through many drinking water treatment processes (Autin *et al.*, 2012, 2013; Semitsoglou-Tsiapou *et al.*, 2016; Tang *et al.*, 2016).

Consequently, new water treatment technologies and adaptation of existing water treatment facilities are required to effectively remove metaldehyde from water (Wols and Hofman-Caris, 2012; Reddy and Kim, 2015; Jefferson *et al.*, 2016). There has been a growing interest in AOPs over the last twenty years, since they are promising technologies for the removal of recalcitrant pollutants and pesticides including metaldehyde (Autin *et al.*, 2013; Cheng *et al.*, 2016; Martinez *et al.*, 2016).

AOPs are oxidation processes that produce free OH radicals ($\bullet\text{OH}$), which are highly reactive and unselective (Pérez *et al.*, 2006; Tizaoui *et al.*, 2007; Ranade and Bhandari, 2014; Ribeiro *et al.*, 2015). During AOPs, the radicals react with the dissolved constituents, initiating a series of oxidation reactions which aim to completely mineralize the micropollutants. Ultimately, these can be degraded into carbon dioxide, water and inorganics (Badawy, Ghaly and Gad-Allah, 2006; Ribeiro *et al.*, 2015; Cheng *et al.*, 2016). However, in many cases complete mineralisation may not be achieved. Therefore, further treatments such as GAC filtration usually need to be applied after AOPs in order to adsorb the by-products formed.

Similarly, due to the non-selectivity and the strong oxidising capacity of the $\bullet\text{OH}$ radicals, AOPs have the potential to degrade almost all organic compounds in water (Tizaoui *et al.*, 2011). As a result, these processes can be used to prevent the downstream formation of DBPs – which are formed from the reaction between OM and disinfectants (Richardson and Ternes, 2011) – by degrading their precursors. However, as OM is typically present in the mg/L concentration range in water, AOPs have been reported to partially oxidise it when applied with the typical UV and oxidant doses used for micropollutant removal which are typically in the ng/L or $\mu\text{g/L}$ concentration range (Metz *et al.* 2011). As a result, increases in DBP formation have been observed following AOP treatments using those dose conditions (Bond, 2009; Metz *et al.*, 2011; Sarathy *et al.*, 2011). Therefore, a comprehensive assessment of the impact of AOPs on DBP formation is of particular importance.

As metaldehyde by-passes conventional water treatment processes, the DWI stated that by the end of 2019, water companies should implement processes in their water treatment works (WTWs) to reduce its concentration and meet the regulatory levels. As AOPs have been identified as efficient processes for this purpose, Severn Trent Water decided to undertake trials of two commercially available AOPs at pilot scale to determine the role that AOPs might play in treating their water sources. This thesis reports on the results obtained from these

trials, which will inform on the selection of technology to be implemented at their treatment plants for removing metaldehyde.

This thesis is structured in the form of two research papers. It comprises of an introduction stating the context of this work in Chapter 1. A literature review on the current state of the art on the efficiency of AOPs for metaldehyde removal and their impact on DBPs was undertaken in Chapter 2. The aims and objectives of the thesis are described in Chapter 2.5. The two paper-style research chapters are presented in Chapter 3 and 4. The first paper compared the efficiency of the UV/H₂O₂ and the O₃/H₂O₂ - UV/H₂O₂ AOPs for removing metaldehyde in water. The influence of the operating conditions on metaldehyde removal was assessed and the suitable process conditions for metaldehyde compliance were determined. The second paper assessed the impact of the two AOPs on downstream DBP formation. The influence of the operating conditions and the quality of the inlet water were studied. The transformations of background OM that can lead to changes in disinfection by-products formation potential (DBP FP) were also investigated. These two research papers are followed by an overall discussion in Chapter 5 and conclusions in Chapter 6. Finally, recommendations for further research are given in Chapter 7.

2 Literature review

2.1 Impact of process conditions on pesticide removal

This research and review focused on two specific AOPs: UV irradiation coupled with hydrogen peroxide (UV/H₂O₂) and UV irradiation coupled with ozone and hydrogen peroxide (O₃/H₂O₂ - UV/H₂O₂). These AOPs have been selected by the sponsor of the project because of their technology readiness in comparison to many other AOPs. Both the UV/H₂O₂ and the O₃/H₂O₂ - UV/H₂O₂ processes are commercially available at the scale required for municipal supply of drinking water.

During the UV/H₂O₂ process, micropollutants can be degraded according to an indirect and unselective reaction with •OH radicals (Ijpelaar *et al.*, 2002; Zaviska *et al.*, 2009; Tizaoui *et al.*, 2011). Hydrogen peroxide has a high absorbance between 200 and 250 nm (Figure 1). When irradiated by UV light, it produces •OH radicals according to equation (2-1) (Ijpelaar *et al.*, 2002; Zaviska *et al.*, 2009). The yield of •OH radicals is optimal between wavelengths of 200 and 250 nm as the UV light absorption is maximised within this range. Micropollutants in water can also be degraded by direct UV photolysis or by direct oxidation by hydrogen peroxide (Zaviska *et al.*, 2009). Among these mechanisms, the degradation by •OH radicals is the predominant one due to their high reactivity.

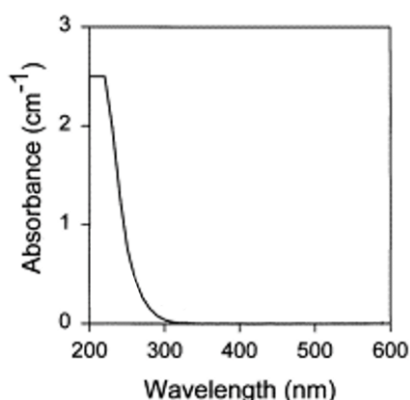


Figure 1. Absorption profile of hydrogen peroxide (Wang *et al.*, 2000)

It has been reported in the literature that during the UV/H₂O₂ process, the metaldehyde degradation rate increased with increasing the UV dose (Autin *et al.*, 2012, 2013; James *et al.*, 2014; Jefferson *et al.*, 2016) and the hydrogen peroxide concentration up to a certain limit, reported as 3.4 g/L (Autin *et al.*, 2012). Above this optimum concentration, the degradation rate dropped. This was believed to be due to the scavenging of •OH radicals by the excess hydrogen peroxide (equation(2-2)) (Autin *et al.*, 2012).



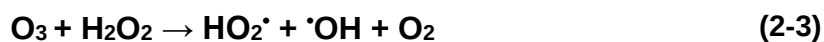
Autin *et al.* (2012) and Jefferson *et al.* (2016) both reported an optimal hydrogen peroxide dose of 272 mg/L to achieve more than 95% metaldehyde removal whereas Semitsoglou-Tsiapou *et al.* (2016) suggested an optimal dose of 15 mg/L (Table 1). It can be noted that a wide range of conditions lead to more than 95% metaldehyde removal. A possible reason for that is the wide range of initial metaldehyde concentrations tested in the different works. In addition it can be pointed out that the UV doses applied to reduce the dissolved organic carbon (DOC) were up to 20 times higher than the doses used to degrade metaldehyde.

Table 1. Optimal process conditions of the UV/H₂O₂ AOP for metaldehyde and DOC removal.

Initial metaldehyde concentration	Optimal [H ₂ O ₂]	UV dose	Removal achieved	Reference
0.3 mg/L	15 mg/L	1000 mJ/cm ²	97% (metaldehyde)	(Semitsoglou-Tsiapou <i>et al.</i> , 2016)
0.2 µg/L	> 2 mg/L	> 2000 mJ/cm ²	> 90% (metaldehyde)	(James <i>et al.</i> , 2014)
1 mg/L	272 mg/L	600 mJ/cm ²	95% (metaldehyde)	(Autin <i>et al.</i> , 2012)
		14,000 mJ/cm ²	40% DOC	
10 µg/L	272 mg/L	5000 mJ/cm ²	100% (metaldehyde)	(Jefferson <i>et al.</i> , 2016)
		40,000 mJ/cm ²	60% DOC	

The combination of UV, ozone and hydrogen peroxide in the same process may be attractive as the degradation of the micropollutants can occur according to several direct and indirect mechanisms (Lester *et al.*, 2011). During the O₃/H₂O₂ - UV/H₂O₂ process, the micropollutants can react with •OH radicals according to an indirect and unselective mechanism (Zaviska *et al.*, 2009; Tizaoui *et al.*, 2011; Ribeiro *et al.*, 2015; Shokri *et al.*, 2016). They can also be degraded directly by selective reactions with molecular ozone (Lester *et al.*, 2011; Tizaoui *et al.*, 2011; Ribeiro *et al.*, 2015; Shokri *et al.*, 2016); oxidised by the hydrogen peroxide (Zaviska *et al.*, 2009); or degraded by UV photolysis (Zaviska *et al.*, 2009; Lester *et al.*, 2011). Due to their high reactivity, the degradation by •OH radicals is the predominant pathway for micropollutant degradation.

During AOPs combining the use of ozone, hydrogen peroxide and UV irradiation, •OH radicals can be generated through different reactions. This can enhance their removal efficiency in comparison to other AOPs. The formation of •OH radicals can occur by reaction of hydrogen peroxide with ozone according to equation (2-3) (Lucas *et al.*, 2010; Lester *et al.*, 2011) or through direct photolysis of the hydrogen peroxide (equation (2-1) (Lucas *et al.*, 2010; Lester *et al.*, 2011).



Qin *et al.* (2015) reported that the performance of the O₃/H₂O₂ - UV/H₂O₂ process for removing micropollutants was mainly influenced by the hydrogen peroxide and ozone dosages as well as the contact time. Lucas *et al.* (2010) found that the degradation efficiency was enhanced when the hydrogen peroxide concentration was increased. However, above an optimum hydrogen peroxide concentration, a decline in the removal efficiency was observed. They reported that an optimal chemical oxygen demand (COD) to hydrogen peroxide mass ratio of 2 could reduce the total organic carbon (TOC) by 88%. This reduction in the removal efficiency may have come from the auto decomposition of the hydrogen peroxide according to equation (2-4) and the recombination of •OH radicals according to equation ((2-5) (Shokri *et al.*, 2016).





In addition, as in the UV/H₂O₂ process, the residual hydrogen peroxide can scavenge •OH radicals (equation (2-2)). All of these secondary reactions lead to a decrease in micropollutant removal when the hydrogen peroxide concentration was too high (Lucas *et al.*, 2010; Shokri *et al.*, 2016).

In the O₃/H₂O₂ AOP, the ozone dose and more specifically the H₂O₂/O₃ ratio had an influence on the removal efficiency. Paillard *et al.* (1988) suggested an optimum H₂O₂/O₃ mass ratio of 0.5 (Zaviska *et al.*, 2009), which agrees with Ijpelaar *et al.* (2002) who reported an optimal ratio between 0.5 and 1.

2.2 Relation between OM characteristics and DBP FP

The formation of DBPs during the final stage of drinking water treatment is another matter of concern for water companies (Jefferson *et al.*, 2016). DBP formation results from the reactions between disinfectants, such as chlorine, and natural organic matter (NOM), other organic contaminants or inorganic species (Richardson and Ternes, 2011). Among DBPs, two classes, trihalomethanes (THMs) and haloacetic acids (HAAs) are the most abundant on a weight basis in drinking water (Krasner *et al.*, 2006). It has been established that DBPs present health risks at elevated concentrations with suspected links to cancer, as well as reproductive and developmental effects (Richardson and Ternes, 2011). Nonetheless, the concentrations encountered in drinking water are much lower than the doses proven to cause damage to health.

In the UK, the maximum concentration for the sum of tribromomethane, bromodichloromethane, dibromochloromethane, and trichloromethane at the consumer's tap has been set at 100 µg/L (Council Directive 98/83/EC, 2000). The US Environmental protection agency set the limit at 80 µg/L as an average of samples for total THMs. HAAs are also regulated in the US, where the total of the five HAA species monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dichloroacetic

acids (DBAA) is currently regulated to a threshold of 60 µg/L (Bond *et al.*, 2011). It has been widely discussed in Europe and in the UK that future regulations may become more stringent and cover a wider range of DBPs, including HAAs (Bond *et al.*, 2009).

One of the approaches to limit DBP formation is to remove their precursors before disinfection (Bond *et al.*, 2011). As a result, many researchers have shown interest in characterising NOM and identifying DBP precursors. Although it is well established that the OM material present in water is the main precursor of DBPs, the composition of NOM is diverse and complex and its composition varies widely depending on the location and the season (Sharp *et al.*, 2006). The major chemical groups in NOM are humic species, carboxylic acids, amino acids, proteins and carbohydrates (Croue, Korshin and Benjamin, 2000, p.7). Among them, humic acids are the most abundant and they are part of the hydrophobic fraction of the NOM. Carbohydrates, amino acids and carboxylic acids are contained in the hydrophilic fraction of NOM (Bond, 2009).

The OM in water is generally characterised by the measure of the DOC and the UV absorbance at 254 nm. The combination of these two measures can also give information on the characteristics of the OM. The specific UV absorbance (SUVA) is defined as the UV absorbance at 254 nm per milligram of DOC. It gives an indication of the aromatic content of the OM as aromatic compounds and conjugated double bonds structures are mainly responsible for the UV absorbance at 254 nm (Lamsal *et al.*, 2011). Valencia *et al.* (2013) and Özdemir (2014) suggested that high SUVA values are related to hydrophobic compounds with higher apparent molecular weight. In disagreement with this, Zhao *et al.* (2006) reported a rise in SUVA values when the molecular weight of the OM decreased. Fluorescence spectroscopy can also be used to characterize the OM. As NOM compounds possess fluorescence characteristics, FEEM can give information on the chemical structure, and the functional groups that the OM is comprised of (Hao *et al.*, 2012). FEEM can be obtained by scanning the fluorescence intensity over a range of excitation and emission wavelengths. The different regions of the FEEM have been linked to the nature of the OM.

Even if the general link between the OM and the DBP formation is well known, the identity and the chemical structure of DBP precursors is not well established, making DBP formation in drinking water unpredictable (Bond *et al.*, 2011). Moreover, Bond *et al.* (2009) reported the absence of relationships between OM physicochemical properties and DBP formation.

Humic species and in particular humic and fulvic acids, have been identified as the major source of DBP precursors. Hao *et al.* (2012) reported positive relationships ($r^2 > 0.90$) between THM FP and HAA FP and humic and fulvic acids concentrations. Valencia *et al.* (2013), Yang *et al.* (2015) and Li *et al.* (2016) have all found a strong correlation ($r^2 > 0.890$, $r^2 > 0.874$ and $r^2 > 0.73$ respectively) between the fluorescence intensity of humic-like compounds and the THM FP.

Bond (2009) suggested that the potential of OM compounds to form DBPs was defined by their chemical structure. Generally, DBP precursors have unsaturated structures (Hao *et al.*, 2012; Özdemir, 2014; Yang *et al.*, 2015). Activated aromatics (substituted benzene, substituted phenol), β -dicarbonyls, and amino acids have been identified as the major classes of DBP precursors (Bond, 2009). Among them, activated aromatics produce significant amounts of THMs and TCAA and are therefore the most important DBP precursors (Bond, 2009). Specifically, resorcinol, a hydrophobic compound, is one important THM precursor (Bond, 2009). One mole of resorcinol can form 0.96 moles of THMs (Bond *et al.*, 2009). Similarly, Zhao *et al.* (2006) reported a linear correlation between the aromatic carbon content of the OM and the halogenated DBP formation. Bond (2009) also considered β -diketones and β -ketoacids as important DBP precursors. On the other hand, several researchers reported the poor correlation between protein-like species and DBP FP (Beggs *et al.*, 2009; Li *et al.*, 2016).

There are conflicting reports about the hydrophobic nature of THM and HAA precursors in natural waters (Liang *et al.*, 2003). Bond *et al.* (2011) and Kent *et al.* (2011) observed that the major source of DBP precursors (75%) was associated with the hydrophobic fraction and specifically the hydrophobic acid fraction of NOM. On the other hand, Metz *et al.* (2011) found that the hydrophilic

and polar NOM could produce significant amounts of DBPs especially HAAs. Finally, Bond (2009) suggested that the transphilic fraction may also contain reactive THM precursors as it has a high content of β -dicarbonyl acids species.

Gerrity *et al.* (2009), Özdemir (2014) and Zhao *et al.* (2006) all observed a correlation between the presence of low molecular weight compounds (< 1000 Da) and high THM FP, indicating that low molecular weight OM are important THM precursors. Similarly, Özdemir (2014) reported an increase in the THM FP when the molecular weight was reduced.

2.3 Impact of AOPs on OM degradation and DBP formation

As AOPs are unselective processes, they are also able to degrade OM (Bond *et al.*, 2009). It has been reported that they are capable of mineralizing DBP precursors (Chin and Bérubé, 2005; Toor and Mohseni, 2007). As an example, Bond (2009) reported that a range of NOM surrogates could be completely mineralised by the UV/H₂O₂ AOP at a UV dose of 50 000 mJ/cm². However, this dose is much higher than doses that would be economically feasible for water treatment. For example, the UV doses used for disinfection are typically in the range 50 - 200 mJ/cm².

Despite their relative unselectivity, $\bullet$ OH radicals tend to react faster with compounds containing unsaturated bonds than with those comprising single bonds (Westerhoff *et al.*, 1999). In addition, Sarathy *et al.* (2011) reported that AOPs could open the aromatic rings contained in the NOM and reduce their degree of substitution.

Li *et al.* (2013) observed that the protein-like compounds were more easily removed by the Fenton AOP than humic-like compounds. Valencia *et al.* (2013) found that the UV/TiO₂ AOP preferentially broke down the high molecular weight OM compounds with a high UV absorbance at 254 nm to form lower molecular weight compounds. This is consistent with the findings of Bond *et al.* (2009) who reported that the degradation of NOM by UV/H₂O₂ AOP treatment mainly lead to the formation of small acidic compounds. Valencia *et al.* (2013) also reported a reduction in aromatic halogen attack sites, and the elimination of quinones during

UV/TiO₂ treatment. Moreover, the UV/TiO₂ AOP caused a reduction in the fluorescence intensity of humic-like OM.

Although AOPs are promising technologies for the removal of DBP precursors, Metz *et al.* (2011), Bond (2009) and Sarathy *et al.* (2011) all reported an increase in DBP formation when AOPs were applied with low oxidant or UV doses. These conditions lead to incomplete mineralisation of NOM. Indeed, weak oxidation conditions (low oxidant or UV doses) can fragment the aromatic rings and split the double bonds of OM compounds. The resulting compounds have more reactive sites, which can increase DBP formation during chlorination (Metz *et al.* 2011). Specifically, Bond (2009) observed that incomplete mineralisation of amino-acids produced a significant increase in HAA FP. As a result, AOPs need to be applied with sufficient UV and chemical doses to oxidise NOM more completely and hence reduce DBP FP (Toor and Mohseni, 2007; Sarathy *et al.*, 2011; Mayer *et al.*, 2015). In agreement with these findings, Toor and Mohseni, (2007) reported that following the UV/H₂O₂ AOP, the THM FP increased for weak oxidation conditions (UV < 1000 mJ/cm² and [H₂O₂] = 4 mg/L) whereas it decreased for strong oxidation conditions (UV > 1500 mJ/cm² and [H₂O₂] = 23 mg/L) (Table 2). Gerrity *et al.* (2009) made similar findings for the UV/TiO₂ AOP: they reported an increase in THM FP for UV doses lower than 5 kWh/m³ and a decrease in THM FP at UV doses higher than 20 kWh/m³. A similar trend has been observed for HAAs during the UV/H₂O₂ AOP (Table 2). Therefore, it is important to assess the impact of AOPs on DBP precursors in addition to evaluating their performance for micropollutant removal.

Table 2. Impact of the process conditions of the UV/H₂O₂ AOP on DBP FP.

Process conditions	Outcome	Reference
UV > 1000 mJ/cm ² [H ₂ O ₂] > 23 mg/L	Decrease in DBP FP	(Toor and Mohseni, 2007)
UV > 2500 mJ/cm ²		(Sarathy <i>et al.</i> , 2011)
UV < 1000 mJ/cm ² [H ₂ O ₂] = 4 mg/L	Increase in THM FP for weak oxidation conditions	(Toor and Mohseni, 2007)
UV > 1500 mJ/cm ² [H ₂ O ₂] = 23mg/L	Decrease in THM FP for strong oxidation conditions	(Toor and Mohseni, 2007)
UV = 3000 mJ/cm ² [H ₂ O ₂] = 10–20 mg/L	Decrease in THM FP	(Bond <i>et al.</i> , 2009)
UV < 1000 mJ/cm ² [H ₂ O ₂] = 4 & 23 mg/L	Increase in HAA FP	(Toor and Mohseni, 2007)
UV > 2500 mJ/cm ²	Decrease in HAA FP	(Toor and Mohseni, 2007)
UV > 500 mJ/cm ² [H ₂ O ₂] = 15 mg/L		(Sarathy and Mohseni, 2010)

2.4 Need for research

Few papers were found on the degradation of metaldehyde in water by AOPs. Among them, only a small number used the UV/H₂O₂ AOP and the others dealt with different AOPs such as UV/TiO₂ (Autin *et al.*, 2012, 2013; Jefferson *et al.*, 2016; Semitsoglou-Tsiapou *et al.*, 2016). Semitsoglou-Tsiapou *et al.* (2016) also reported the scarce information on metaldehyde degradation by the UV/H₂O₂ process in the literature. Additionally, most of the works dealing with degradation of metaldehyde by the UV/H₂O₂ process were performed at bench scale. No published research has been found about AOPs comprising the combination of UV light, ozone and hydrogen peroxide processes for metaldehyde degradation.

Several studies have been found on the performance of UV/H₂O₂ process for removing NOM and DBP precursors. Some papers compared the impact of different AOPs on DBP formation (Jefferson *et al.*, 2016; Chu *et al.*, 2016) but to our knowledge, none of them compared the impact of UV/H₂O₂ and UV/O₃/H₂O₂ AOPs on DBP formation potential as the information about UV/O₃/H₂O₂ processes is scarce.

2.5 Aims and objectives

This work aims to critically evaluate the performance of two different AOPs to determine the key process characteristics required for metaldehyde removal and the resultant impact on DBP formation potential.

This aim has been split into the following objectives:

- Assessing the impact of UV light used in combination with different oxidant chemicals on metaldehyde removal.
- Identifying the UV and oxidant doses that achieve a reduction in metaldehyde concentration below the regulatory level.
- Comparing the efficiency of both AOPs for metaldehyde removal.
- Investigating how the process variables of the AOPs and the quality of the inlet water influence THM FP and HAA FP.
- Understanding the transformations of background OM that can explain a change in DBP FP following the treatment by AOPs.
- Comparing the impact of both AOPs on OM transformation and DBP formation.

3 Comparison of the performance of UV/H₂O₂ and O₃/H₂O₂ - UV/H₂O₂ AOPs at pilot scale for metaldehyde removal

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Abstract

A large scale pilot study was carried out to compare the performance of the UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ process for removing metaldehyde from sources used to produce drinking water. The latter process was a combination of two AOPs: O₃/H₂O₂ AOP followed by UV/H₂O₂. The efficiency of these processes together with the influence of the UV, ozone and hydrogen peroxide doses were assessed for different concentrations of metaldehyde in the inlet water. The performance of the two AOPs was compared at similar UV and hydrogen peroxide doses. Both AOPs were shown to remove metaldehyde efficiently by up to 98%. In the O₃/H₂O₂ - UV/H₂O₂ AOP, most of the removal was achieved by the O₃/H₂O₂ sub-process. The efficiency of the UV/H₂O₂ AOP was improved with increasing the UV and the hydrogen peroxide doses whereas the O₃/H₂O₂ - UV/H₂O₂ AOP was mostly impacted by the ozone and UV doses in the ranges that were tested in this work. Both AOPs were efficient at reducing the metaldehyde concentration below the regulatory level of 0.1 µg/L for initial metaldehyde concentrations of up to 2.10 µg/L with UV doses lower than 1 kWh/m³. The O₃/H₂O₂ - UV/H₂O₂ AOP was up to 33% more efficient than the UV/H₂O₂ AOP at UV doses below 0.60 kWh/m³. However, the costs implied in each AOP to reduce metaldehyde concentration below the regulatory level will be determinant in the choice of process to be implemented at full scale.

Key words:

Hydroxyl radicals, oxidation, micropollutant degradation, pilot study.

3.1 Introduction

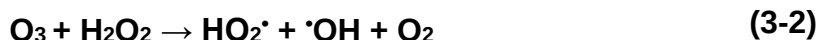
Due to the increase in their occurrence and their impact on human health, micropollutants including pesticides need to be monitored and removed from water sources used to produce drinking water (DWI, 2016a, 2016b, 2016c, 2016d, 2016e, Farré *et al.*, 2008; Morasch *et al.*, 2010; Pal *et al.*, 2010; Stuart *et al.*, 2012; Richardson and Ternes, 2014). The concentration of pesticides in water is regulated in Europe and must be lower than 0.5 µg/L but the amount of each individual pesticide must not exceed 0.1 µg/L (Council Directive 98/83/EC, 2000).

However, some pesticides have been found in drinking water at higher concentrations than the permitted level. For instance, the water quality regulator in England and Wales, the DWI, has reported that metaldehyde was the pesticide that most exceeded the permitted concentration level in the recent years (DWI, 2016a, 2016b, 2016c). Metaldehyde is a molluscicide that can be found in most slug and snail pellets (Autin *et al.*, 2012; Semitsoglou-Tsiapou *et al.*, 2016). In 2015, across all of the water supply regions of England and Wales, metaldehyde was responsible for 94% of the water quality failures associated with pesticides (DWI, 2016a, 2016b, 2016c, 2016d, 2016e). Therefore, metaldehyde is not efficiently removed by conventional water treatment processes such as ozonation oxidation and GAC filtration (Autin *et al.*, 2012, 2013; Semitsoglou-Tsiapou *et al.*, 2016; Tang *et al.*, 2016).

Consequently, new treatment processes have to be implemented in order to control the metaldehyde concentration in water (Wols and Hofman-Caris, 2012; Reddy and Kim, 2015; Jefferson *et al.*, 2016). Due to their non-selectivity, AOPs have shown to be efficient at removing recalcitrant pollutants such as metaldehyde (Autin *et al.*, 2013; Cheng *et al.*, 2016; Martinez *et al.*, 2016). AOPs are oxidation processes that produce highly reactive and unselective free •OH radicals (Pérez *et al.*, 2006; Ranade and Bhandari, 2014; Ribeiro *et al.*, 2015). The radicals oxidise the micropollutants by a succession of oxidation reactions which aim to completely degrade the pollutants into carbon dioxide, water and inorganics (Badawy *et al.*, 2006; Ribeiro *et al.*, 2015; Cheng *et al.*, 2016). This research has investigated two commercial AOP technologies at pilot-scale:

UV/H₂O₂ and O₃/H₂O₂ followed by UV/H₂O₂. The O₃/H₂O₂ process was followed by the UV/H₂O₂ AOP to see how metaldehyde was degraded across two different processes and if there was any benefit in having the O₃/H₂O₂ AOP before the UV/H₂O₂ process. These AOPs have been selected following a comprehensive technology assessment because of their technology readiness in comparison to many other AOPs.

In the UV/H₂O₂ process, the •OH radicals are produced when the hydrogen peroxide is irradiated by UV light between 200 and 250 nm (equation (3-1)) (Ijpelaar *et al.*, 2002, Zavisla *et al.* 2009). The combination of UV, ozone and hydrogen peroxide in the O₃/H₂O₂ - UV/H₂O₂ process may be attractive as •OH radicals can be generated through different pathways: in addition to their production through direct photolysis of the hydrogen peroxide (equation (3-1)), •OH radicals can be produced by the reaction of hydrogen peroxide with ozone according to equation (3-2) (Lucas *et al.*, 2010; Lester *et al.*, 2011).



The effectiveness of the UV/H₂O₂ AOP for removing metaldehyde from water has already been proven in the past. Autin *et al.* (2012), James *et al.* (2014), Jefferson *et al.* (2016) and Semitsoglou-Tsiapou *et al.* (2016) all reported metaldehyde removals greater than 90% under optimised UV and hydrogen peroxide doses. Few studies have been found on metaldehyde removal by AOP treatment combining the use of ozone, hydrogen peroxide and UV (Vulpe *et al.*, 2015) but the combination of these variables has been shown to efficiently remove several pharmaceuticals in water (Lester *et al.*, 2011; Qin *et al.*, 2015).

This study builds on previous findings by critically evaluating and comparing the performance of two different AOPs at pilot-scale in order to determine the key process characteristics required for metaldehyde removal. To this end, the impact of the UV irradiation applied in combination with different oxidant chemicals was

studied as well as the operating conditions required to reduce the metaldehyde concentration below the regulatory concentration of 0.1 µg/L.

3.2 Materials and methods

3.2.1 Chemicals and reagents

The metaldehyde (99%) and the extrapure sodium sulphite were acquired from Fisher Scientific. The metaldehyde spiking solution was prepared in ultrapure water (Purelab Option – S7/15, TOC < 3 ppb).

3.2.2 Description of pilot-scale experiments

Two AOPs were assessed at pilot-scale. The UV/H₂O₂ pilot plant was supplied by Trojan Technologies. The UVPhox 8AL20 pilot unit comprised 8 low pressure lamps and could treat between 1 and 5 m³/h of water. The dimensions of the unit were 3.38 m (L) x 1.32 m (W) x 1.93 m (H). Mixing was performed before the reactor. The second process assessed was supplied by Xylem Water Solutions and comprised two individual AOPs in series: O₃/H₂O₂ followed UV/H₂O₂. The water was first treated by ozone and an excess of hydrogen peroxide and was then transferred to a UV reactor. In the UV reactor, the hydroxyl radicals were formed by reaction with the residual hydrogen peroxide from the first AOP. The O₃/H₂O₂ AOP was carried out in a Wedeco Promix system of dimensions 2.90 m (L) x 0.95 m (W) x 1.38 m (H). This unit was designed to enhance the ozone transfer efficiency thanks to its multiple transfer points. The ozone and the hydrogen peroxide were mixed with the water in this unit before it went to the UV reactor. The ozone was transferred to the system as a gas and the dose was measured by deducting the off gas from the inlet concentration. The second AOP was performed in a MiPRO photo Wedeco UV system LBX 10 of 13 L which comprised 3 Spektrotherm® UV lamps and was able to treat water between 0.5 and 4 m³/h. The residence times varied between 19 and 78 seconds in the LBX 10 UV reactor. All the lamps used in these pilots were new at the beginning of the trial. The pilot plants were supplied with partially treated reservoir water from the real WTWs in which they were located (in the midlands, UK). The water feeding the pilot plants had been treated by coagulation, clarification and rapid

gravity filtration (RGF). Following the treatment by the AOPs, the water was filtered through a GAC contactor. Samples were collected before the AOPs, between AOPs and GAC and after GAC filtration (Figure 2). A sample was also collected between the two individual sub-processes of the O_3/H_2O_2 - UV/H_2O_2 AOP. The residual hydrogen peroxide was measured onsite in the samples collected between AOP and GAC using a Palintest Photometer with potassium iodide reagent tablets. The reaction was quenched with sodium sulphite using the concentration required to stoichiometrically neutralise the hydrogen peroxide. 3.7 mg/L of sodium sulphite were added per mg/L of hydrogen peroxide measured in each sample. The samples were then kept in cold boxes onsite until they were transferred to a cold room in the laboratory before their analysis. The variables in both AOPs were the initial metaldehyde concentration, the oxidant doses, the flow rate and the UV dose (Table 3). In the Trojan pilot-plant, the UV irradiation was set by adjusting the power of the UV lamps. As the UV dose delivered by unit of surface was not provided, the UV electric consumption of both processes was normalised by the flow rate. Therefore, the UV doses were expressed in this work in kWh/m^3 to enable the comparison of both AOPs at similar operating conditions.

Table 3. Process variables applied to AOP pilot plants.

Process variables	AOP Treatment Processes	
	UV/ H_2O_2	H_2O_2/O_3 - H_2O_2/UV
Initial metaldehyde concentration	0.10 - 0.15 $\mu g/L$ (Environmental concentration) to 2 $\mu g/L$	
Hydrogen peroxide dose	10 - 45 mg/L	8 - 30 mg/L
Ozone dose	-	2 - 10 mg/L
Flow rate	2 - 3.5 m^3/h	0.6 - 2.5 m^3/h
UV dose	0.35 - 1.00 kWh/m^3	0 - 1.10 kWh/m^3

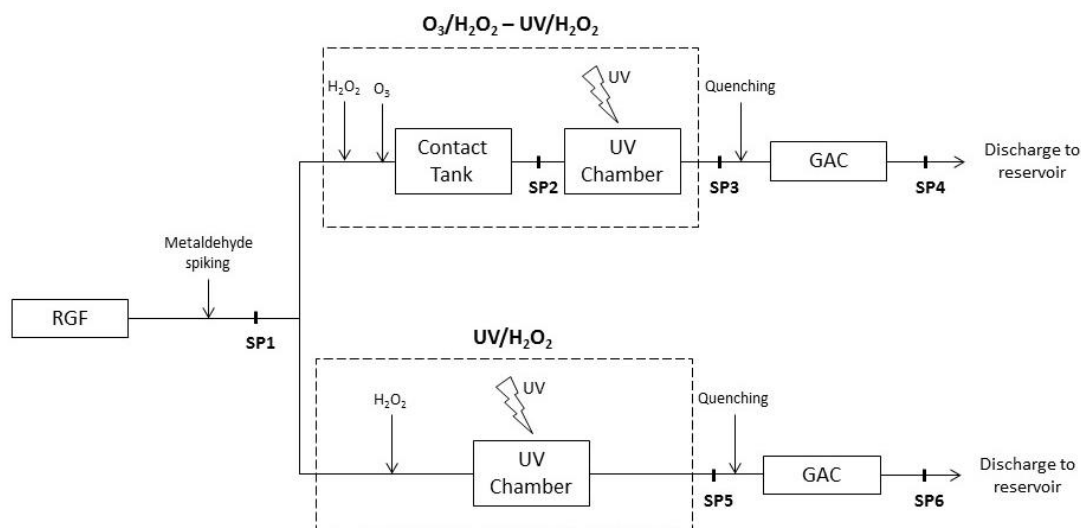


Figure 2. Process flow diagrams of the AOP pilot plants. SP1 - SP8 represent the sample points across the pilots.

3.2.3 Analytical methods

The absorbance at 254 nm was measured in the samples with a Jenway 6715 UV-Vis spectrophotometer, the turbidity with a Hach 2100N Turbidity Meter and the DOC was measured as non-purgeable organic carbon (NPOC) using a Shimadzu TOC-V CSH TOC analyser. The metaldehyde concentration was determined by liquid chromatography - tandem mass spectrometry (LC-MS-MS) on an Agilent LC-MSMS 6490 by Affinity Water Laboratory. The metaldehyde was detected in positive mode using the transitions $215 > 39$ and $199 > 67$. 99 μL of sample were injected at a flowrate of 0.45 mL/min on a Poroshell 120 EC-C18 2.7m 75 mm x 2.1 mm column. The mobile phase was a gradient of acetonitrile and a solution of 0.1% acetic acid. The limit of detection was 0.009 $\mu\text{g/L}$. The analysis were carried out in duplicate. The standard errors in measurement were 6.4% and 3.1% for DOC and UV absorbance respectively.

3.2.4 Statistical tests

The statistical analysis of the data set was performed using the Primer software, which comprises resemblance-based methods, with PERMANOVA+ add-on package. The distance-based linear model (DISTLM) was selected as it can analyse and model the relationships between response variables and predictor

variables. For this purpose, a resemblance matrix, which describes the dissimilarities among a set of samples depending on the values of their response variables, is calculated (Anderson *et al.*, 2008). The DISTLM was used to assess whether the operating conditions (flow rate and UV, ozone and hydrogen peroxide doses) and the predictor variables (DOC, Turbidity, and UV absorbance at 254 nm measured in the inlet) explained a significant proportion of the variation in the values of the response variable (metaldehyde removal).

The DISTLM comprised two different tests: the marginal and the sequential tests. The marginal tests indicated how much each of the variable taken alone explained the variation in the response variables. In this test each variable was assessed independently of the other variables. In the sequential tests, each test examined whether adding one particular variable contributed significantly to the explained variation, given that the previous variables were already included in the model (Anderson *et al.*, 2008).

In the marginal tests, the 'Prop.' value indicated the proportion of the variation in response variables that was explained by each variable and the P value indicated how statistically significant was that proportion. The P-values indicate the veracity of the hypothesis of no relationship between the process variables or predictor variables and the response variables (Anderson *et al.*, 2008). P values lower than 0.05 were considered as statistically significant in this work. In the sequential tests, the 'Prop.' value indicated the increase in the proportion of explained variation attributable to each variable that was added, and the 'Cumul.' value provided a running cumulative total (Anderson *et al.*, 2008). The 'res.df' value indicated the residual degrees of freedom of each test.

3.3 Results and discussion

3.3.1 Metaldehyde removal efficiency of the AOPs

Both AOPs were efficient at degrading metaldehyde with removals of up to 97% and 98%. The maximum removals were obtained for the highest oxidant and UV doses tested and were similar for both processes (Table 4). The metaldehyde

removal achieved by the UV/H₂O₂ AOP varied between 38% - for an inlet of 0.53 µg/L, a hydrogen peroxide dose of 13 mg/L and a UV dose of 0.41 kWh/m³ at a flow rate of 3 m³/h - and 98% - for an inlet of 2.11 µg/L a hydrogen peroxide dose of 45 mg/L and a UV dose of 0.94 kWh/m³ at a flow rate of 2 m³/h. The maximum removal obtained was similar to that reported by Semitsoglou-Tsiapou *et al.* (2016) however it was obtained at a lower hydrogen peroxide dose of 15 mg/L compared to 45 mg/L in this work. A further increase in the removal was observed after the GAC treatment where an overall removal between 94% and 99.6% was achieved. Turning to the O₃/H₂O₂ - UV/H₂O₂ AOP, the removal after the overall process varied between 55% - for an inlet of 0.80 µg/L, a hydrogen peroxide dose of 10 mg/L, an ozone dose of 3 mg/L and a UV dose of 0.83 kWh/m³ at a flow rate of 2.5 m³/h - and 97% - for an inlet of 2.11 µg/L, a hydrogen peroxide dose of 24 mg/L, an ozone dose of 7.2 mg/L and a UV dose of 1.03 kWh/m³ applied at a flow rate of 2.5 m³/h. Qin *et al.* (2015) reported a similar removal of 94.1% by the O₃/UV/H₂O₂ AOP for the pharmaceutical berberine hydrochloride.

When broken down into its two individual sub-processes, it was apparent that the O₃/H₂O₂ sub-process achieved more removal than the UV/H₂O₂ sub-process. This was because the latter received a lower metaldehyde concentration than the former. The O₃/H₂O₂ sub-process removed between half and all of the total metaldehyde degraded during this AOP. It decreased metaldehyde concentration between 38% - for an inlet of 0.14 µg/L, a hydrogen peroxide dose of 11 mg/L, an ozone dose of 2.1 mg/L and a UV dose of 0.83 kWh/m³ at a flow rate of 2.5 m³/h - and 96% - for an inlet of 2.23 µg/L, a hydrogen peroxide dose of 24 mg/L and an ozone dose of 5.4 mg/L at a flow rate of 0.6 m³/h. A further increase in the metaldehyde removal was observed after the UV/H₂O₂ process as more radicals were formed and could degrade metaldehyde during the second sub-process. The maximum metaldehyde removal achieved by the UV/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP was 79% for an initial metaldehyde inlet of 0.53 µg/L, an initial hydrogen peroxide dose of 18 mg/L, an initial ozone dose of 6.0 mg/L and a UV dose of 1.10 kWh/m³ applied at a flow rate of 2.5 m³/h. This removal is lower than the highest removal achieved by the O₃/H₂O₂ process

because it received a lower metaldehyde concentration. A further increase in the removal was observed after the GAC treatment where a removal between 98% and 99.6% was achieved.

However, for both AOPs, a high metaldehyde removal did not necessarily imply the production of a metaldehyde-compliant water. This was dependent on the concentration of metaldehyde in the inlet. For a metaldehyde inlet concentration of 0.14 µg/L, a removal of 29% was enough to reduce metaldehyde below the regulatory concentration of 0.1 µg/L but the metaldehyde removal required for an initial metaldehyde concentration of 2.30 µg/L was 96%.

Table 4. Operating conditions observed to achieve maximum metaldehyde removal for each AOP and sub-process.

		AOP		
		UV/H ₂ O ₂	O ₃ /H ₂ O ₂ - UV/H ₂ O ₂	
			Overall	O ₃ /H ₂ O ₂
Operating conditions	Maximum removal (%)	98%	97%	96%
	H ₂ O ₂	45 mg/L	24 mg/L	24 mg/L
	O ₃	-	7.2 mg/L	5.4 mg/L
	UV	0.94 kWh/m ³	1.03 kWh/m ³	-
	Flow rate	2 m ³ /h	2.5 m ³ /h	0.6 m ³ /h
	Metaldehyde inlet	2.11 µg/L	2.11 µg/L	2.23 µg/L

3.3.2 Influence of the process variables on metaldehyde removal

In the UV/H₂O₂ AOP, increasing the hydrogen peroxide dose enhanced metaldehyde removal (Figure 3a, Figure 3b, Figure 3c), which is in agreement with what has been found in the literature (James *et al.* 2014). For a metaldehyde inlet concentration of 0.5 µg/L and a UV dose of 0.41 kWh/m³ applied at a flow rate of 3 m³/h, an increase in the hydrogen peroxide dose from 13 to 42 mg/L raised the metaldehyde removal by 23% (Figure 3b). However, at UV doses higher than 0.66 kWh/m³, raising the hydrogen peroxide dose between 30 and 40 mg/L only resulted in a slight improvement in the efficiency, and in some cases, the metaldehyde removal was decreased (Figure 3a, Figure 3c). Raising the UV dose of the UV/H₂O₂ AOP up to 0.85 kWh/m³ also enhanced the metaldehyde removal. The later was increased by up to 44% when the UV dose was raised from 0.36 to 0.89 kWh/m³ at a flow rate of 3.5 m³/h for an inlet of 0.139 µg/L and a hydrogen peroxide dose between 15 and 20 mg/L (Figure 3a). A

further increase in the UV dose between 0.85 and 1.00 kWh/m³ only resulted in a slight or no increase in metaldehyde removal, especially for hydrogen peroxide doses higher than 30 mg/L. Despite the consistent trend of enhancing the removal when increasing the UV dose, an exception was observed for all of the trials performed. For example, at 0.60 kWh/m³, the removal was higher than for a UV dose of 0.66 kWh/m³ (Figure 3a, Figure 3b, Figure 3c). This was because these UV doses were not applied at the same flow rate: the former UV dose was applied at 2.5 m³/h whereas the latter was applied at 2 m³/h. This phenomenon was clearly shown when plotting the metaldehyde removal at different flow rates for the same UV dose (Figure 3d, Figure 3e). An increase in the flow rate between 2.5 and 3.5 m³/h enhanced the efficiency of the process by up to 10%. The reason for this was thought to be that there was more turbulence in the UV reactor at the higher flow rates. Hence the hydrogen peroxide could be more homogeneously spread within the water hence enhancing the •OH radicals' production and the removal. The general trends could be seen in Figure 3 but additional graphs were obtained on different days of the trial and are presented in Appendix A.

The DISTLM tests confirmed that the UV dose, the hydrogen peroxide dose and the flow rate taken independently had a significant impact on metaldehyde removal in the UV/H₂O₂ AOP. They explained respectively 32%, 13% and 13 % of the total variation in metaldehyde removal with P values of 0.0001. When considering the variables and their interactions, the change in the hydrogen peroxide dose added 11% of the total variation in metaldehyde removal once the UV dose was already fitted to the model. Together, these two variables significantly explained 43% of the total variation in metaldehyde change with P values of 0.0001. These tests were performed on a total of 127 samples. The full DISTLM test results are presented in Appendix B.

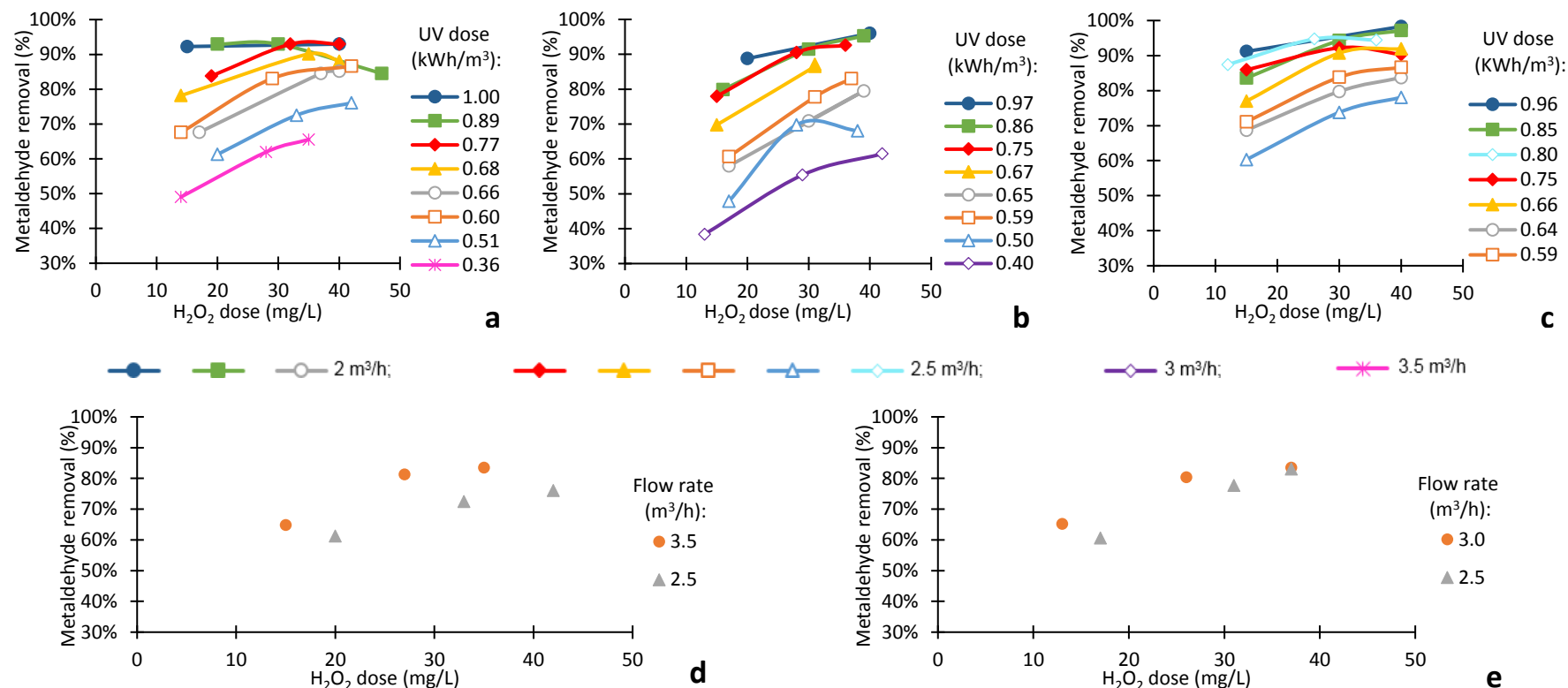


Figure 3. Influence of the operating conditions of the UV/H₂O₂ AOP on metaldehyde removal: Influence of the hydrogen peroxide and UV doses for metaldehyde inlet concentrations of 0.14 µg/L (a), 0.53 µg/L (b) and 2.2 µg/L (c). The UV doses were applied at different flowrates. Influence of the flow rate and the hydrogen peroxide dose for an inlet of 0.14 µg/L metaldehyde and a UV dose of 0.50 kWh/m³ (d) and for an inlet of 0.5 µg/L metaldehyde and a UV dose of 0.57 kWh/m³ (e). The lines linking the data points are for illustrative purpose only. The values of the UV dose and the flow rate in the legend are the mean of the measured values of each data point.

In the O_3/H_2O_2 - UV/ H_2O_2 AOP, a simultaneous increase in the ozone and hydrogen peroxide doses enhanced the metaldehyde removal (Figure 4a, Figure 4b, Figure 4c). An increase in the hydrogen peroxide dose from 10 to 19 mg/L with a constant H_2O_2/O_3 mass ratio of 3, at a UV dose of 0.81 kWh/m³ and a metaldehyde concentration in the inlet of 0.80 µg/L resulted in an increase in the metaldehyde removal by 35% (Figure 4b). The reason for this was that when the ozone and hydrogen peroxide doses were increased at a constant ratio, more •OH radicals were produced hence the metaldehyde degradation was enhanced. The performance of the O_3/H_2O_2 - UV/ H_2O_2 AOP was also influenced by the UV dose. An increase in the UV dose from 0.56 to 1.03 kWh/m³, for a metaldehyde initial concentration of 2.14 µg/L, an hydrogen peroxide dose of 14 mg/L and an ozone dose of 3.3 mg/L, resulted in 9% more metaldehyde removal (Figure 4c). The hydrogen peroxide dose did not seem to have a major impact on the metaldehyde removal for constant ozone doses (Figure 4d, Figure 4e, Figure 4f). The general trends can be seen in Figure 4 but additional graphs were obtained on different days of the trial and are presented in Appendix A.

The DISTLM tests confirmed that the UV, ozone and hydrogen peroxide doses taken independently had a significant impact on the metaldehyde removal in the overall O_3/H_2O_2 - UV/ H_2O_2 AOP. They explained 54%, 45% and 34% of the total variation in metaldehyde removal respectively, with P values lower than 0.0002. When considering the variables and their interactions, the ozone dose added 25% of the total variation in metaldehyde removal once the UV dose was already fitted to the model. The addition of the hydrogen peroxide dose in the model only added 3% of the total variation. This was because the ozone dose was controlling the •OH radical production in both sub-processes. Indeed the ozone dose defined the hydrogen peroxide consumed in the first sub-process hence having an impact on the hydrogen peroxide available to form radicals in the second sub-process. The •OH radicals are formed by the reaction of 1 mole of hydrogen peroxide with 1 mole of ozone (3-2). Therefore, the stoichiometric H_2O_2/O_3 mass ratio to form •OH radicals is 0.7. Similarly, the optimum H_2O_2/O_3 mass ratios found in literature were between 0.5 and 1 (Ijpelaar *et al.*, 2002; Paillard *et al.* 1988 in Zaviska *et al.*, 2009). However in this trial, the ratios assessed were higher than 1. The

reason for that was the need to have a residual hydrogen peroxide concentration after the first sub-process in order to form $\bullet\text{OH}$ radicals upon irradiation by UV in the second sub-process. At these ratios, the hydrogen peroxide was in excess compared to the ozone. As a result, the ozone dose was driving the production of $\bullet\text{OH}$ radicals in the first sub-process hence impacting the residual hydrogen peroxide available for $\bullet\text{OH}$ formation in the second sub-process. An alternative to optimise the efficiency of the process would be to add the stoichiometric $\text{H}_2\text{O}_2/\text{O}_3$ mass ratio of 0.7 in the $\text{O}_3/\text{H}_2\text{O}_2$ AOP, and to add a second dosing of hydrogen peroxide in the UV reactor for the second AOP. Together, the UV and ozone doses significantly explained 79% of the total variation in the metaldehyde removal with P values of 0.0001. These tests were performed on a total of 64 samples. The full DISTLM test results are presented in Appendix B.

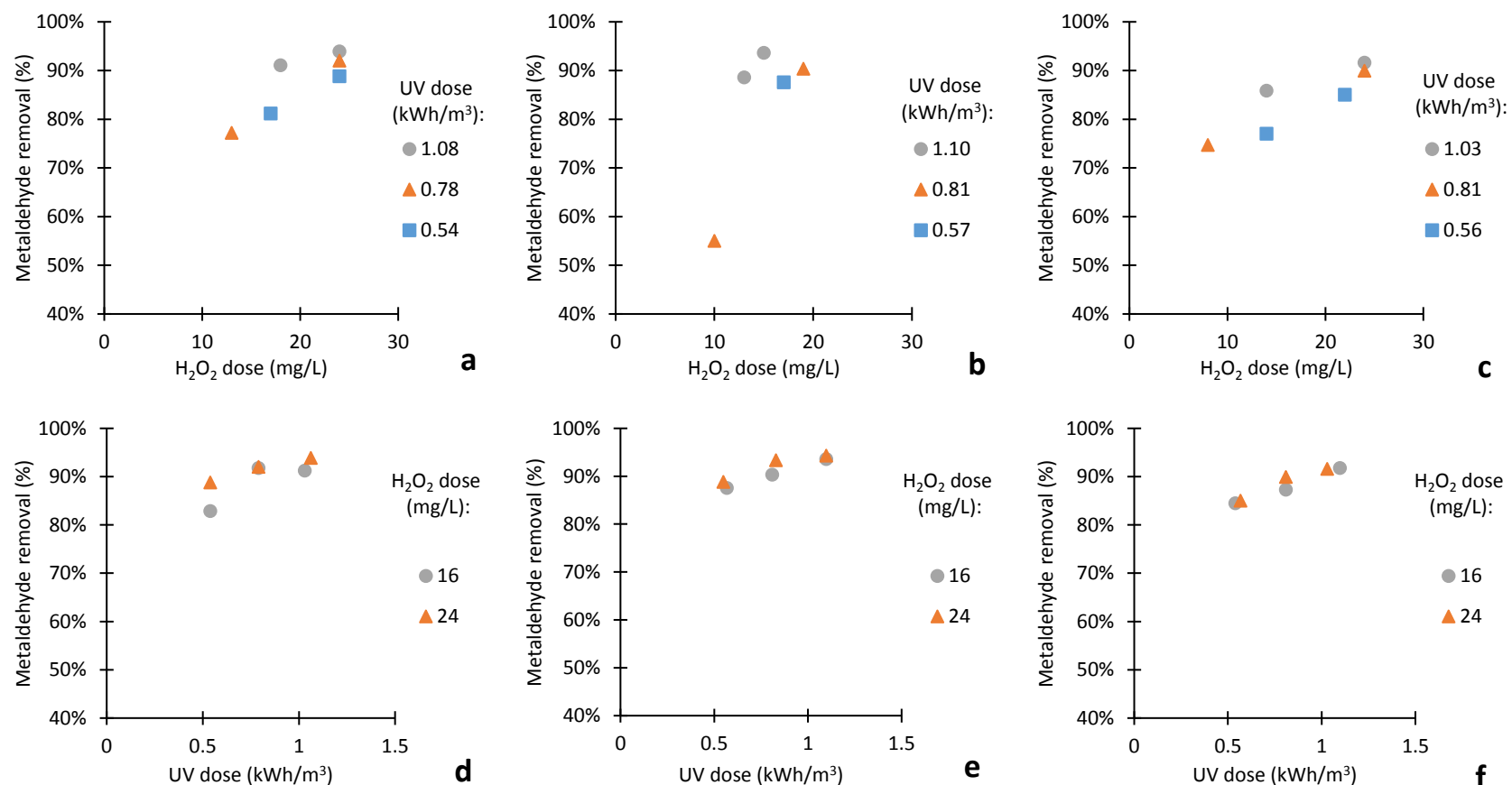


Figure 4. Influence of the operating conditions of the overall O₃/H₂O₂ - UV/H₂O₂ AOP on the metaldehyde removal for initial concentrations of 0.53 µg/L (a, d), 0.80 µg/L (b, e) and 2.14 µg/L (c, f). Influence of the hydrogen peroxide and UV doses at constant H₂O₂/O₃ mass ratios: ratio of 3 (a, c) and ratio of 2 (b). Influence of the UV and hydrogen peroxide doses at constant ozone doses of 7.7 mg/L (d), 5.7 mg/L (e) and 5.2 mg/L (f).

The impact of the operating conditions on the metaldehyde removal was also assessed individually for the two sub-processes of the overall O_3/H_2O_2 - UV/ H_2O_2 AOP. During the O_3/H_2O_2 sub-process, an increase in the ozone dose enhanced the metaldehyde removal (Figure 5a, Figure 5b, Figure 5c). When increasing the ozone dose between 5.0 and 6.9 mg/L for a metaldehyde inlet of 2 $\mu\text{g/L}$ and a hydrogen peroxide dose of 16 mg/L, the efficiency of the process raised by 12% (Figure 5c). Increasing the hydrogen peroxide dose while keeping the ozone dose constant only had a small influence on the metaldehyde removal. As the hydrogen peroxide was in excess compared to the ozone, increasing the hydrogen peroxide dose did not enhance the production of $\bullet\text{OH}$ radicals as all the ozone was already consumed. In contrast, an increase in the ozone dose decreased the H_2O_2/O_3 mass ratio hence increasing the production of $\bullet\text{OH}$ radical and the degradation of metaldehyde. Experimentally, no trend could be observed in metaldehyde removal when changing the H_2O_2/O_3 mass ratio up to 2 units between values of 2 to 6. The change in the metaldehyde removal when increasing the H_2O_2/O_3 mass ratio varied between -22% and +32% but in most experiments (82%), changing the H_2O_2/O_3 mass ratio only resulted in a small change in metaldehyde removal between -6% and +6%.

The UV and the initial hydrogen peroxide doses influenced the UV/ H_2O_2 sub-process, which was consistent with what was observed for the UV/ H_2O_2 AOP. An increase in the initial hydrogen peroxide dose between 8 mg/L and 23 mg/L resulted in 34% more metaldehyde removal for an initial concentration of 0.14 $\mu\text{g/L}$ and a UV dose between 0.55 and 0.58 kWh/m^3 (Figure 5d). Similarly, the metaldehyde removal was enhanced by up to 18% when increasing the UV dose from 0.54 to 1.08 kWh/m^3 for an initial concentration of 0.5 $\mu\text{g/L}$ metaldehyde and 15 mg/L hydrogen peroxide (Figure 5e). The general trends can be seen in Figure 5 and complementary graphs are presented in Appendix A.

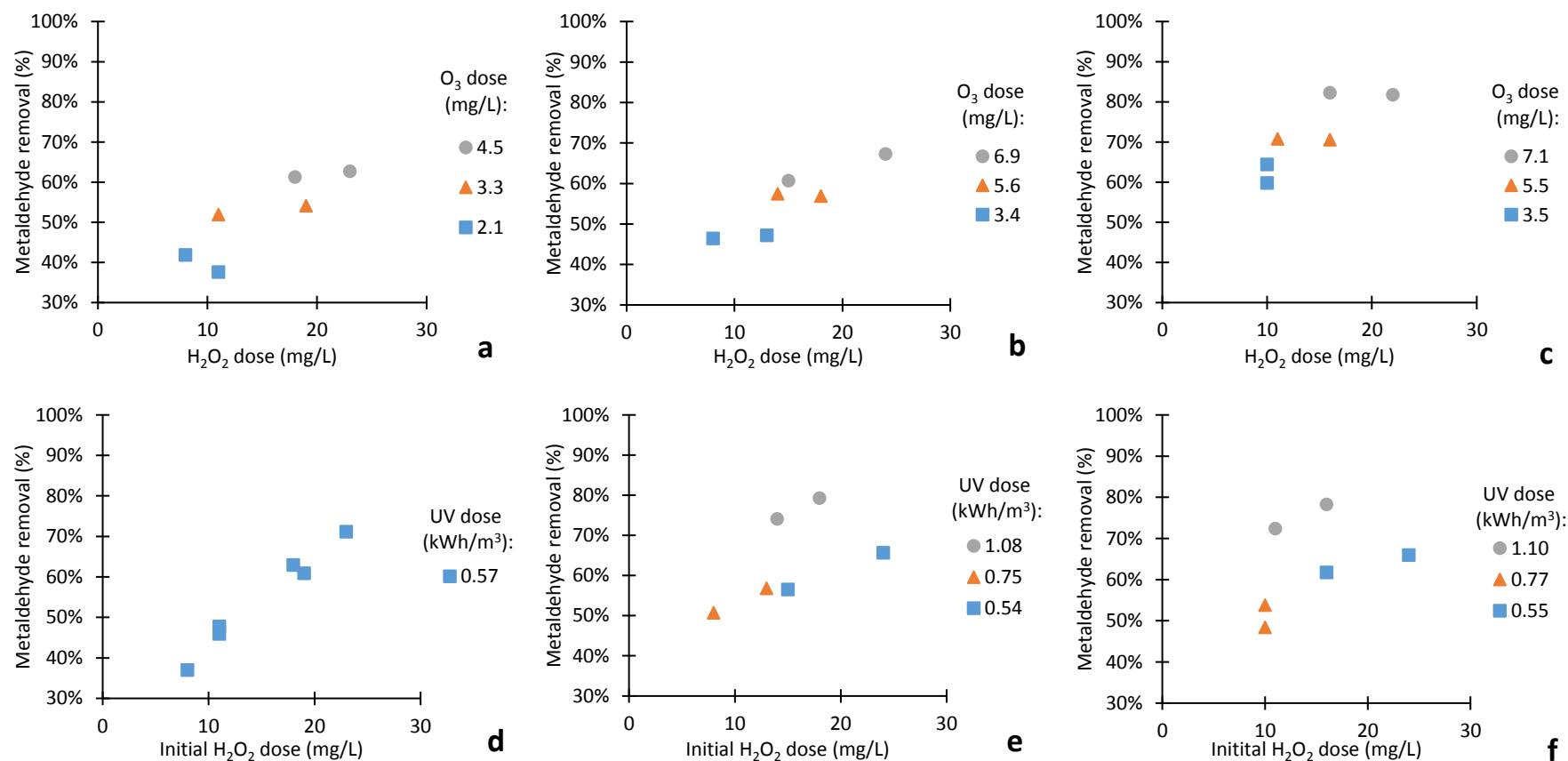


Figure 5. Influence of the operating conditions on metaldehyde removal for each sub-process of the O_3/H_2O_2 - UV/ H_2O_2 . Influence of the ozone and hydrogen peroxide doses of the O_3/H_2O_2 sub-process for different metaldehyde concentrations in the inlet: 0.14 $\mu g/L$ (a), 0.53 $\mu g/L$ (b) and 2.0 $\mu g/L$ (c). Influence of the UV and hydrogen peroxide doses of the UV/ H_2O_2 sub-process for different initial metaldehyde concentrations: 0.14 $\mu g/L$ (d), 0.53 $\mu g/L$ (e) and 2.0 $\mu g/L$ (f). The values of the ozone and UV doses in the legend are the mean of the measured values of each data point.

3.3.3 Suitable process conditions for compliance for each AOP depending on the concentration of metaldehyde in the inlet.

Figure 6 presents key findings of this study that could be of interest for water companies. It indicates the minimum UV and oxidant doses that can be applied to the selected AOPs in order to reduce metaldehyde concentration below the permitted level depending on the initial metaldehyde concentration. For a metaldehyde initial concentration below 0.20 $\mu\text{g/L}$, the minimum hydrogen peroxide dose tested of 15 mg/L could reduce metaldehyde sufficiently for compliance at all the UV doses tested in the UV/H₂O₂ AOP (Figure 6a). At this hydrogen peroxide dose, the metaldehyde concentrations obtained after the UV/H₂O₂ AOP varied between 0.01 and 0.07 $\mu\text{g/L}$. For greater initial metaldehyde concentrations between 0.50 and 0.80 $\mu\text{g/L}$, the higher the UV dose, the less hydrogen peroxide was required (Figure 6a). For UV doses below 0.60 kWh/m³, the minimum hydrogen peroxide dose required was around 40 mg/L whereas this dose dropped to 20 mg/L for UV doses close to 1 kWh/m³. When the metaldehyde inlet reached 2 $\mu\text{g/L}$, only high UV doses above 0.75 kWh/m³ and hydrogen peroxide doses greater than 36 mg/L could produce metaldehyde-compliant water (Figure 6a, Table 6). When the metaldehyde inlet concentration was over 2.20 $\mu\text{g/L}$, none of the operating conditions tested could reduce metaldehyde sufficiently for compliance. Nonetheless, the downstream GAC filtration further reduced metaldehyde concentration below 0.01 $\mu\text{g/L}$ for all the sets of conditions tested. One limitation of the GAC filtration was that the GAC media used for the trials was virgin. Hence it is hypothesised that a non-virgin media would lead to lower metaldehyde removals. This is because it has been shown that GAC has a low capacity for this pesticide (Autin *et al.*, 2012).

The O₃/H₂O₂ sub-process could reduce metaldehyde concentration below the permitted level for a metaldehyde inlet of 0.14 $\mu\text{g/L}$ only, with the exception of one set of conditions for an initial concentration of 2.30 $\mu\text{g/L}$ (Figure 6b). However for this sample, the oxidant doses required were very high (an ozone dose of 5.4 mg/L and a hydrogen peroxide dose of 24 mg/L). Figure 6b suggests that when the ozone dose was increased, the hydrogen peroxide dose needed to be

increased as well to achieve a sufficient reduction in the metaldehyde removal. However, this is only an artefact of the experimental plan: in these trials, only $\text{H}_2\text{O}_2/\text{O}_3$ ratios higher than 1 were tested in order to have a residual hydrogen peroxide in the system for the second sub-process. This means that when the ozone dose applied was increased, a higher hydrogen peroxide dose was applied. Therefore, the trend observed is only a result of the conditions tested in this trial.

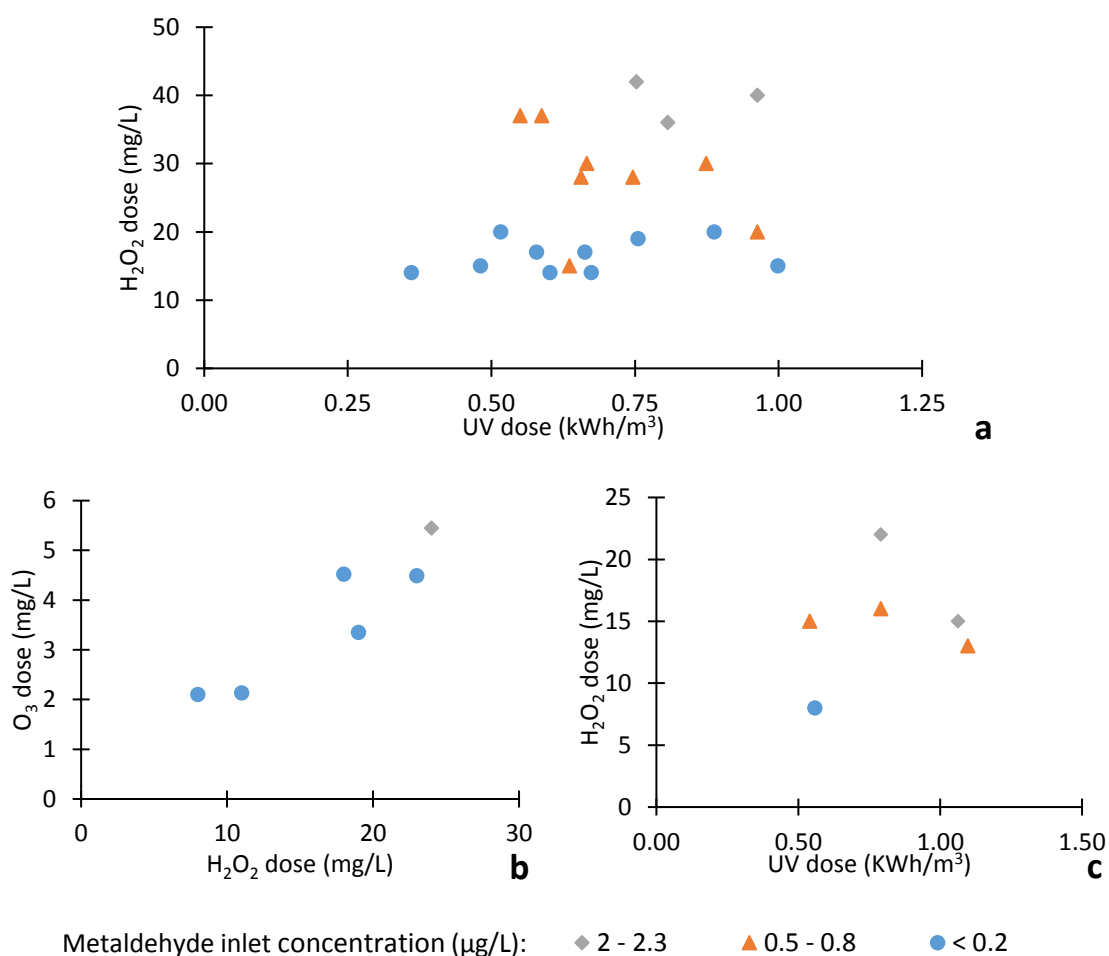


Figure 6. Minimum inputs to the AOPs to produce metaldehyde-compliant water for different initial concentrations. UV/H₂O₂ AOP (a). O₃/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP (b). Overall O₃/H₂O₂ - UV/H₂O₂ AOP (c). The legend referring to the metaldehyde inlet is common to the 3 graphs.

Figure 6c only showed one set of conditions able to achieve metaldehyde compliance at a metaldehyde inlet concentration lower than 0.2 µg/L for the

overall O₃/H₂O₂ - UV/H₂O₂ AOP. This was because for this inlet, UV doses higher than 0.55 kWh/m³ were not assessed. However, it was very likely that higher UV doses would have also reduced metaldehyde concentration below the regulatory level of 0.1 µg/L. The minimum hydrogen peroxide and ozone doses required at this UV dose were 8 mg/L and 2 mg/L respectively (Figure 6c, Table 6). For higher metaldehyde concentration between 0.50 and 0.80 µg/L, the hydrogen peroxide dose required was around 15 mg/L for all the UV doses tested and the ozone need was between 5 and 6 mg/L. When the metaldehyde spiking of the inlet was increased between 2 and 2.1 µg/L, only UV doses higher than 0.79 kWh/m³ could reduce the metaldehyde concentration below the permitted level, and this was achieved for hydrogen peroxide doses between 15 and 22 mg/L and ozone doses between 7 and 8 mg/L (Table 6). In addition, the hydrogen peroxide dose required was reduced for a higher UV dose (Figure 6c). None of the conditions tested could reduce metaldehyde concentration below the regulatory level for metaldehyde inlet concentrations greater than 2.10 µg/L. After GAC filtration, all the metaldehyde concentrations obtained were below 0.1 µg/L.

3.3.4 Comparison of the performance of the UV/H₂O₂ and O₃/H₂O₂ - UV/H₂O₂ processes for removing metaldehyde.

In order to compare both AOPs at similar operating conditions, 5 groups comprising different sets of conditions were established. Each set of conditions was defined by a range of hydrogen peroxide and UV doses (Table 5). For this comparison, the efficiency of the overall O₃/H₂O₂ - UV/H₂O₂ AOP was considered. Hence the combination of the effect of the two individual AOPs was taken into account. For a metaldehyde inlet concentration of 0.14 µg/L, no reliable comparison could be made because of the insufficient data collected and the lack of similarity between the operating conditions of the two processes (Figure 7a). For an inlet between 0.50 and 0.80 µg/L of metaldehyde, the O₃/H₂O₂ - UV/H₂O₂ AOP showed a better removal efficiency for UV doses between 0.50 and 0.60 kWh/m³ (sets of conditions 1 and 2) (Figure 7b, Figure 7c). This was expected as in the O₃/H₂O₂ - UV/H₂O₂ AOP, the addition of ozone can enhance the •OH

radical production hence the metaldehyde removal. The O_3/H_2O_2 - UV/H_2O_2 AOP was between 10% and 33% more efficient than the UV/H_2O_2 AOP at hydrogen peroxide doses between 10 and 20 mg/L and this difference decreased to between 5 and 19% for hydrogen peroxide doses in the range 24 - 34 mg/L. For higher UV doses (sets of conditions 3, 4 and 5), the efficiency of both processes was similar (Figure 7b, Figure 7c). This was because at high UV doses, the $\bullet OH$ radicals were formed in excess and were hence able to degrade metaldehyde to the same level as seen in the UV/H_2O_2 AOP. The same observation was made for an initial metaldehyde concentration between 2.10 and 2.30 $\mu g/L$. The O_3/H_2O_2 - UV/H_2O_2 AOP was between 6% and 32% more efficient than the UV/H_2O_2 AOP for removing metaldehyde at UV doses between 0.50 and 0.60 kWh/m^3 and hydrogen peroxide doses in the range 10 - 20 mg/L. The difference in metaldehyde removal between both AOPs decreased to about 10% when the hydrogen peroxide dose was increased to 24 - 34 mg/L (Figure 7b, Figure 7c). Nonetheless, several limitations to this comparison exist. The first is that although a lot of data was obtained during the trials, only a small number of conditions could be used to compare processes at similar operating conditions. The second limitation is that to compare enough data to enable the comparison of both AOPs, groups of conditions were made. This means that the processes were not compared at exactly the same operating conditions. Finally, the O_3/H_2O_2 - UV/H_2O_2 AOP comprised of two individual AOPs and used ozone as an additional oxidant. The addition of ozone can enhance metaldehyde degradation by enhancing $\bullet OH$ radical production but it can also make the O_3/H_2O_2 - UV/H_2O_2 AOP prohibitive due to the elevated cost of generating ozone. Water companies will want to consider a trade-off between the metaldehyde removal efficiency and the cost of operation for a future implementation in WTWs.

Considering the operating costs only, the electricity consumption of the UV lamps is the main expense for the AOP processes. Therefore, this is the main variable to compare between both processes. When comparing the minimum doses required to reduce the metaldehyde concentration to below the permitted level for the same concentration of metaldehyde in the inlet, the UV doses are lower for the UV/H_2O_2 AOP than for the O_3/H_2O_2 - UV/H_2O_2 AOP which suggests that

the UV/H₂O₂ AOP was more economically viable (Table 6). A simple estimation of the operating cost for both processes considering the price of the hydrogen peroxide and oxygen supply and the electricity consumption for the generation of ozone and for the UV irradiation confirmed that hypothesis. For a metaldehyde inlet of 0.14 µg/L, the minimum operating cost to treat 1000 m³ of water was £38.50 for the UV/H₂O₂ AOP against £58.34 for the O₃/H₂O₂ - UV/H₂O₂ AOP (Table 6). The difference in the operating cost between the two processes was smaller for a metaldehyde concentration between 0.50 and 0.80 µg/L with minimum operating costs of £62.19 and £63.13 to treat 1000 m³ of water. For higher initial metaldehyde concentrations between 2.00 and 2.30 µg/L, the minimum operating cost for treating 1000 m³ of water was £8 lower for the UV/H₂O₂ AOP than for the O₃/H₂O₂ - UV/H₂O₂ AOP. Therefore, on the basis of metaldehyde removal efficiency and cost efficiency, the UV/H₂O₂ AOP appeared to be more viable than the O₃/H₂O₂ - UV/H₂O₂ AOP.

Table 5. Definition of the sets of conditions used in Figure 7.

Sets of conditions	1	2	3	4	5
H ₂ O ₂ (mg/L)	10 - 20	24 - 34	10 - 20	24 - 34	10 - 20
UV (kWh/m ³)	0.50 - 0.60	0.50 - 0.60	0.75 - 0.85	0.75 - 0.85	0.95 - 1.05

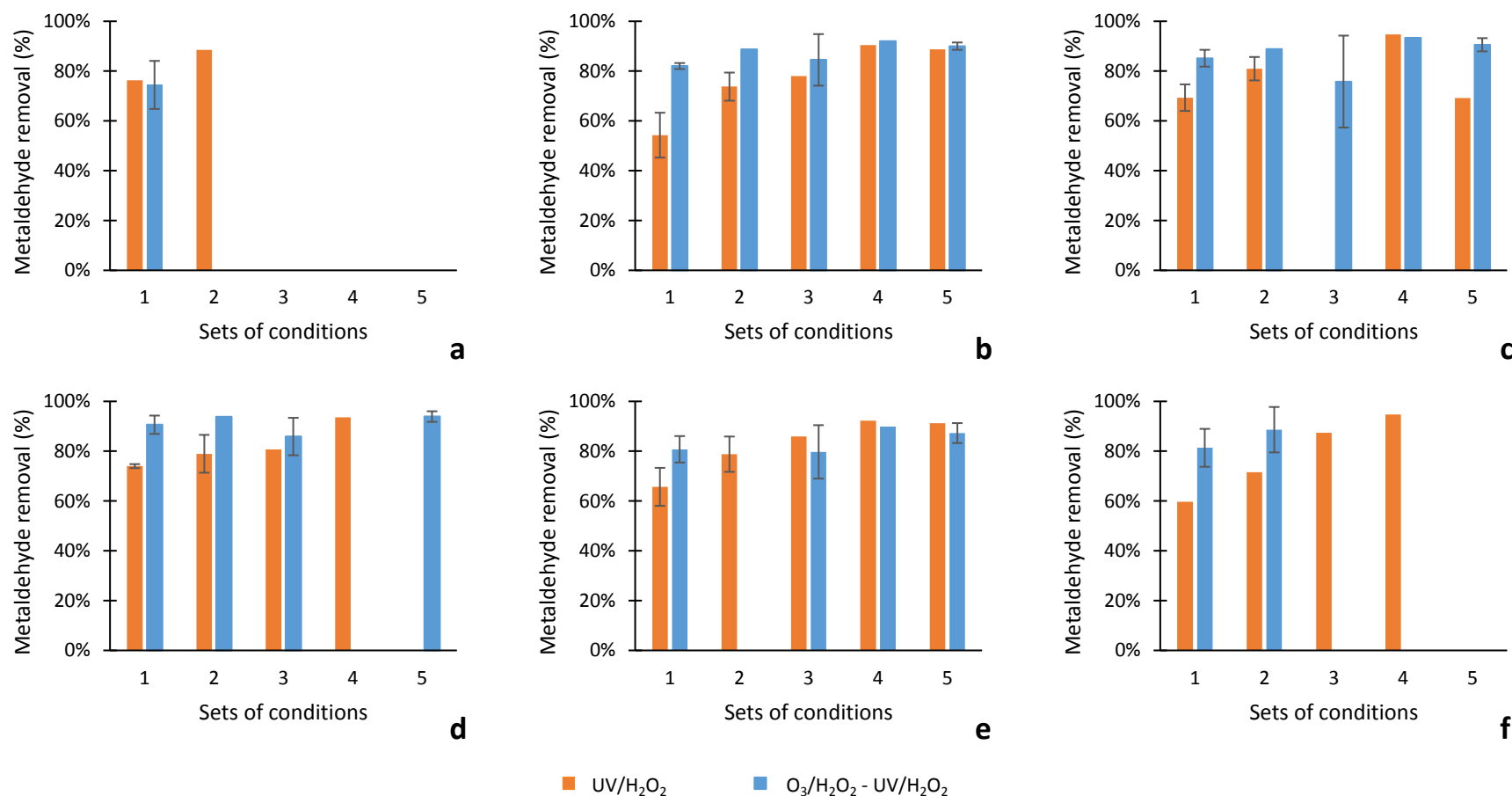


Figure 7. Comparison of the UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOPs at similar UV and hydrogen peroxide doses for different metaldehyde initial concentrations: 0.14 µg/L (a), 0.53 µg/L (b), 0.80 µg/L (c), 2.11 µg/L (d), 2.14 µg/L (e) and 2.30 µg/L (f). The values represented are the average of the removals obtained for the different samples from the same sets of conditions. The error bars represent the standard deviation. The sets of conditions corresponding to each number are defined in Table 5.

Table 6. Minimum inputs to the UV/H₂O₂ and O₃/H₂O₂ - UV/H₂O₂ AOPs to reduce metaldehyde concentration below the regulatory concentration of 0.1 µg/L and their corresponding operating cost for the treatment of 1000 m³ of water. The values used for the cost estimation are 0.216 £/kg H₂O₂ for the hydrogen peroxide supply, 0.0225 £/kg O₂ for the oxygen supply to generate ozone, 12 Wh/g O₃ for the electricity required for ozone generation, and 0.09855 £/kWh for the electricity. These values were obtained from Lucas, Peres and Li Puma (2010) and converted to pounds sterling with a conversion rate from euros to pound sterling of 0.90.

	UV/H ₂ O ₂				O ₃ /H ₂ O ₂ - UV/H ₂ O ₂				
Metaldehyde inlet concentration	H ₂ O ₂ dose (mg/L)	UV dose (kWh/m ³)	Flow rate (m ³ /h)	Operating cost (£/1000 m ³)	O ₃ dose (mg/L)	H ₂ O ₂ dose (mg/L)	UV dose (kWh/m ³)	Flow rate (m ³ /h)	Operating cost (£/1000 m ³)
< 0.14 µg/L	14	0.36	2	38.50	2	8	0.55	0.6	58.34
0.50 - 0.80 µg/L	37	0.55	2.5	62.19	6	17	0.53	2.5	63.13
	28	0.67	2.5	72.08	5	14	1.06	2.5	113.51
2.00 - 2.20 µg/L	42	0.75	2.5	82.98	7	22	0.79	2.5	91.04
	36	0.81	2	87.60	8	15	1.06	2.5	117.34

3.4 Conclusions

Both AOPs could reduce the metaldehyde concentration effectively in this work with removals of up to 98%, which were similar to that reported in the literature. In the $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 AOP, the $\text{O}_3/\text{H}_2\text{O}_2$ sub-process degraded metaldehyde to a greater extent than the UV/ H_2O_2 sub-process. It removed between half and all of the total metaldehyde degraded by this overall process. The performance of the UV/ H_2O_2 AOP was enhanced by increasing the hydrogen peroxide and the UV doses up to 30 mg/L and 0.85 kWh/m³ respectively. A further increase in these doses only resulted in a slight increase in the metaldehyde removal. Increasing the flow rate between 2.5 and 3.5 m³/h also enhanced the efficiency of the process by up to 10%. For the $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 AOP, a simultaneous increase in the ozone and hydrogen peroxide doses resulted in an increase in the metaldehyde removal by up to 35%. In the range assessed, the hydrogen peroxide dose only had a small influence on the removal achieved by this process as it was added in excess. The efficiency of the $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 AOP was also increased with increasing the UV dose. Both processes were able to reduce metaldehyde concentration below the regulatory level of 0.1 µg/L at similar UV doses for all the initial metaldehyde concentrations tested. For initial metaldehyde concentrations below 0.2 µg/L, minimum UV doses as low as 0.36 and 0.55 kWh/m³ were required for the UV/ H_2O_2 and the $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 process respectively. The minimum UV dose needed was increased to 0.55 kWh/m³ for both AOPs when the inlet concentration was raised to 0.5 - 0.8 µg/L. For a metaldehyde initial concentration of 2 µg/L, UV doses of 0.75 and 0.79 kWh/m³ were needed for the UV/ H_2O_2 and $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 AOP respectively. In the UV and oxidant ranges of doses assessed, these AOPs were not able to consistently reduce the metaldehyde concentration to below the regulatory concentration of 0.1 µg/L when the initial metaldehyde concentration was above 2.2 µg/L. In this work, the $\text{O}_3/\text{H}_2\text{O}_2$ sub-process could only reduce metaldehyde for compliance when the initial concentration was lower than 0.2 µg/L. The $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 AOP showed a better removal efficiency than the UV/ H_2O_2 AOP for UV doses below 0.60 kWh/m³. For higher UV doses, the efficiency of

both processes was similar. The cost of the electricity to produce UV irradiation is the major source of operating expenses in these AOPs, followed by the cost of ozone generation. As both processes showed similar efficiencies especially at higher UV doses, the costs implied should be considered in order to select the process to implement in WTWs. In addition, the O_3/H_2O_2 sub-process of the O_3/H_2O_2 - UV/ H_2O_2 AOP was shown to remove metaldehyde by up to 96%. In this trial, and under the conditions tested, it was only able to consistently reduce the metaldehyde concentration below compliance levels for initial metaldehyde concentrations below 0.2 $\mu\text{g/L}$. However, this AOP should be assessed individually with an optimised H_2O_2/O_3 ratio and increased ozone and hydrogen peroxide doses to enhance the production of $\bullet\text{OH}$ radicals hence the metaldehyde removal. As no UV light is required in this process, this AOP would be economically more competitive than the two others providing that it can produce metaldehyde-compliant water for inlet concentrations higher than 0.2 $\mu\text{g/L}$. A downstream GAC filtration could also help to this end.

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4 Impact of UV/H₂O₂ and O₃/H₂O₂ - UV/H₂O₂ AOPs at pilot scale on DBP formation and background OM transformation

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Abstract

This work assessed and compared the impact of the UV/H₂O₂ and the O₃/H₂O₂-UV/H₂O₂ AOPs at pilot-scale on background OM and downstream DBP formation in water. The impact of these AOPs on DBP formation was evaluated by comparing the THM FP and HAA FP before and after each AOP upon chlorination for seven days. Different oxidant and ozone doses were tested on different days in order to assess the influence of the process conditions as well as the impact of the quality of the inlet water. To investigate the effect of the AOPs on the character and the size of the background OM, FEEM and HPSEC chromatograms of the samples collected at different stages of the treatment were obtained. The UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOP had a similar impact on the DBP FP. They either increased or decreased the THM FP and the HAA FP between -85% and +155% and a slight positive correlation was observed between the THM FP and the HAA FP. The quality of the inlet water appeared to be a more influential factor in these changes rather than the UV and oxidant doses that were applied. These AOPs were shown to change the reactivity of the OM and decrease their aromatic content. During the O₃/H₂O₂ - UV/H₂O₂ AOP, the O₃/H₂O₂ sub-process was responsible for most of the transformation of the OM that occurred during the overall process and tended to decrease both the THM FP and the HAA FP. The UV/H₂O₂ and the O₃/H₂O₂ - UV/H₂O₂ processes mostly removed humic-like substances and degraded higher molecular weight OM into smaller compounds. These changes in the structure and character of the OM could explain the potential of AOPs to increase DBP formation. However in

the range of oxidant and UV doses applied in this work, AOPs did not appear to be effective for preventing downstream DBP formation.

Key words:

Oxidation, pilot study, trihalomethanes, haloacetic acids, natural organic matter, chlorination

4.1 Introduction

Due to the occurrence of recalcitrant micropollutants in water above the regulatory concentrations, there has been an increasing interest in AOPs. (DWI, 2016a, 2016b, 2016c, 2016d, 2016e, Autin *et al.*, 2013; Cheng *et al.*, 2016; Martinez *et al.*, 2016). The efficiency of the AOPs relies on the production of the highly reactive and unselective free $\bullet\text{OH}$ radicals (Pérez *et al.*, 2006; Ranade and Bhandari, 2014; Ribeiro *et al.*, 2015). These can be produced by UV irradiation of the hydrogen peroxide between 200 and 250 nm (Ijpelaar *et al.*, 2002, Zaviska *et al.*, 2009) or by reaction of hydrogen peroxide with ozone (Lucas *et al.*, 2010; Lester *et al.*, 2011). The radicals oxidise the micropollutants by a succession of oxidation reactions which aim to completely degrade the pollutants into carbon dioxide, water and inorganics (Badawy *et al.*, 2006; Ribeiro *et al.*, 2015; Cheng *et al.*, 2016).

Another matter of concern in drinking water treatment is the formation of DBPs upon chlorination (Jefferson *et al.*, 2016). They result from the reaction between disinfectants, such as chlorine, and natural OM, organic contaminants or inorganic species (Richardson and Ternes, 2011). THMs and HAAs, are the most abundant DBP classes on a mass basis in drinking water (Krasner *et al.*, 2006). The maximum concentration of THMs (including tribromomethane, bromodichloromethane, dibromochloromethane, and trichloromethane) is set at 100 $\mu\text{g/L}$ in drinking water in the UK (Council Directive 98/83/EC, 2000). As they are unselective, $\bullet\text{OH}$ radicals can also react with the background OM in water, the only difference being the higher concentration of OM in water compared to

micropollutants. Therefore AOPs have the potential to degrade the background OM including DBP precursors and change the DBP FP. Several researchers reported that AOPs were able to mineralize DBP precursors (Chin and Bérubé, 2005; Toor and Mohseni, 2007). However, the partial oxidation of the OM has been showed to increase the DBP formation when AOPs were applied at insufficient oxidant or UV doses for the mineralisation of DBP precursors (Metz *et al.* 2011, Sarathy *et al.* 2011). Therefore, the impact of AOPs on DBP formation should be assessed before implementing processes for micropollutant removal at large scale (Metz *et al.*, 2011).

This research has investigated two commercial AOP technologies at pilot scale: UV/H₂O₂ and O₃/H₂O₂ followed by UV/H₂O₂. These AOPs have been selected following a comprehensive technology assessment because of their technology readiness in comparison to many other AOPs. This study builds on previous findings by critically evaluating the impact that these two AOPs applied for micropollutant removal can have on DBPs. This work aims to compare the changes in the THM FP and the HAA FP during AOPs and investigate the transformations of background OM during these processes. To this end, the impact of UV light used in combination with different oxidant chemicals as well as the influence of the quality of the inlet water on the THM FP and the HAA FP was studied. The changes in OM character and molecular weight following the treatment by AOPs were also determined.

4.2 Materials and methods

4.2.1 Chemicals and reagents

The metaldehyde (99%), the sodium hypochlorite (13% active chlorine), the ammonium chloride (Certified Analytical Reagent) and the extrapure sodium sulphite were acquired from Fisher Scientific. All solutions were prepared in ultrapure water (Purelab Option – S7/15, TOC < 3 ppb).

4.2.2 Description of pilot-scale experiments

Two AOPs were assessed at pilot-scale. The UV/H₂O₂ pilot plant was supplied by Trojan Technologies. The UVPhox 8AL20 pilot unit comprised 8 low pressure lamps and could treat between 1 and 5 m³/h of water. The dimensions of the unit were 3.38 m (L) x 1.32 m (W) x 1.93 m (H). Mixing was performed before the reactor. The second process assessed was supplied by Xylem Water Solutions and comprised two individual AOPs in series: O₃/H₂O₂ followed by UV/H₂O₂. The water was first treated by ozone and an excess of hydrogen peroxide and was then transferred to a UV reactor. In the UV reactor, the hydroxyl radicals were formed by reaction with the residual hydrogen peroxide from the first AOP. The O₃/H₂O₂ AOP was performed in a Wedeco Promix system of dimensions 2.90 m (L) x 0.95 m (W) x 1.38 m (H). This unit was designed to enhance the ozone transfer efficiency thanks to its multiple transfer points. The ozone and the hydrogen peroxide were mixed with the water in this unit before it went to the UV reactor. The ozone was transferred to the system as a gas and the dose was measured by deducting the off gas from the inlet concentration. The second AOP was performed in a MiPRO photo Wedeco UV system LBX 10 of 13 L which comprised 3 Spektrotherm[®] UV lamps and was able to treat water between 0.5 and 4 m³/h. The residence times varied between 19 and 78 seconds in the LBX 10 UV reactor. All the lamps used in these pilots were new at the beginning of the trial. The pilot plants were supplied with partially treated reservoir water from the real WTWs where they were located (in the midlands, UK). The water feeding the pilot plants had been treated by coagulation, clarification and rapid gravity filtration (RGF). Following the treatment by the AOPs, the water was filtered through a GAC contactor. Samples were collected before the AOPs, between AOPs and GAC and after GAC filtration (Figure 8). A sample was also collected between the two individual sub-processes of the O₃/H₂O₂ - UV/H₂O₂ AOP. The residual hydrogen peroxide was measured onsite in the samples collected between AOP and GAC using a Palintest Photometer with potassium iodide reagent tablets. The reaction was quenched with sodium sulphite using the concentration required to stoichiometrically neutralise the hydrogen peroxide. 3.7 mg/L of sodium sulphite were added per mg/L of hydrogen peroxide measured in

each sample. The samples were then kept in cold boxes onsite until they were transferred to a cold room in the laboratory before their analysis. The variables in both AOPs were the initial metaldehyde concentration, the oxidant doses, the flow rate and the UV dose (Table 7). In the Trojan pilot-plant, the UV irradiation was set by adjusting the power of the UV lamps. As the UV dose delivered by unit of surface was not provided, the UV electric consumption of both processes was normalised by the flow rate. Therefore, the UV doses were expressed in this work in kWh/m³ to enable the comparison of both AOPs at similar operating conditions. Different concentrations of the pesticide metaldehyde in the inlet water were assessed in this study. This is because this work was part of a larger study assessing the performance of AOPs for metaldehyde removal.

Table 7. Process variables applied to AOP pilot plants.

Process variables	AOP Treatment Processes	
	UV/H ₂ O ₂	H ₂ O ₂ /O ₃ - H ₂ O ₂ /UV
Initial metaldehyde concentration	0.10 - 0.15 µg/L (Environmental concentration) to 2 µg/L	
Hydrogen peroxide dose	10 - 45 mg/L	8 - 30 mg/L
Ozone dose	-	2 - 10 mg/L
Flow rate	2 - 3.5 m ³ /h	0.6 - 2.5 m ³ /h
UV dose	0.35 - 1.00 kWh/m ³	0 - 1.10 kWh/m ³

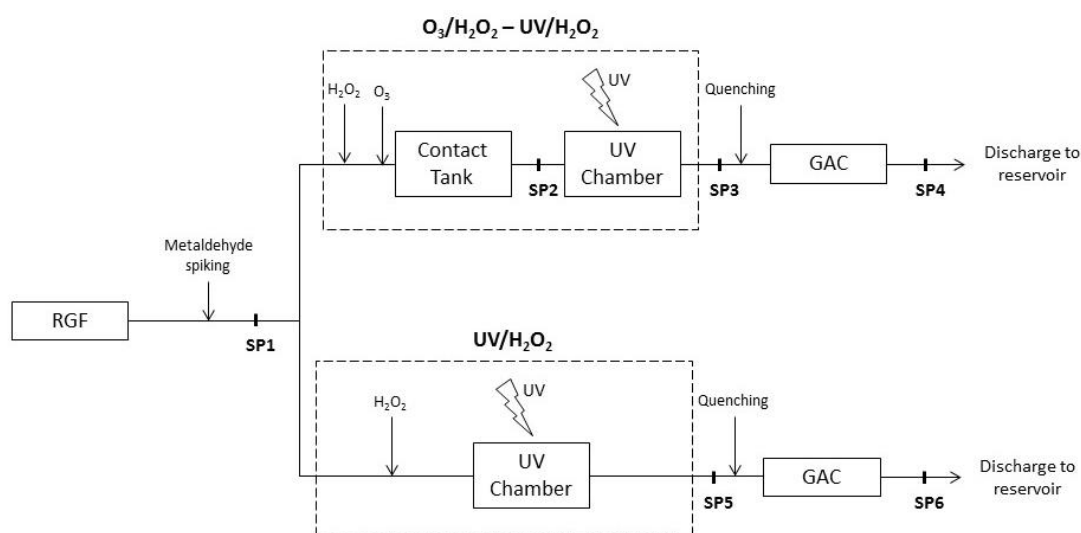


Figure 8. Process flow diagrams of the AOP pilot plants. SP1 - SP8 represent the sample points across the pilots.

4.2.3 Analytical methods

The absorbance at 254 nm was measured in the samples with a Jenway 6715 UV-Vis spectrophotometer, the turbidity with a Hach 2100N Turbidity Meter and the DOC was measured as NPOC using a Shimadzu TOC-V CSH TOC analyser. In order to measure the THM FP and the HAA FP, the samples were first diluted to 1 mg/L of DOC and were then chlorinated with 5 mg/L of chlorine. After seven days of contact in the dark, the residual chlorine was quenched with 100 mg/L of sodium sulphite prior to THM extraction and with 100 mg/L of ammonium chloride

prior to HAA extraction. The formed THMs and HAAs were extracted according to the United States Environmental Protection Agency (USEPA) methods 551.1 and 552.3 and were analysed by gas chromatography with an electron capture detector (GC-ECD). For this purpose, a Hewlett Packard gas chromatograph HP 6890 was used. 1 μ L of sample was injected in split ratio at a flow rate of 14.4 mL/min in an Agilent 122-1033 DB-1 column. Helium was used as the carrier gas. The 4 THMs monitored were trichloromethane, dibromochloromethane, bromodichloromethane and tribromomethane. The 9 HAAs analysed were MCAA, MBAA, DCAA, TCAA, DBAA, bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA) and tribromoacetic acid (TBAA). The FEEM of selected samples were acquired using a HORIBA Fluoromax spectrofluorometer. The excitation wavelength varied from 200 nm to 400 nm with an increment of 5 nm and a slit width of 5 nm and the emission wavelength was increased from 280 nm to 500 nm with an increment of 2 nm and a slit width of 5 nm. The integration time was 0.1 s and the first and second order Rayleigh scatter were corrected directly on the software of the spectrofluorometer. The molecular weight distribution was determined by HPSEC with a Shimadzu liquid chromatograph LC-10 AD and a UV/Vis detector set at a wavelength of 254 nm. 500 μ L of sample were injected in a Phenomenex BioSep-Sec-S 3000 300mmx7.8mm at a flow rate of 1 mL/min and a solution of 0.01 M of sodium acetate was used as the solvent. The analysis were carried out in duplicate. The standard errors in measurement were 6.4%, 3.1%, 3.7% and 7.8% for DOC, UV absorbance, THM FP and HAA FP respectively.

4.2.4 Statistical tests

The statistical analysis of the set of data was performed using the Primer software, which comprises resemblance-based methods, with PERMANOVA+ add-on package. The DISTLM was selected as it analyses and models the relationship between response variables and predictor variables. For this purpose, a resemblance matrix, which describes the dissimilarities among a set of samples depending on the values of their response variables, is calculated (Anderson *et al.*, 2008). The DISTLM was used to assess whether the operating

conditions (flow rate and UV, ozone and hydrogen peroxide doses) and predictor variables (DOC, Turbidity, and UV absorbance at 254 nm measured in the inlet and after AOPs) explained a significant proportion of the variation in the values of the response variables (change in DOC, THM FP and HAA FP following AOPs).

The DISTLM comprised two different tests: the marginal and the sequential tests. The marginal tests indicated how much each of the variable taken alone explained the variation in the response variables. In this test each variable was assessed independently of the other variables. In the sequential tests, each test examined whether adding one particular variable contributed significantly to the explained variation, given that the previous variables were already included in the model (Anderson *et al.*, 2008).

In the marginal tests, the 'Prop.' value indicated the proportion of the variation in the response variables that was explained by each variable and the P value indicated how statistically significant was that proportion. The P-values indicate the veracity of the hypothesis of no relationship between the process variables or predictor variables and the response variables (Anderson *et al.*, 2008). P values lower than 0.05 were considered as statistically significant in this work. In the sequential tests, the 'Prop.' value indicated the increase in the proportion of explained variation attributable to each variable that was added to the model, and the 'Cumul.' value provided a running cumulative total (Anderson *et al.*, 2008). Finally, the 'res.df' value indicated the residual degrees of freedom of each test.

4.3 Results and discussion

4.3.1 Changes in THM FP and HAA FP following AOPs

The THM FP in the inlet water varied between 234 and 609 µg/L depending on the day of the trial. The HAA FP varied between 174 and 322 µg/L. These values seem high in comparison to the maximum regulatory THM concentration of 100 µg/L. This is because the samples were in contact with high amounts of chlorine

for a long time, hence the DBP FP was maximised. Hutton and Chung (1994) suggested a conversion factor of 0.199 from the THM FP to the THM concentration after chlorination (Jefferson *et al.*, 2016). Both AOPs were found to both reduce and increase THM FP and HAA FP depending on the samples and the day of the trial. The maximum THM FP and HAA FP obtained after both AOPs were similar for both processes and in the range of 600 µg/L and 300 µg/L respectively (Table 8). The difference in the HAA FP in the samples collected before and after both AOPs varied between -164 and +131 µg/L with respect to the inlet. The THM FP increased by a higher magnitude during the O₃/H₂O₂ - UV/H₂O₂ AOP than following the UV/H₂O₂ AOP, forming up to 255 µg/L more of THMs than in the inlet (in comparison with 133 µg/L for the UV/H₂O₂ AOP). The GAC filtration reduced the THM FP below 246 µg/L and the HAA FP below 78 µg/L. When comparing the sub-processes of the O₃/H₂O₂ - UV/H₂O₂ AOP, the magnitude of the increase in THM FP and HAA FP was higher for the UV/H₂O₂ sub-process than for the first sub-process. The O₃/H₂O₂ sub-process only slightly increased the THM FP and HAA FP by up to 69 and 22 µg/L respectively.

Table 8. Magnitude of change in DBP and HAA FP after each AOP and sub-process.

		AOP			
		UV/H ₂ O ₂	O ₃ /H ₂ O ₂ - UV/H ₂ O ₂		
			Overall	O ₃ /H ₂ O ₂	UV/H ₂ O ₂
Maximum concentration after AOP	THM FP	638 µg/L	616 µg/L	549 µg/L	616 µg/L
	HAA FP	305 µg/L	316 µg/L	245 µg/L	316 µg/L
Absolute magnitude of change between inlet and post-AOP	THM FP	-234 to +133 µg/L	-268 to +255 µg/L	-282 to +69 µg/L	-187 to +246 µg/L
	HAA FP	-164 to +131 µg/L	-163 to +124 µg/L	-164 to +22 µg/L	- 158 to +95 µg/L
% Magnitude of change between inlet and post-AOP	THM FP	-85% to +30%	-58% to +155%	-62% to +164%	-49% to +139%
	HAA FP	-85% to +76%	-61% to +64%	-51% to +10%	-65% to +120%

Irrespective of the sample point, trichloromethane was the most abundant THM by mass in the water, representing between 60 and 90% of the total THMs. Bromodichloromethane was the second most abundant THM and tribromomethane concentration was less than 2.5 µg/L in all the samples collected. DCAA and TCAA were the most abundant of HAAs in our samples with proportions in the ranges 38 - 58% and 10 - 33% respectively with respect to the sum of HAAs. TBAA and MCAA were not detected in any of our samples. These results may be explained by the low levels of bromide in the water used in these trials. As a result, trichloromethane, DCAA and TCAA were the DBPs that exhibited the most change through both AOPs.

4.3.2 Influence of process variables on THM FP and HAA FP

In both processes, no trend was apparent between the change in the THM FP and the HAA FP and the process operating conditions (Figure 9). Neither the UV, the hydrogen peroxide nor the ozone doses seemed to influence the THM FP and the HAA FP. This was confirmed by the DISTLM tests: the hydrogen peroxide dose taken independently only explained 14% of the total variation in THM FP change after the overall O_3/H_2O_2 - UV/ H_2O_2 AOP and 11% for the UV/ H_2O_2 AOP. In addition, the latter was not statistically significant ($P = 0.09$). The DISTLM tests also showed that the UV and hydrogen peroxide doses taken independently explained less than 4% of the variation in the HAA FP change after the UV/ H_2O_2 AOP, and these proportions were not statistically significant. However, the H_2O_2/O_3 mass ratio taken independently significantly explained 37% of the variation in the HAA FP change after the overall O_3/H_2O_2 - UV/ H_2O_2 AOP ($P=0.0018$). A possible reason for this was that in the O_3/H_2O_2 sub-process, the HAA FP changed by a higher magnitude than in the UV/ H_2O_2 sub-process. The full DISTLM tests are presented in Appendix B.

Many researchers have reported the efficiency of AOPs for decreasing the DBP FP at high chemical and UV inputs but highlighted their potential to increase DBP FP at lower doses (Kleiser and Frimmel, 2000; Toor and Mohseni, 2007; Kent *et al.*, 2011; Sarathy *et al.*, 2011; Mayer *et al.*, 2015). Kleiser and Frimmel (2000) showed that the potential of NOM to form DBPs was increased in the presence of low amounts of $\bullet OH$ radicals. Similarly, Metz *et al.* (2011) suggested that AOPs applied at limited energy and chemical inputs could result in incomplete NOM oxidation which could increase the number of chlorine reactive sites and therefore increase DBP formation. On the other hand, Mayer *et al.* (2015) reported that when AOPs were applied with sufficient energy and chemical inputs, the oxidation of the NOM was more complete and significantly reduced the DBP concentrations. This has been attributed to the high levels of $\bullet OH$ radicals produced (Toor and Mohseni, 2007). However, the UV doses applied to reduce DBP formation were higher than $10\,000\text{ mJ/cm}^2$ which is greater than the range of doses we used in this work (Bond *et al.*, 2009; Jefferson *et al.*, 2016). As a result, the inability of AOPs to prevent DBP formation in this work was likely due

to the fact that the UV ranges assessed were too low for DBP control. The lack of influence of process variables on THM FP and HAA FP suggested that in the range of UV doses tested, the change in DBP FP was not driven by the UV and oxidant doses but may have been more impacted by the quality of the inlet water and more specifically by the composition and characteristics of the NOM in the inlet.

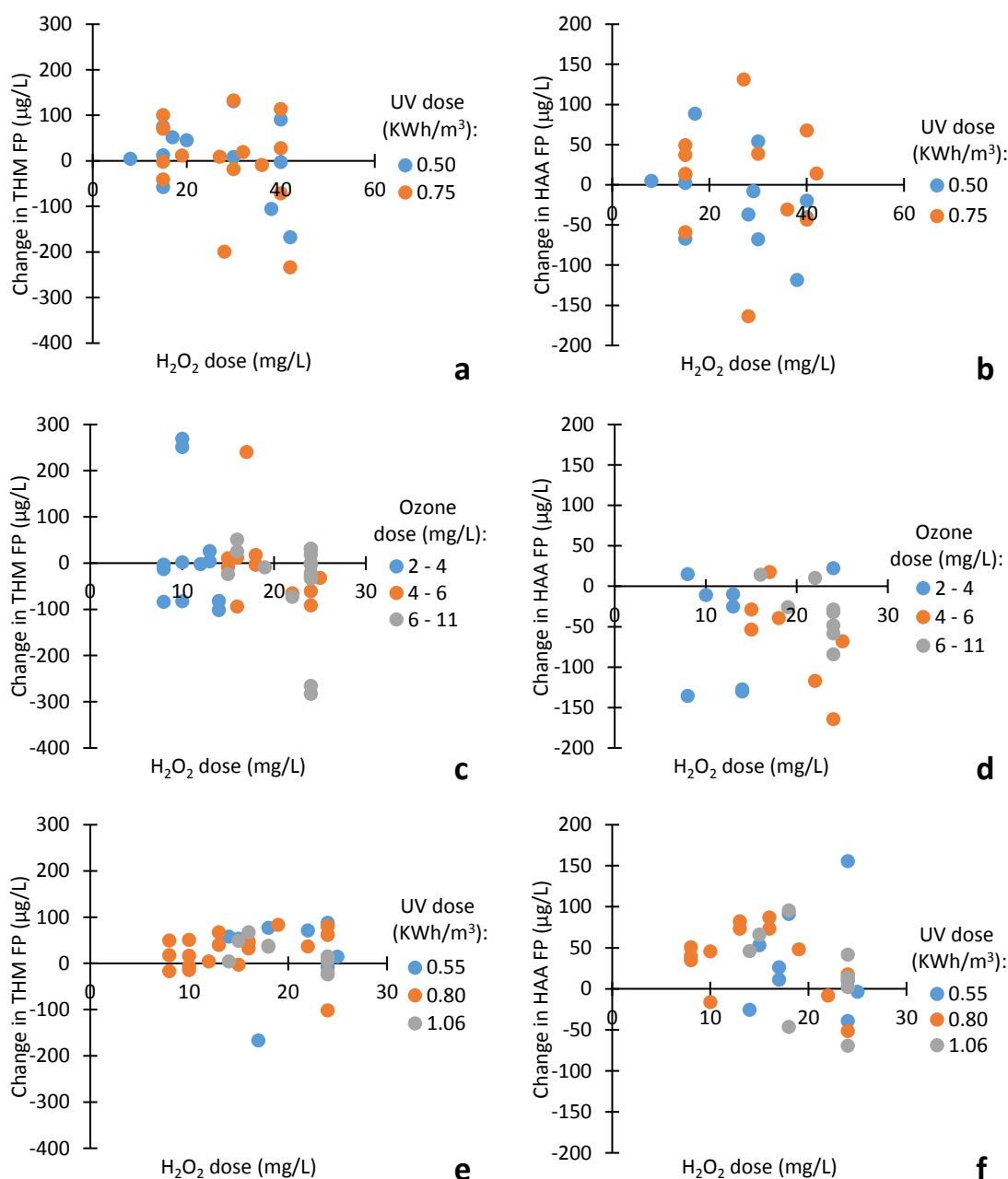


Figure 9. Influence of the operating conditions on the change in THM FP and HAA FP following AOPs. Influence of the UV and hydrogen peroxide doses of the UV/H₂O₂ AOP on the change in THM FP (a), and HAA FP (b). Influence of the ozone and hydrogen peroxide doses on changes in THM FP (c) and HAA FP (d) during the O₃/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP. Influence of the UV and hydrogen peroxide doses on the change in THM FP (e), and HAA FP (f) during the UV/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP.

4.3.3 Correlation between the change in the THM FP and the HAA FP following AOPs

A slight positive correlation ($r^2 = 0.327$) was observed between the change in the THM FP and in the HAA FP following AOPs with respect to the inlet (Figure 10a, Figure 10c). This link means that when the THM FP increased after the AOP, the HAA FP tended to be increased as well. The data factored by AOP showed no difference between the change in the THM FP and the HAA FP following the UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOP (Figure 10a). However splitting the O₃/H₂O₂ - UV/H₂O₂ AOP into its sub-processes illustrated that the O₃/H₂O₂ AOP tended to reduce both the THM FP and the HAA FP whereas the UV/H₂O₂ sub-process showed a tendency to increase both groups of DBPs (Figure 10b). This is in agreement with the conclusions of Kleiser *et al.* (2000) who reported that ozone-based AOPs such as O₃/H₂O₂ are more advantageous for controlling DBP formation than the UV/H₂O₂ AOP.

Additionally, the day of sampling influenced the changes in THM FP and HAA FP. It was observed that the data points from the same day were gathered in the same region of the graph (Figure 10c). The differences between each day of the trial were the metaldehyde spiking and the quality of the feeding water. It is unlikely that the metaldehyde concentration influenced the DBP FP as it was present in water between 0.14 and 2.30 µg/L whereas the NOM was present in the mg/L order. However, Sharp *et al.* (2006) have reported a wide seasonal variation in the NOM composition. The difference in the quality of the inlet water and more specifically the difference in the composition and character of the OM could explain the difference in the changes in THM FP and the HAA FP obtained for the different sampling days. This was supported by the data presented in Figure 11a and Figure 11b. On day 5, AOPs tended to reduce both the THM FP and HAA FP whereas on days 1, 2 and 4, both groups of DBPs tended to increase. However, the same operating conditions were applied for each sampling day. This confirms that the quality of the inlet water and the variation in the composition of the OM influenced the effect of the AOPs on the THM FP and the HAA FP. No reliable correlation could be observed between the changes in the THM FP and HAA FP and the water quality parameters measured in the inlet

such as the turbidity, the DOC, the UV absorbance at 254 nm nor the THM FP or the HAA FP. This was because the techniques used were not sensitive enough to detect the small changes in the DBP precursors, and because of the small number of samples collected from the inlet. Nonetheless, these results suggested that the DBP precursors present in the inlet water on day 5 were different and more treatable by AOPs than the precursors present in the water on the other days of the trial. It is likely that the inlet water contained more humic substances, or unsaturated organic compounds on days 2 and 4 compared to day 5. In addition, Sakai *et al.* (2013) reported that some NOM surrogates including leucine were responsible for increased HAA FP after UV/H₂O₂ treatment whereas some others such as resorcinol showed a decrease in HAA FP. Therefore the composition of NOM in the inlet water has an effect on the formation of DBPs. Despite the relatively small number of data, it could be observed that the SUVA values of the inlet water were higher on days 2 and 4 (1.87 and 1.90 L/(mg.m) respectively) than on day 5 (1.32 L/(mg.m)), which is in agreement with this hypothesis.

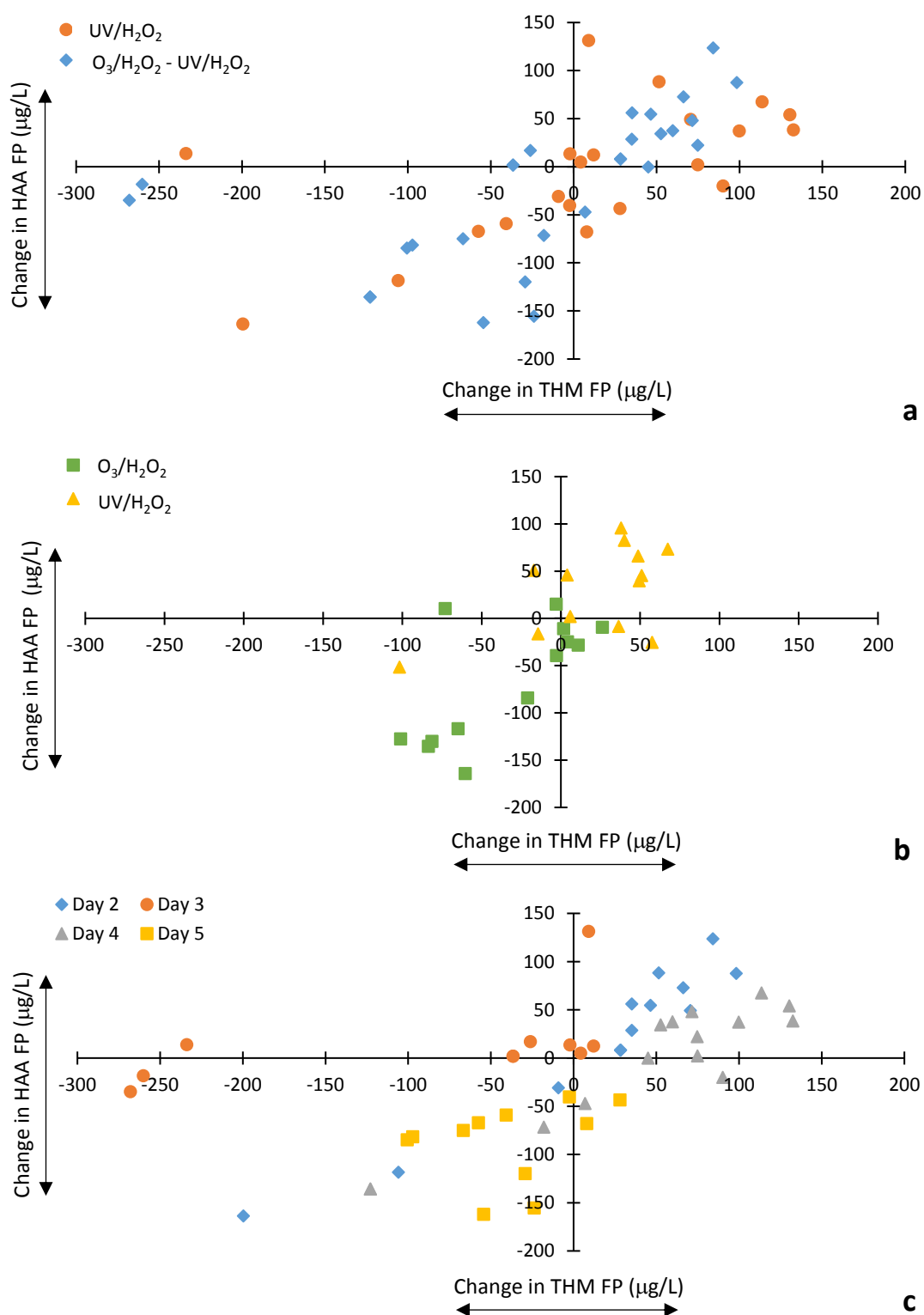


Figure 10. Change in THM FP and HAA FP following AOPs with respect to the inlet. Data factored by AOP (a), by sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP (b), and by day of trial (c). These graphs gather all the data obtained, irrespective of the operating conditions and the sampling day.

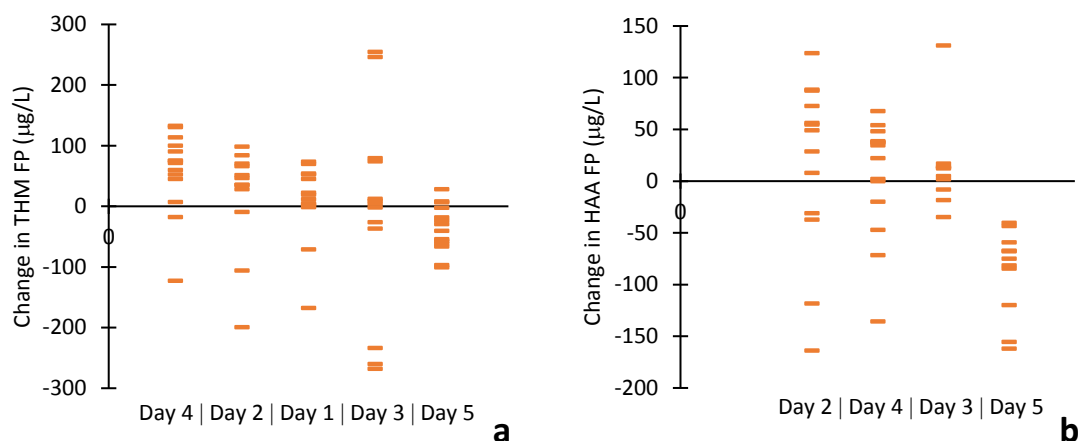


Figure 11. Impact of the sampling day on the change in THM FP (a) and HAA FP (b) following AOPs. These graphs gather all the data obtained for both AOPs irrespective of the operating conditions.

4.3.4 Background OM transformation during AOP

The change in the THM FP following AOPs was weakly linked to the change in the DOC when considering both of the AOPs together (Figure 12a). Removing the 6 data points that showed atypical reductions in THM FP (these data points correspond to both AOPs, different sampling days and different UV doses but they are all related to hydrogen peroxide doses higher than 24 mg/L and an ozone dose of 8 mg/L for the O_3/H_2O_2 - UV/ H_2O_2 AOP) increased the value of the r^2 from 0.345 to 0.781. This correlation was weaker for the HAA FP (Figure 12b). This is in agreement with the findings of Li *et al.* (2016) who reported a strong correlation between DOC and THMs ($r^2 = 0.89$) and a lower correlation with HAAs ($r^2 = 0.62$). These results suggested that the formation of DBPs was related to the variation in the amount of OM in the water. However, this correlation did not imply that a decrease in DOC would necessarily lead to a decrease in the THM FP during AOPs. It was observed that even when the DOC remained unchanged following AOPs, the formation of THMs and HAAs was increased for some samples (Figure 12a, Figure 12b). Sakai *et al.* (2013) reported similar results for HAAs. This indicated that the AOPs changed the reactivity of the OM towards chlorine. This is supported by the findings of Metz *et al.* (2011) and Kleiser *et al.* (2000), who suggested that the reaction of the $\bullet OH$ radicals on the background OM and especially on aromatic compounds could change their structure hence increasing

their reactivity with chlorine compared to the OM in the inlet water. SUVA values decreased during AOP, which illustrated that AOPs reduced the aromatic content of the OM. This is consistent with the findings of Lamsal *et al.* (2011) and Metz *et al.* (2011) who observed that AOPs could fragment aromatic compounds hence decreasing the aromatic content of the OM. A slight trend ($r^2 = 0.15$) was observed between the reduction in the SUVA values following AOPs and the change in the THM FP (Figure 12c), which means that the higher the reduction in SUVA values, the more potential to increase the THM FP. This trend was more modest for HAA FP than for THM FP (Figure 12d). This observation suggested that there was more probability to observe an increase in the THM FP for greater decreases in the aromatic content of the OM. High decreases in SUVA values were achieved for samples having a higher SUVA in the inlet. Indeed, the higher the initial SUVA, the higher the aromatic content in the OM, and Valencia *et al.* (2013) found that AOPs preferentially broke down the OM compounds with a high UV absorbance at 254 nm. Therefore when a greater decrease in SUVA values was observed, more breakdown products from aromatic compounds were formed. Metz *et al.* (2011) reported that the degradation of aromatic structures could lead to more reactive sites which can explain the potential of AOPs to increase the DBP FP.

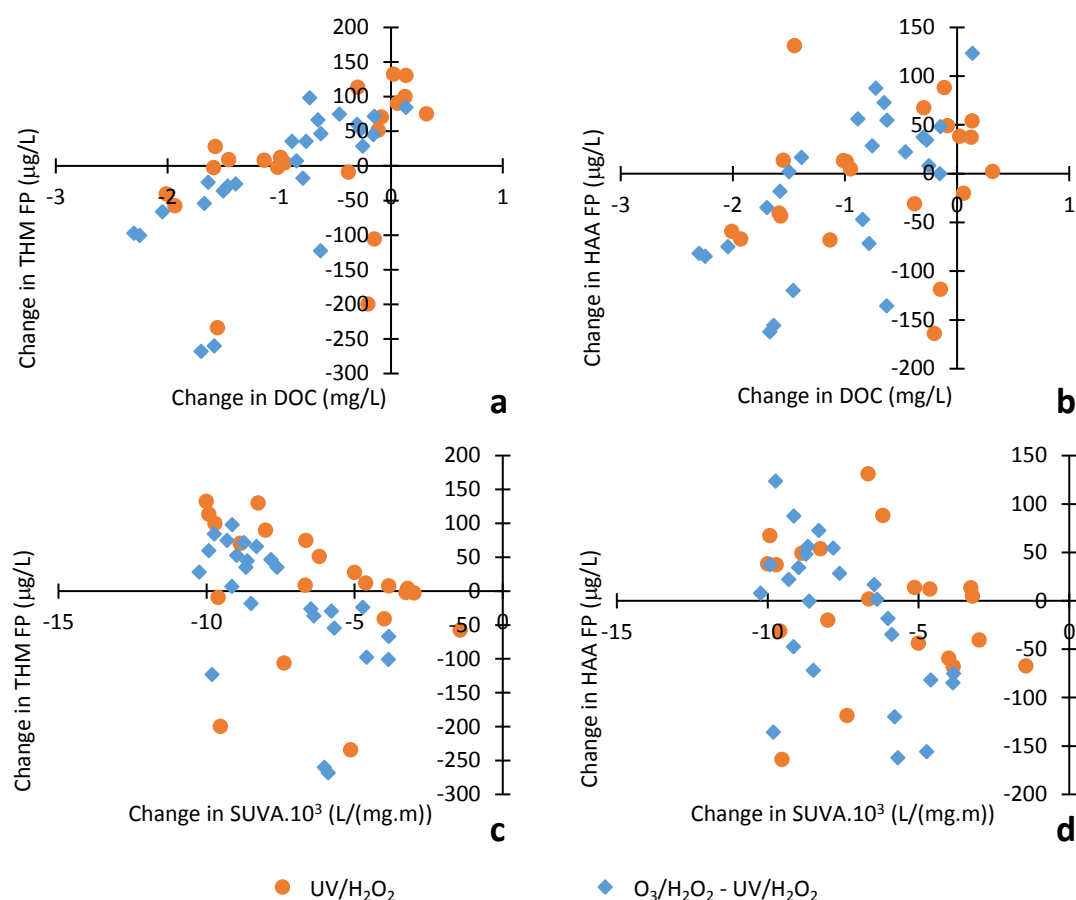


Figure 12. Correlation between the change in the OM character and the changes in THM FP and HAA FP following AOPs. Correlation with the change in DOC (a, b), Correlation with the change in SUVA (c, d). These graphs gather the data from both AOPs, irrespective of the operating conditions.

FEEM were obtained from selected samples collected before AOPs, after AOPs and after GAC filtration to investigate the changes in the character of the OM during AOPs. In order to assess the impact of each step of the treatment processes on the OM, the FEEM of the samples collected between each process were subtracted. The original FEEM were only presented for the inlet water to show the material removed by the processes. The position of the peaks on the FEEM indicate different OM character (Figure 13). Peaks A and C refer to humic-like OM whereas peaks T and B are related to protein-like OM. In particular, peak C indicates more similarity with humic-acid and peak A is more related to fulvic acid-like OM. Also, peak T indicates more similarity with tryptophan-like proteins and peak B with tyrosine-like proteins. Protein-like materials are linked with

bacterial activity (Hudson *et al.*, 2007) whereas humic substances are mixtures of materials formed by biochemical and chemical reactions during the decay and transformation of plant remains (International Humic Substances Society, 2017). The FEEM of the inlet samples all exhibited similar profiles with intense peaks corresponding to humic-like OM (Figure 14a, Figure 15a). In particular, the peak corresponding to humic acid-like material was more intense than the peak related to fulvic acid-like OM.

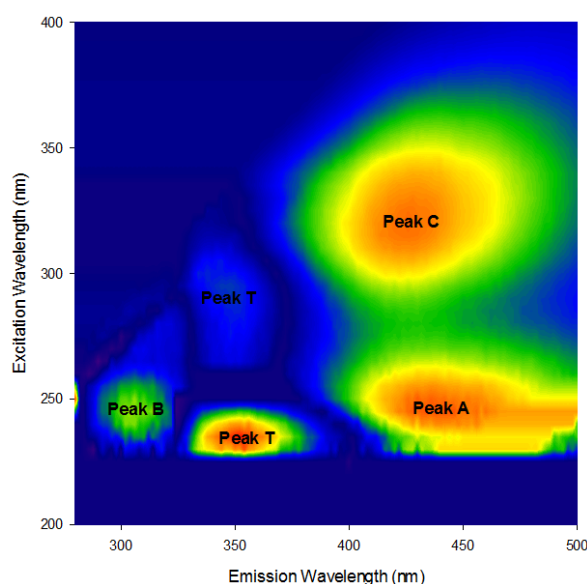


Figure 13. Position of the OM specific peaks on FEEM (Hudson *et al.*, 2007).

The main trends on the FEEM are illustrated in Figure 14 and Figure 15, but additional FEEM were obtained and are presented in Appendix C. All of the samples collected after the UV/H₂O₂ AOP showed a decrease in the peaks related to humic-like material (Figure 14b). It could be noted that the region of the FEEM that was removed after this treatment was very large and covered a part of the protein-like region as well. The same change was observed after the O₃/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP (Figure 15b). This indicated that the UV/H₂O₂ AOP and the O₃/H₂O₂ sub-process mostly removed or transformed the humic-like OM, which is in agreement with the findings of Ahn *et al.* (2017). After the UV/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP, 2 of the 3 samples selected exhibited a decrease in peaks corresponding to tryptophan-like material (Figure 15c), and the last sample showed only a small decrease in humic-related peaks (Appendix C). It is hypothesised that this

difference was due to the amount of humic-like and protein-like OM initially present in the samples however this difference could not be observed on the FEEM of the inlet samples due to the sensitivity of the instrument. The O_3/H_2O_2 sub-process was the treatment that transformed the OM the most in the O_3/H_2O_2 - UV/H_2O_2 AOP. In comparison, the UV/H_2O_2 sub-process only exhibited a small change in the OM character. The FEEM of post-GAC samples all exhibited a further but smaller decrease in the peaks related to humic-like material and a slight decrease in the peak corresponding to tyrosine-like OM (Figure 14c, Figure 15d). An increase in the tryptophan-like peak was also observed after the GAC filtration and was due to the potential of the GAC media to release bacteria. These results revealed how the background OM was transformed during AOP, however, no correlation could be established between the changes in the DOC, the THM FP, the HAA FP and the changes in the intensity of the FEEM peaks. This was most likely due to the sensitivity of the spectrofluorometer which did not allow to pick up the small molecules changes.

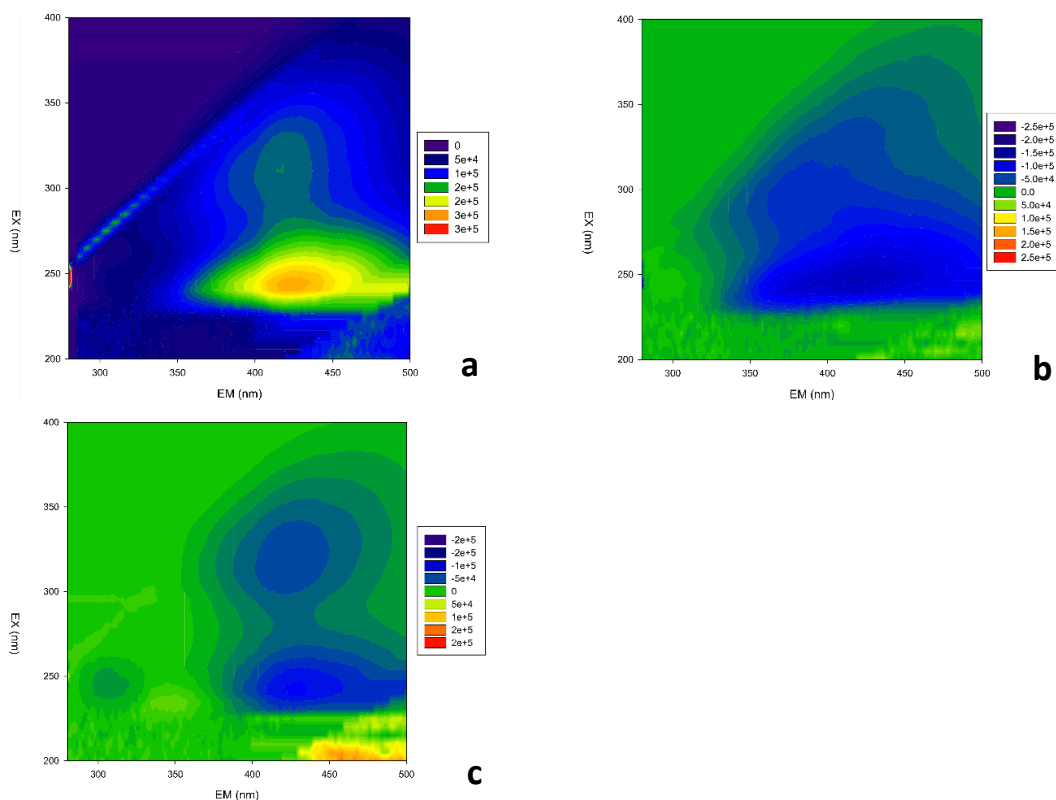


Figure 14. FEEM of the sample collected before UV/H_2O_2 AOP (a). Subtracted FEEM between post- UV/H_2O_2 and inlet (b). Subtracted FEEM between post-GAC and post- UV/H_2O_2 (c). The Rayleigh scatter has been corrected on the FEEM.

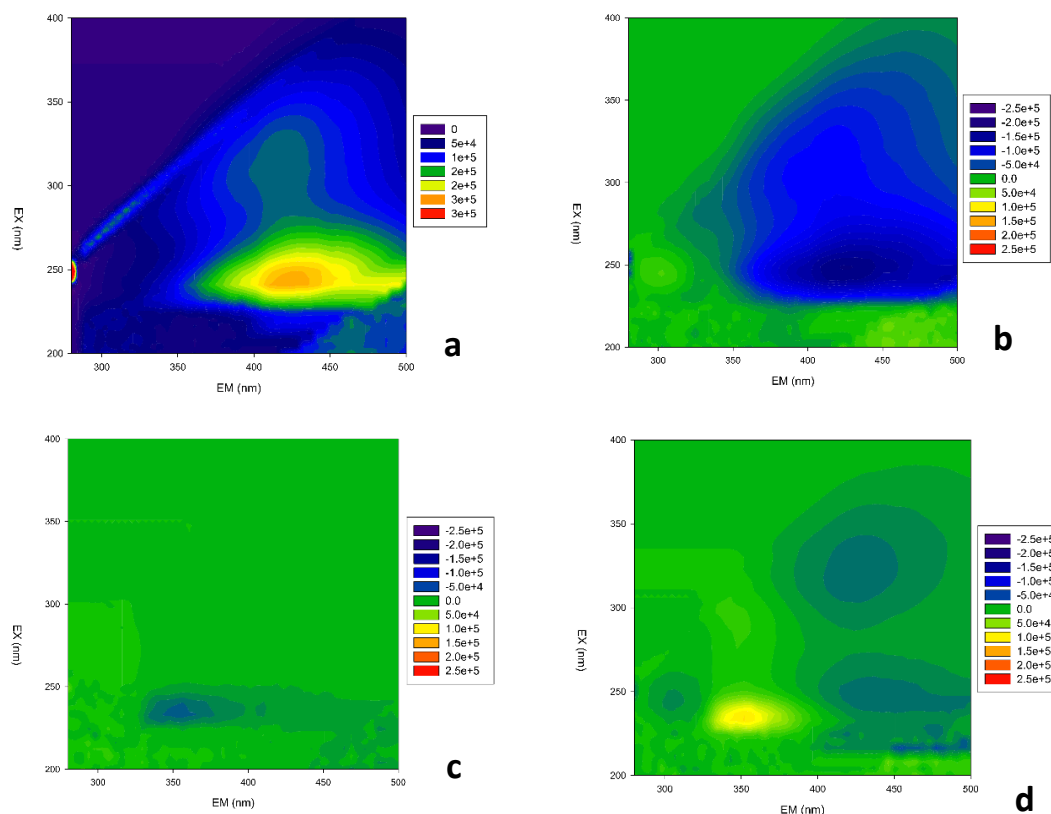


Figure 15. FEEM of the sample collected before AOP (a). Subtracted FEEM between post-O₃/H₂O₂ and inlet (b). Subtracted FEEM between post-UV/H₂O₂ and post-O₃/H₂O₂ (c). Subtracted FEEM between post-GAC and post-UV/H₂O₂ (d). The Rayleigh scatter has been corrected on the FEEM.

The HPSEC chromatograms of the inlet samples all showed similar profiles with a higher peak at low retention times corresponding to bigger molecules and a lower peak at higher retention times corresponding to smaller molecules (Figure 16a, Figure 16b). The general trend on the chromatograms are illustrated by Figure 16 but the additional chromatograms were obtained and are presented in Appendix D. As the wavelength of the detector was set at 254 nm, these chromatograms only showed compounds that absorbed at this wavelength, which are mainly unsaturated and aromatic OM compounds. Following the UV/H₂O₂ and the O₃/H₂O₂ - UV/H₂O₂ treatments, the intensity of both peaks was decreased. This indicated that the AOPs reduced the amount of compounds that absorbed at 254 nm. These were likely degraded into other compounds that did not absorb at this wavelength. This is supported by Westerhoff *et al.* (1999) who

reported that compounds containing double bonds hence absorbing light at 254 nm were degraded faster by AOPs. As a result, the breakdown products may have presented less aromaticity and a lower absorbance at 254 nm. In addition, it could be noted that the reduction in the peak corresponding to the OM of higher molecular weight was greater than that of the peak related to smaller OM compounds (Figure 16a, Figure 16b). This demonstrated that these AOPs preferentially broke down the larger OM compounds. The degradation of larger molecules lead to the formation of more low molecular weight compounds although they did not appear on the chromatogram as they might not absorb UV at 254nm. This is in agreement with the findings of Valencia *et al.* (2013), Bond *et al.* (2009) and Ahn *et al.* (2017), who found that the AOPs preferentially broke down the high molecular weight OM compounds with a high UV absorbance at 254 nm to form smaller compounds. This could explain the increase in DBP FP after AOPs that we observed in some samples as Özdemir (2014) observed an increase in the THM FP when the molecular weight was reduced. Additionally, the O₃/H₂O₂ sub-process of the O₃/H₂O₂ - UV/H₂O₂ AOP had more impact on the OM than the UV/H₂O₂ sub-process (Figure 16b). Most of the decrease in the peaks occurred after the O₃/H₂O₂ sub-process and the UV/H₂O₂ sub-process only achieved a small further decrease in both peaks. Overall, the chromatograms of both AOPs exhibited a similar decrease in the size of the OM compounds suggesting a similar transformation of the unsaturated and aromatic OM.

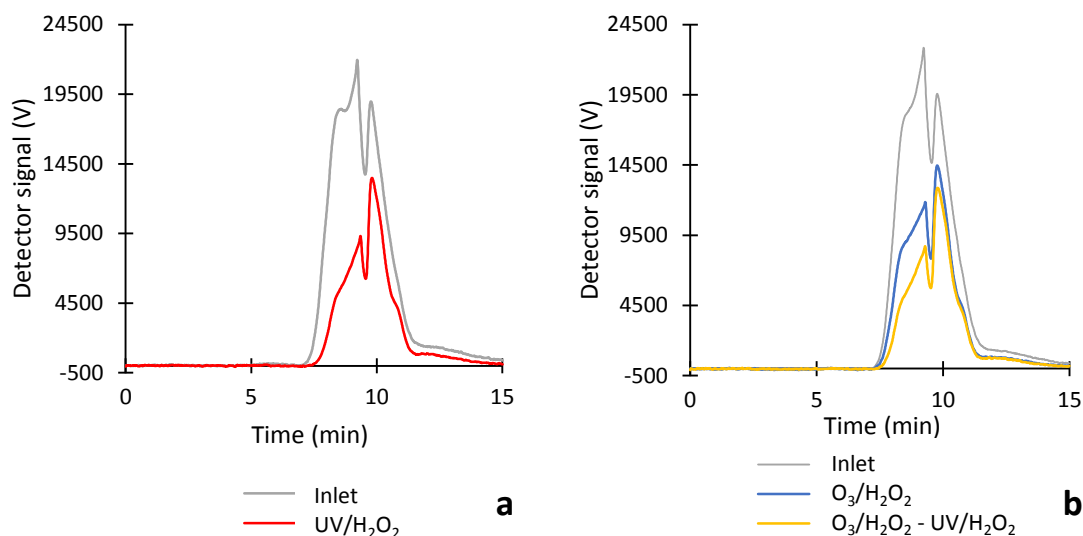


Figure 16. Characteristic HPSEC chromatograms of the samples collected at each stage of the AOP treatments. Samples collected during UV/H₂O₂ AOP (a) and during O₃/H₂O₂ - UV/H₂O₂ AOP (b).

4.3.5 Comparison of the impact of UV/H₂O₂ and O₃/H₂O₂ - UV/H₂O₂ AOPs on THM FP and HAA FP

In order to compare the impact of both AOPs on THM FP and HAA FP, Student tests were performed. For both tests, the calculated t values were smaller than the critical t value (Table 9). This demonstrated that there was no significant difference between the impact of the UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOPs on the THM FP and the HAA FP. This is in agreement with the previous findings demonstrated by the FEEM and the HPSEC chromatograms that both AOPs had a similar impact on the transformation of the OM (including DBP precursors).

Table 9. Characteristic t-test values obtained for the comparison of the impact of UV/H₂O₂ and O₃/H₂O₂ - UV/H₂O₂ AOPs on the change in THM FP and HAA FP.

	Change in THM FP after AOP		Change in HAA FP after AOP	
	UV/H ₂ O ₂	O ₃ /H ₂ O ₂ - UV/H ₂ O ₂	UV/H ₂ O ₂	O ₃ /H ₂ O ₂ - UV/H ₂ O ₂
Mean	-0.2523	12.27099	-6.27245	-15.7918
Variance	8723.899	10065.7	4419.559	6098.634
Observations	27	39	23	25
Degrees of Freedom	59		46	
Calculated t value	-0.51946		0.455842	
Critical t value	2.000995		2.012896	
P value	0.605381		0.650648	

4.4 Conclusions

The AOPs assessed in this work have been found to both increase or decrease the DBP FP. Nonetheless, the changes in THM FP and HAA FP were not influenced by the process operating conditions. The quality of the inlet water and more specifically the character and the composition of the OM in the inlet could better explain the differences in the changes in THM FP and HAA FP following AOPs. Therefore, in the range of UV and oxidant doses assessed, these AOPs could not control the DBP formation. The UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOP had a similar impact on the THM FP and the HAA FP. The HAA FP tended to increase when the THM FP increased. There was a weak link between the change in THM FP and the change in the DOC during AOPs which suggested that the amount of OM in water had an influence on the THM FP. This work demonstrated that the AOPs changed the reactivity of the OM with chlorine.

Particularly, it was observed that the AOPs decreased the SUVA values hence the aromatic content of the OM. Also the AOPs preferentially transformed the high molecular weight aromatic compounds into smaller non aromatic compounds. These transformations of the background OM could explain the potential of AOPs to increase the THM FP and the HAA FP. The UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOP mostly removed or transformed the humic-like OM. Overall, the two AOPs assessed had a similar impact on the OM transformation. It could be pointed out that the O₃/H₂O₂ sub-process was the treatment that transformed OM the most in the O₃/H₂O₂ - UV/H₂O₂ AOP. In addition, the O₃/H₂O₂ sub-process tended to decrease both the THM FP and the HAA FP whereas the UV/H₂O₂ sub-process showed a trend to increase both groups of DBPs. Therefore the potential of this individual AOP to prevent DBP FP should be further investigated.

4.5 Acknowledgments

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5 Overall discussion

In this work, no relation was observed between the UV and chemical doses applied during AOPs and the resultant DBP FP. Therefore, the AOPs were not efficient at controlling the downstream DBP formation in this study. This can be attributed to the low range of UV doses tested compared to some doses applied in the literature although they are doses that are used practically at full-scale WTWs. Jefferson *et al.* (2016) and Bond *et al.* (2011) observed that the THM FP and the degradation of OM during AOPs were dependant on the UV dose. However, these conclusions were based on experiments performed at lab-scale, hence within more controlled conditions than at pilot-scale. In addition, the doses tested were much higher than the energy inputs that were used in the present work. Jefferson *et al.* (2016) reported a reduction in the THM FP after an irradiation of 10 000 mJ/cm² and Bond *et al.* (2009) observed that the OM was almost completely mineralised at UV doses close to 50 000 mJ/cm². As a result, the inability of AOPs to prevent DBP formation in this work was likely due to the fact that the UV ranges assessed were too low for DBP control.

Additionally, because of time constraints imposed by the sponsors, the trials were performed over several days only. As a result, a consequent number of samples had to be collected in a short period of time. Although some time was given between each change in the operating conditions to allow for stabilisation in the systems, this might have not been sufficient to observe trends in the change in DBP FP.

AOPs are promising technologies for preventing the downstream formation of DBPs as long as they are applied at high oxidant and UV doses. The high costs involved are prohibitive in many cases but the development in UV-LED technologies might reduce the cost of delivery of UV and make the use of high UV doses more amenable (Autin, 2012). In the meantime, subsequent treatment such as GAC filtration, or additional preliminary treatments to remove DBP precursors must be implemented to prevent excess downstream DBP formation.

In this study, the impact of AOPs on DBPs was influenced by the quality of the inlet water. To strengthen this observation, more parameters related to the OM character could have been measured in the inlet water. Also, some identification techniques comprising the use of mass spectrometry could have helped to identify and quantify chemical groups or precursors responsible for significant changes in the DBP FP following AOPs. Ideally, samples of the inlet should have been collected for each set of conditions tested. In this trial and due to time constraints, samples of the inlet were collected only twice a day which did not allow for the observation of significant and reliable trends between the parameters measured in the inlet such as DOC, UV absorbance at 254 nm or SUVA and the changes in the THM FP and the HAA FP.

As the metaldehyde removal depended on the process variables whereas the DBP FP did not for the range that was assessed here, there was no correlation between the metaldehyde removal and the changes in the THM FP and the HAA FP. As a result, the comparison of both AOPs mainly relied on their efficiency to remove metaldehyde. The UV/H₂O₂ AOP achieved metaldehyde removals up to 98% for metaldehyde initial concentrations of up to 2 µg/L. This is in consistent with the findings of Semitsoglou-Tsiapou *et al.* (2016) who reported an optimum metaldehyde removal of 97% by this AOP under similar ranges of UV and hydrogen peroxide doses. In addition, the observed enhancement of the removal efficiency with increasing UV and hydrogen peroxide doses was consistent with the work of other researchers (Autin *et al.*, 2012, 2013; Jefferson *et al.*, 2016). To our knowledge, no study has been published on the performance of the O₃/H₂O₂ - UV/H₂O₂ AOP on metaldehyde removal. This AOP proved to be at least as efficient as the UV/H₂O₂ AOP for reducing metaldehyde concentrations below the regulatory level of 0.1 µg/L and achieved removals of up to 97%. This AOP was found to be mainly influenced by the ozone and UV doses applied in the range that we assessed. The O₃/H₂O₂ - UV/H₂O₂ AOP showed better removal efficiencies than the UV/H₂O₂ AOP at UV doses lower than 0.60 kWh/m³. Nonetheless, these were achieved using ozone as an additional chemical. The cost of ozone generation might be prohibitive for the implementation of this AOP even though it reduced the need for hydrogen peroxide.

In addition, AOPs should be compared according to their potential to reduce metaldehyde concentration below the regulatory level of 0.1 $\mu\text{g/L}$. Both AOPs were efficient for this purpose, however the oxidant and UV doses required were different. For selecting a process to be implemented in WTWs, the cost efficiency also needs to be taken into account. Considering the operating costs only, the electricity consumption of the UV lamps is the major source of expenses, and the cost of the generation of ozone is more expensive than the supply of hydrogen peroxide. Therefore, a comprehensive economic study of these two processes would be beneficial for informing the best choice of AOP to be implemented at large scale.

The assessment presented in this work gives a fair indication of the removal efficiency that can be achieved together with the chemical and UV doses required, however there are some limitations to scaling up these AOPs for an implementation in WTWs. From pilot to full-scale, the volume of the reactors will increase hence increasing the path length of the UV and reducing the efficiency of the AOP. Nonetheless, this pilot-scale study gives a good insight and a reliable comparison of the potential of these AOPs.

This work highlighted the potential of the $\text{O}_3/\text{H}_2\text{O}_2$ sub-process of the $\text{O}_3/\text{H}_2\text{O}_2$ - UV/ H_2O_2 AOP both for metaldehyde removal and to control downstream DBP formation. This sub-process achieved most of the metaldehyde removal of the overall process and showed a trend to decrease the THM FP and the HAA FP. This individual AOP did not reduce metaldehyde concentration sufficiently to meet the regulatory level. However, the $\text{H}_2\text{O}_2/\text{O}_3$ mass ratios applied in this trial were not optimal because a hydrogen peroxide residual was needed for the second sub-process. An increase in the ozone and hydrogen peroxide doses as well as an adjustment of the $\text{H}_2\text{O}_2/\text{O}_3$ mass ratio could enhance the metaldehyde removal. In addition, the operating cost of that AOP would be considerably lower than that of the two other AOPs as it would not comprise the use of UV irradiation.

6 Conclusions

Both AOPs were efficient at reducing metaldehyde concentration below the regulatory concentration of $0.1 \mu\text{g/L}$. Maximum removals of 98% and 97% were obtained for an initial metaldehyde concentration of $2 \mu\text{g/L}$ at UV doses of about 1 kWh/m^3 for the UV/H₂O₂ AOP and the O₃/H₂O₂ - UV/H₂O₂ AOP respectively. An increase in the UV and hydrogen peroxide doses as well as an increase in the flow rate from 2.5 to 3.5 m³/h enhanced the efficiency of the UV/H₂O₂ AOP. The performance of the O₃/H₂O₂ - UV/H₂O₂ AOP for removing metaldehyde was enhanced by increasing the hydrogen peroxide and UV doses simultaneously and by raising the UV dose. However, the UV and ozone doses were the most influent variables in the process as the •OH radical production during the first sub-process and the hydrogen peroxide dose of the second sub-process were both dependant on the ozone dose. The O₃/H₂O₂ - UV/H₂O₂ AOP was found to be more efficient than the UV/H₂O₂ AOP for removing metaldehyde when applied at UV doses lower than 0.60 kWh/m^3 . The minimum UV doses required in the UV/H₂O₂ AOP to achieve metaldehyde compliance were similar to that of the O₃/H₂O₂ - UV/H₂O₂ AOP for metaldehyde inlets from 0.14 to $2.30 \mu\text{g/L}$. However, the minimum oxidant doses required were different, and therefore an economic study would inform of the choice of AOP to be implemented at full-scale taking into account the operating and capital expenses. One drawback of the two processes assessed in this research was their potential to increase DBP FP. AOPs were found to change the THM FP between -85% and +155% and the HAA FP between -85% and +76%. However the impact of AOPs on DBP formation was not related to the UV and oxidant doses applied. The change in THM FP and HAA FP was more influenced by the quality of the inlet water. Depending on the sampling day, the quality of the inlet water and especially the composition of the NOM was different. It is believed that different DBP precursors that were more or less treatable by AOPs were present in the inlet water depending on the sampling day. Although the change in the DBP FP was slightly correlated to the change in the amount of OM in the water during AOPs, these processes transformed the NOM and changed their characteristics hence changing their reactivity with

chlorine. The changes in the amount, structure, character and size of the OM could explain the potential of AOPs to increase DBP FP. No significant difference was observed between the impact of the two AOPs on THM FP and HAA FP and on the transformation of the background OM. As these AOPs cannot be used to control downstream DBP formation, it is recommended to implement additional treatments either before or after the AOPs in order to prevent the formation of elevated levels of DBPs upon chlorination. Downstream GAC filtration appeared to be a suitable alternative to better control the THM FP and the HAA FP following AOPs.

7 Further research

This work has shown that AOPs transformed the OM by changing their structure and reactivity. However, these changes could not be directly related to increases or decreases in the THM FP and the HAA FP. The water quality of the inlet has also shown to influence the DBP FP changes following AOPs. Therefore, further work should focus upon linking the changes in OM to increases or decreases in the DBP FP. The use of more sensitive equipment or different techniques such as HPSEC with organic carbon detection (HPSEC-OCD), liquid chromatography with quadrupole time of flight detection (LC-QTOF), Fourier-transform infrared spectroscopy (FTIR) or nuclear magnetic resonance (NMR) would be beneficial for understanding the changes in the structure and character of the OM during AOPs. Some degradation experiments performed on OM surrogates would be beneficial for investigating how they are oxidised during AOPs and whether their by-products present more reactivity towards chlorine than the parent compounds. Also, further characterisation of the OM in the inlet water would contribute to understanding the impact of AOPs on DBP FP. The use of qualitative techniques would enable the identification and quantification of chemical groups or precursors responsible for significant changes in the DBP FP after the AOPs.

Further research into the impact of AOPs on DBPs using different disinfection techniques could also be beneficial. Indeed, Yang *et al.* (2012) reported that chloramination produced many fewer DBPs than chlorination following ozone oxidation and O_3/H_2O_2 AOP. They also observed that the HAA FP could be reduced by 20% when using chloramination in comparison to chlorination. Therefore, using different disinfection techniques could reduce the impact of AOPs on DBP formation.

Both the UV/ H_2O_2 and the O_3/H_2O_2 - UV/ H_2O_2 AOPs have proven to be efficient at reducing metaldehyde concentration below the regulatory level for initial metaldehyde concentrations up to 2.10 $\mu\text{g/L}$. However, due to the nature of these AOPs, different oxidant and UV doses were required for each AOP to produce metaldehyde-compliant water. Therefore a detailed cost analysis including the

operating costs as well as the capital costs required to operate these AOPs would be useful for assessing which technology is the most economically viable and therefore helping in deciding the AOP to be implemented at full-scale in WTWs for metaldehyde removal.

Finally, the O_3/H_2O_2 AOP, which was a sub-process of the O_3/H_2O_2 - UV/ H_2O_2 process, showed promising performance both for metaldehyde removal and for controlling downstream DBP formation. This AOP was responsible for most of the metaldehyde removal achieved by the overall O_3/H_2O_2 - UV/ H_2O_2 process. In this work the O_3/H_2O_2 AOP was only able to reduce metaldehyde below the regulatory level of $0.1 \mu\text{g/L}$ when the inlet was lower than $0.2 \mu\text{g/L}$. However, the H_2O_2/O_3 ratio was not optimal in this trial as a residual hydrogen peroxide was needed for the subsequent AOP. It is likely that the $\bullet\text{OH}$ radical production hence the metaldehyde removal would be increased with optimising this ratio. In addition, as this AOP do not comprise the use of UV irradiation, higher doses of oxidants could be used to enhance metaldehyde degradation while still making this AOP economically viable. In comparison to the UV/ H_2O_2 AOP and the overall O_3/H_2O_2 - UV/ H_2O_2 process, the O_3/H_2O_2 process has shown a beneficial impact on DBP FP as it tended to decrease both the THM FP and the HAA FP. Therefore, further trials would be of interest to assess the impact of optimising and increasing the oxidant doses applied in this process on metaldehyde removal and on DBP formation.

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APPENDICES

Appendix A Influence of AOP process variables on metaldehyde removal

A.1 Influence of process variables on the UV/H₂O₂ AOP

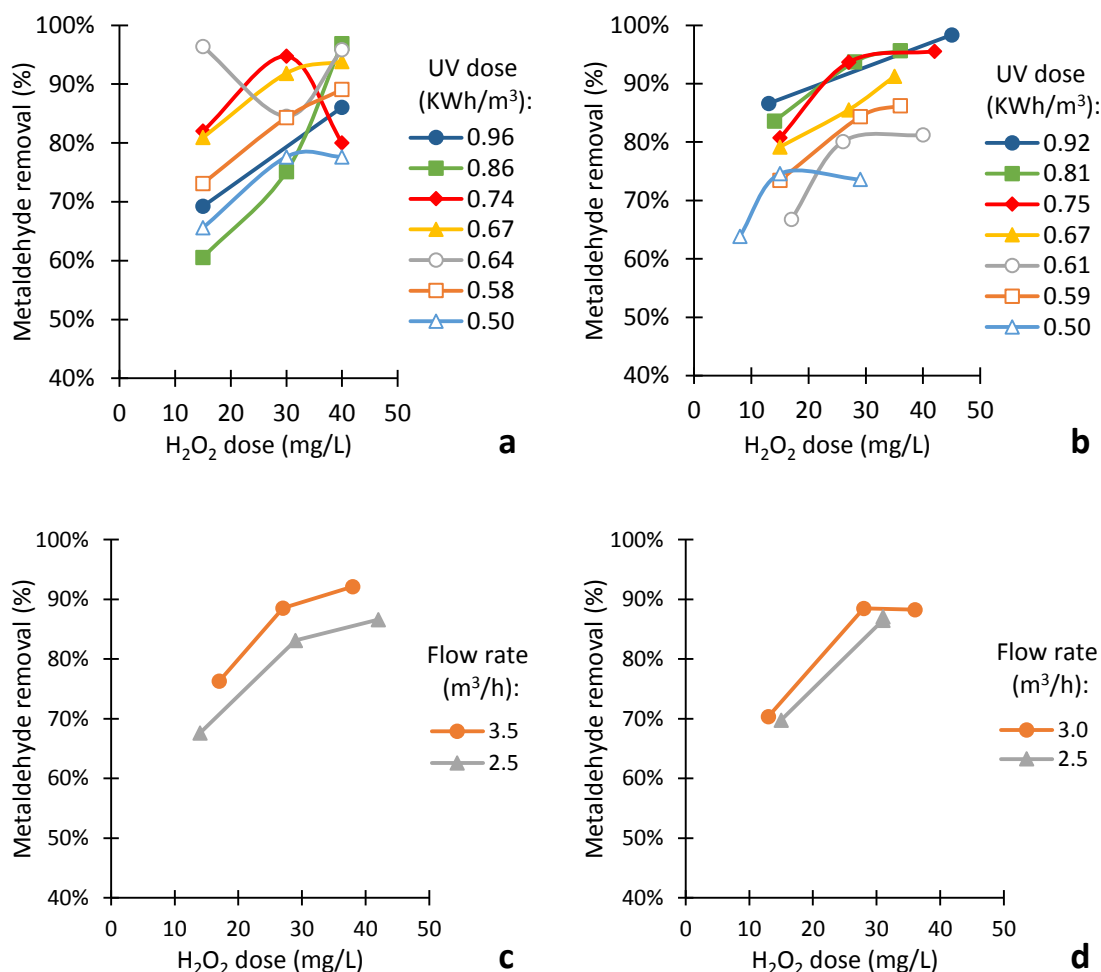


Figure A-1. Influence of the operating conditions of the UV/H₂O₂ AOP on metaldehyde removal: Influence of the hydrogen peroxide and UV doses for metaldehyde inlet concentrations of 0.80 µg/L (a) and 2.112 µg/L (b). Influence of the flow rate and the hydrogen peroxide dose for an inlet of 0.14 µg/L and a UV dose of 0.59 kWh/m³ (c) and for an inlet of 0.53 µg/L and a UV dose of 0.67 kWh/m³ (d). The lines linking the data points are for illustrative purpose only. The values of the UV dose and the flow rate in the legend are the mean of the measured values of each data point.

A.2 Influence of the process variables on the O₃/H₂O₂ - UV/H₂O₂ AOP

A.2.1 Influence of the process variables on the efficiency of the overall O₃/H₂O₂ - UV/H₂O₂ AOP

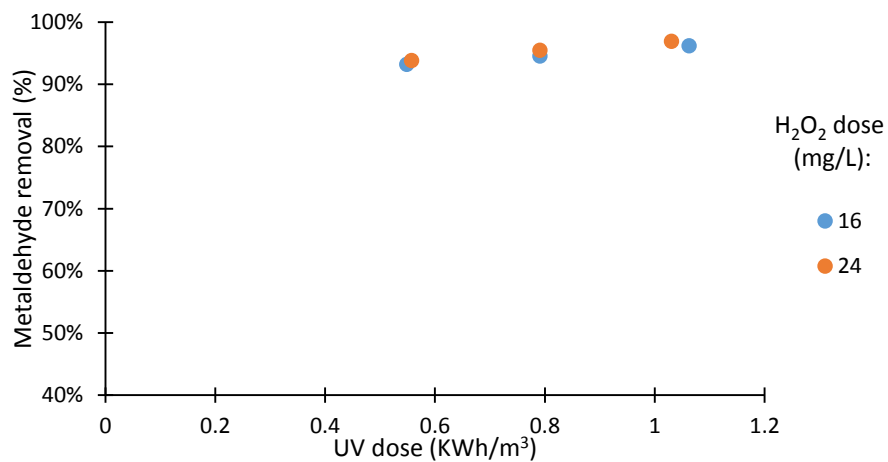


Figure A-2. Influence of the hydrogen peroxide and UV doses on the metaldehyde removal by the overall O₃/H₂O₂ - UV/H₂O₂ AOP at constant ozone dose of 7.3 mg/L for a metaldehyde inlet of 2.04 µg/L.

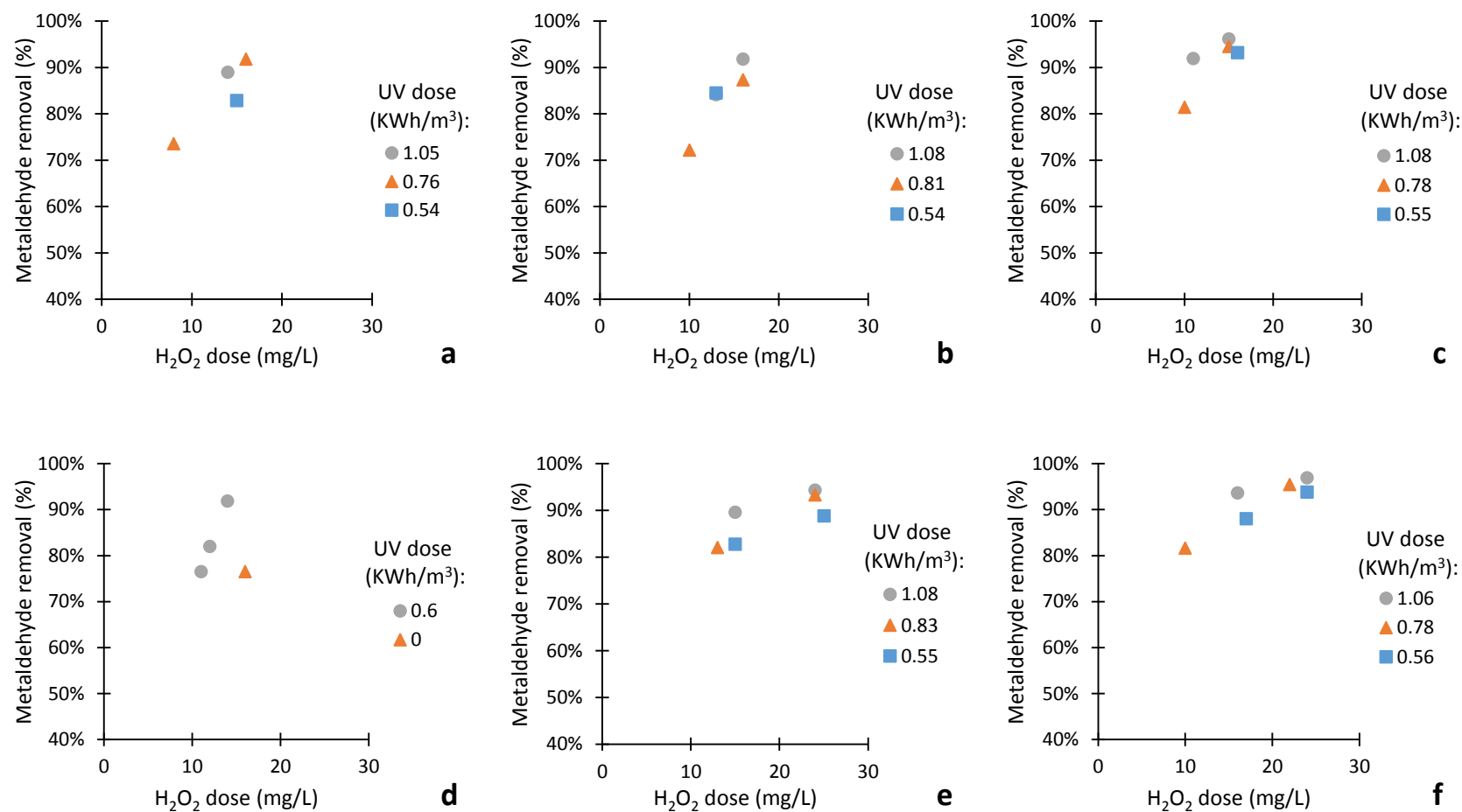


Figure A-3. Influence of the operating conditions on the metaldehyde removal by the overall O_3/H_2O_2 - UV/ H_2O_2 AOP at constant H_2O_2/O_3 mass ratios: Ratio of 2 (a, b, c, d) and 3 (e, f) for different metaldehyde inlet concentrations: 0.53 $\mu g/L$ (a), 2.14 $\mu g/L$ (b), 2.04 $\mu g/L$ (c, f), 2.30 $\mu g/L$ (d) and 0.80 $\mu g/L$ (e).

A.2.2 Influence of the process variables on the efficiency of the O₃/H₂O₂ sub-process

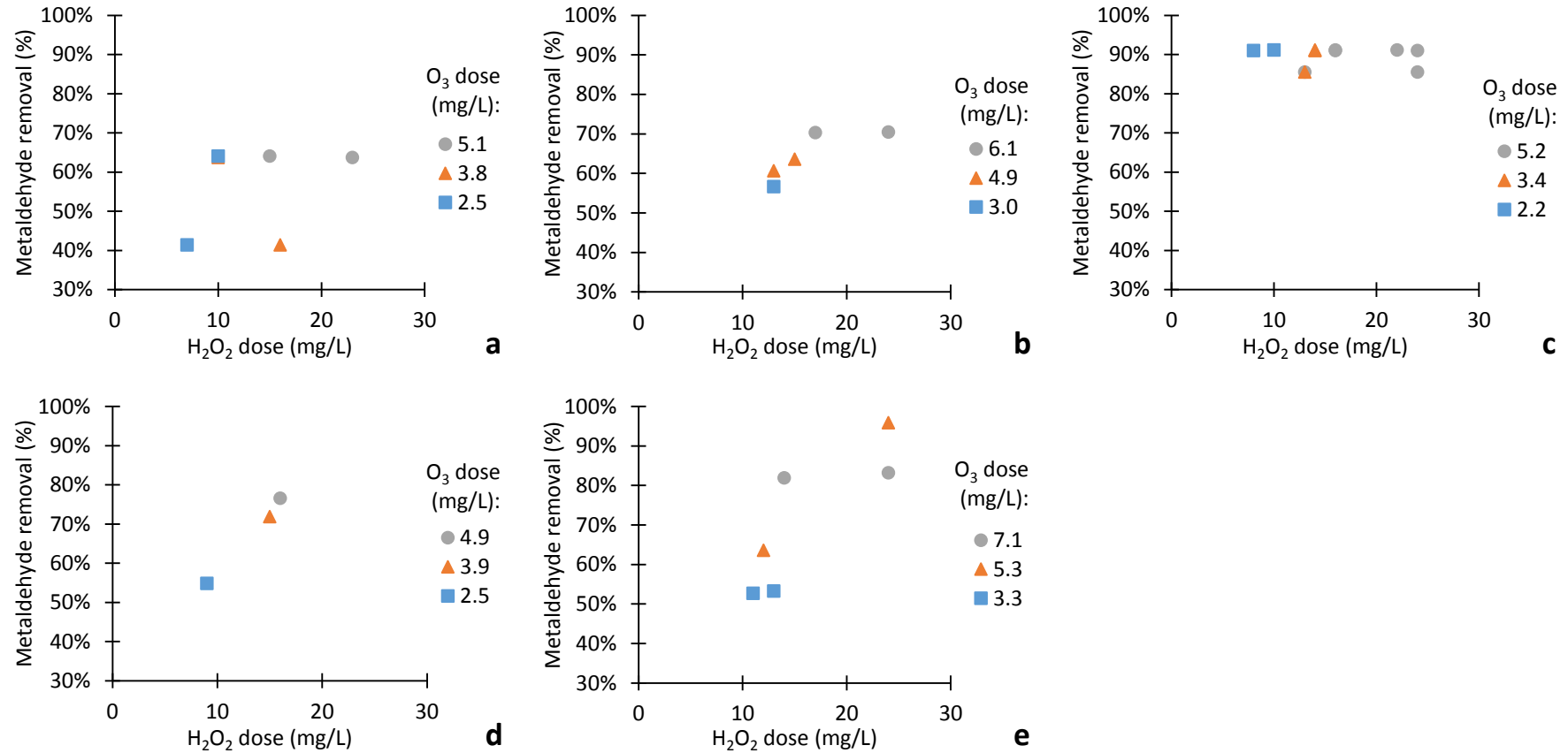


Figure A-4. Influence of the ozone and hydrogen peroxide doses of the O₃/H₂O₂ sub-process on metaldehyde removal at a flow rate of 2.5 m³/h for different metaldehyde inlet concentrations: 0.53 µg/L (a), 0.80 µg/L (b), 2.14 µg/L (c) and 2.30 µg/L (d). Influence at a flow rate of 0.6 m³/h for a metaldehyde inlet concentration of 2.30 µg/L (e). The values of the ozone dose in the legend are the mean of the measured values of each data point.

A.2.3 Influence of the process variables on the efficiency of the UV/H₂O₂ sub-process

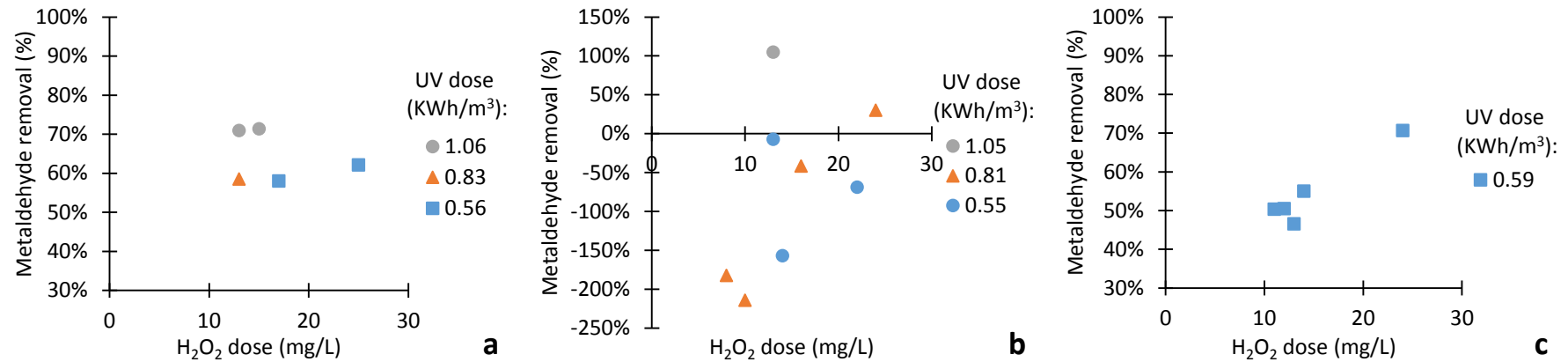


Figure A-5. Influence of the UV and hydrogen peroxide doses of the UV/H₂O₂ sub-process at different concentrations of metaldehyde in the inlet water: 0.80 µg/L (a), 2.14 µg/L (b) and 2.30 µg/L (c). The values of the UV dose in the legend are the mean of the measured values of each data point

Appendix B Results of the DISTLM statistical tests

The variables that statistically explain a significant proportion of the variation of the set of data are in bold. Samples of the inlet water have been taken twice per day and the average of the parameters measured such as DOC, metaldehyde inlet, turbidity and UV absorbance at 254 nm has been done. Therefore, there are less than 10 different values for the each parameter measured in the inlet. As a result, there are some limitations to consider one of these parameters as having a significant impact on the response variables due to the low number of data.

B.1 Influence of the process variables and the water quality parameters on metaldehyde removal

Table B-1. DISTLM Marginal test: Influence of the process variables of the UV/H₂O₂ AOP on metaldehyde removal. Residual degrees of freedom: 125.

Variable	SS(trace)	Pseudo-F	P	Prop.
Flow rate	16.101	18.313	0.0001	0.12779
H₂O₂	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. DISTLM Sequential test: Influence of the process variables of the UV/H₂O₂ AOP on metaldehyde removal.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res.df
UV	39.827	57.771	0.0001	0.31608	0.31608	125
H₂O₂	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

Table B-3. DISTLM Marginal test: Influence of the process variables of the O₃/H₂O₂ - UV/H₂O₂ AOP on metaldehyde removal. Residual degrees of freedom: 62.

Variable	SS(trace)	Pseudo-F	P	Prop.
H ₂ O ₂ /O ₃	1.969	2.0003	0.1561	0.031254
O₃	28.611	51.583	0.0001	0.45415
H₂O₂	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. DISTLM Sequential test: Influence of the process variables of the O₃/H₂O₂ - UV/H₂O₂ AOP on metaldehyde removal.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res.df
UV	33.718	71.395	0.0001	0.53521	0.53521	62
O₃	15.681	70.333	0.0001	0.24891	0.78412	61
H ₂ O 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 ₂ O ₂ /O ₃	0.000103	0.00051	0.9799	1.64E-06	0.81996	56

Table B-5. DISTLM Marginal test: Influence of the process variables of the O₃/H₂O₂ sub-process on metaldehyde removal. Residual degrees of freedom: 48.

Variable	SS(trace)	Pseudo-F	P	Prop.
Flow rate	3.7589	3.9882	0.0528	0.076713
H ₂ O ₂ /O ₃	0.021648	0.021215	0.8806	0.0004418
O ₃	5.0298	5.4907	0.0255	0.10265
H ₂ O 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. DISTLM Sequential test: Influence of the process variables of the O₃/H₂O₂ sub-process on 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
O₃	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 ₂ O ₂ /O ₃	0.24518	0.67275	0.4169	0.005004	0.68018	43
H ₂ O ₂	0.000224	0.000599	0.9822	4.56E-06	0.68019	42

Table B-7. DISTLM Marginal test: Influence of the process variables of the UV/H₂O₂ sub-process on metaldehyde removal. Residual degrees of freedom: 29.

Variable	SS(trace)	Pseudo-F	P	Prop.
O ₃	16.762	17.162	0.2032	0.055872
H ₂ O ₂	0.0847	0.082109	0.786	0.0028233
H ₂ O 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 ₂ O ₂	0.010373	0.010031	0.9243	0.00034576
UV254 Abs post O ₃ /H ₂ O ₂	0.021981	0.021264	0.8742	0.00073269
DOC post O ₃ /H ₂ O ₂	23.633	24.799	0.1227	0.078776

Table B-8. DISTLM Sequential test: Influence of the process variables of the UV/H₂O₂ sub-process on metaldehyde removal.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res .df
DOC post O ₃ /H ₂ O ₂	2.3633	2.4799	0.1228	0.078776	0.07877	29
H ₂ O ₂ /O ₃	1.502	1.6092	0.2179	0.050066	0.12884	28
UV254 Abs post O ₃ /H ₂ O 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 ₂ O ₂	0.53655	0.56968	0.4394	0.017885	0.21512	25
Turbidity post O ₃ /H ₂ O ₂	0.36311	0.3759	0.5468	0.012104	0.22722	24
UV	0.027798	0.027612	0.8656	0.000927	0.22815	23

B.2 Influence of the process variables and the water quality parameters on the THM FP change following AOPs

Table B-9. DISTLM Marginal test: Influence of the process variables of the UV/H₂O₂ AOP on THM FP. Residual degrees of freedom: 25.

Variable	SS(trace)	Pseudo-F	P	Prop.
Flow rate	0.1686	0.16317	0.6906	0.0064846
H ₂ O 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 B-10. DISTLM Sequential test: Influence of the process variables of the UV/H₂O₂ AOP on THM FP.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res. df
H ₂ O 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

Table B-11. DISTLM Marginal test: Influence of the process variables of the O₃/H₂O₂ - UV/H₂O₂ AOP on THM FP. Residual degrees of freedom: 37.

Variable	SS(trace)	Pseudo-F	P	Prop.
H ₂ O ₂ /O ₃	2.8109	2.9555	0.0928	0.073971
O ₃	0.61309	0.60675	0.4366	0.016134
H₂O₂	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 B-12. DISTLM Sequential test: Influence of the process variables of the O₃/H₂O₂ - UV/H₂O₂ AOP on THM FP.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res .df
H₂O₂	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 ₂ O 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

Table B-13. DISTLM Marginal test: Influence of the process variables of the O₃/H₂O₂ sub-process on THM FP. Residual degrees of freedom: 37.

Variable	SS(trace)	Pseudo-F	P	Prop.
Flow rate	1.7337	1.7688	0.1905	0.045625
H ₂ O ₂ /O ₃	0.42498	0.41847	0.4987	0.011184
O ₃	1.9574	2.0094	0.1707	0.051511
H ₂ O ₂	4.0561	4.4213	0.0375	0.10674
Metalddehyde 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 B-14. DISTLM Sequential test: Influence of the process variables of the O₃/H₂O₂ sub-process on THM FP.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res. df
H ₂ O 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 ₂ O 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
Metalddehyde 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

Table B-15. DISTLM Marginal test: Influence of the process variables of the UV/H₂O₂ sub-process on THM FP. Residual degrees of freedom: 18.

Variable	SS(trace)	Pseudo-F	P	Prop.
O ₃	0.23358	0.22404	0.6554	0.012294
H ₂ O ₂	0.0030564	0.002896	0.9598	0.00016086
H ₂ O 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 O₃/H₂O₂	44.093	54.396	0.0368	0.23207
UV254 Abs post O ₃ /H ₂ O ₂	0.42277	0.40963	0.5293	0.022251
DOC post O ₃ /H ₂ O ₂	0.27709	0.26639	0.624	0.014584

Table B-16. DISTLM Sequential test: Influence of the process variables of the UV/H₂O₂ sub-process on THM FP.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res. df
Turbidity post O₃/H₂O₂	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 ₂ O 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 ₂ O ₂ /O ₃	0.25793	0.38667	0.5515	0.0135	0.54359	13
UV254 Abs post O ₃ /H ₂ O ₂	0.002396	0.003317	0.955	0.0001	0.54372	12
H ₂ O ₂	0.001114	0.001413	0.9694	5.9E-05	0.54377	11

B.3 Influence of the process variables and the water quality parameters on the HAA FP change following AOPs

Table B-17. DISTLM Marginal test: Influence of the process variables of the UV/H₂O₂ AOP on HAA FP. Residual degrees of freedom: 21.

Variable	SS(trace)	Pseudo-F	P	Prop.
Flow rate	0.018638	0.017806	0.8973	0.00084718
H ₂ O 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 B-18. DISTLM Sequential test: Influence of the process variables of the UV/H₂O₂ AOP on HAA FP.

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 ₂ O 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

Table B-19. DISTLM Marginal test: Influence of the process variables of the O₃/H₂O₂ - UV/H₂O₂ AOP on HAA FP. Residual degrees of freedom: 23.

Variable	SS(trace)	Pseudo-F	P	Prop.
H ₂ O ₂ /O ₃	8.9524	13.684	0.0018	0.37302
O ₃	1.8137	1.8802	0.1827	0.075572
H ₂ O 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 B-20. DISTLM Sequential test: Influence of the process variables of the O₃/H₂O₂ - UV/H₂O₂ AOP on HAA FP.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res. df
Turbidity inlet	11.905	22.638	0.0001	0.49603	0.49603	23
H ₂ O 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 ₂ O 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

Table B-21. DISTLM Marginal test: Influence of the process variables of the O₃/H₂O₂ sub-process on HAA FP. Residual degrees of freedom: 21.

Variable	SS(trace)	Pseudo-F	P	Prop.
Flow rate	0.097202	0.093196	0.7674	0.004418
H ₂ O ₂ /O ₃	2.7875	3.0468	0.0974	0.1267
O ₃	0.56366	0.55218	0.4633	0.025621
H ₂ O 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 B-22. DISTLM Sequential test: Influence of the process variables of the O₃/H₂O₂ sub-process on HAA FP.

Variable	SS(trace)	Pseudo-F	P	Prop.	Cumul.	res.df
DOC inlet	8.3656	12.885	0.0026	0.38026	0.3802	21
DOC post AOP	2.4477	4.3761	0.0488	0.11126	0.4915	20
Turbidity inlet	2.0844	4.3511	0.0508	0.094747	0.5862	19
H ₂ O ₂	1.2109	2.762	0.1104	0.05504	0.6413	18
UV254 Abs post AOP	1.5548	4.1713	0.0567	0.070672	0.7119	17
H ₂ O ₂ /O ₃	1.4075	4.5688	0.0485	0.063977	0.7759	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	0.8240	14
Flow rate	0.036709	0.12445	0.7341	0.001669	0.8257	13

Table B-23. DISTLM Marginal test: Influence of the process variables of the UV/H₂O₂ sub-process on HAA FP. Residual degrees of freedom: 11.

Variable	SS(trace)	Pseudo-F	P	Prop.
O ₃	0.32409	0.30533	0.5922	0.027008
H ₂ O ₂	0.61259	0.59175	0.4493	0.051049
H ₂ O 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 ₂ O ₂	0.50499	0.48324	0.4979	0.042082
UV254 Abs post O ₃ /H ₂ O ₂	32.975	4.168	0.0649	0.27479
DOC post O ₃ /H ₂ O ₂	10.057	10.062	0.3316	0.083806

Table B-24. DISTLM Sequential test: Influence of the process variables of the UV/H₂O₂ sub-process on HAA FP.

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 ₂ O ₂	0.19083	0.67212	0.4291	0.015902	0.8107	8
DOC post O ₃ /H ₂ O ₂	0.22802	0.78114	0.4091	0.019002	0.8297	7
UV254 Abs post O ₃ /H ₂ O ₂	0.16898	0.54091	0.4917	0.014082	0.8438	6
H ₂ O ₂ /O ₃	0.61739	2.4559	0.1755	0.051449	0.8952	5
H ₂ O ₂	0.34482	1.5121	0.2897	0.028735	0.9239	4

Appendix C Subtracted FEEM of samples collected between each stage of the AOPs

C.1 FEEM of samples from the UV/H₂O₂ AOP

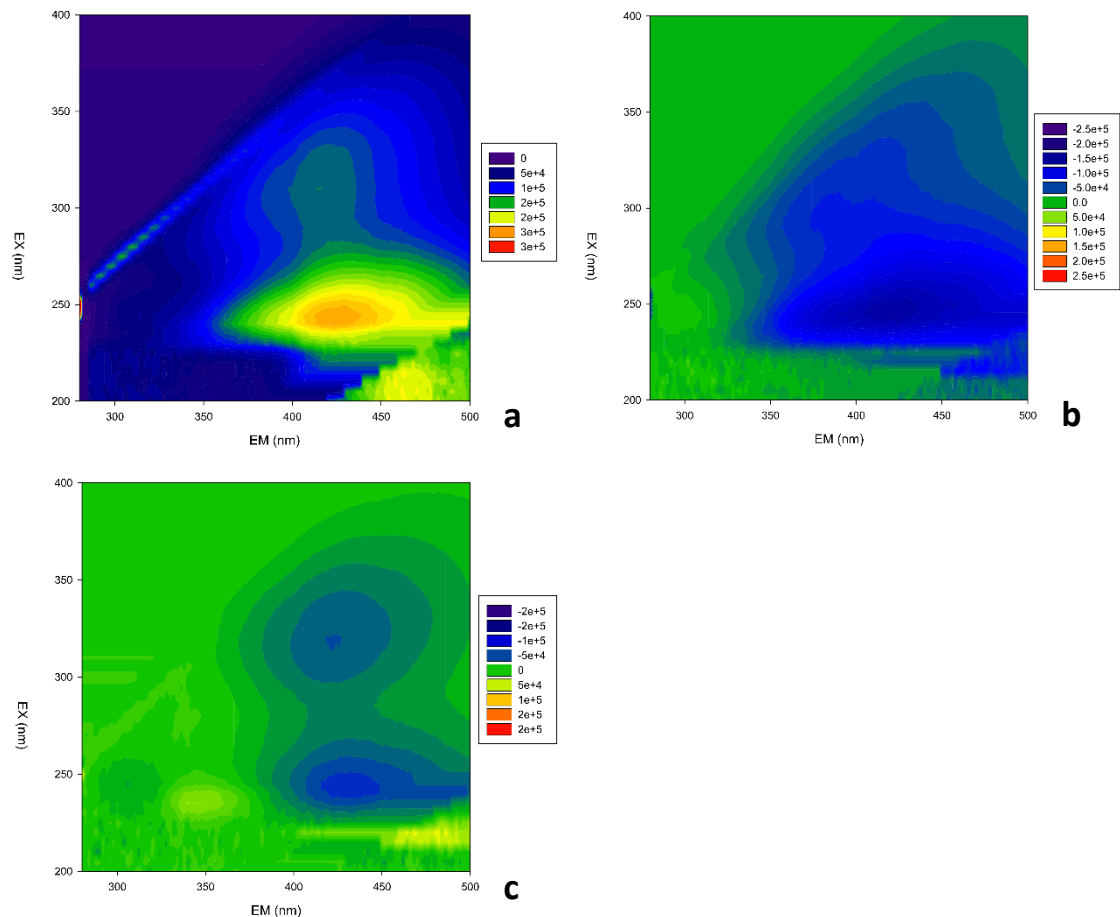


Figure C-1. FEEM of sample collected before AOP (a). Subtracted FEEM between post-UV/H₂O₂ and inlet (b). Subtracted FEEM between post-GAC and post-UV/H₂O₂ (c). Characteristics of the samples: Metaldehyde inlet: 0.80 µg/L; flow rate: 2.5 m³/h; [H₂O₂] = 40 mg/L; UV = 0.51 kWh/m³. The Rayleigh scatter has been corrected on the FEEM.

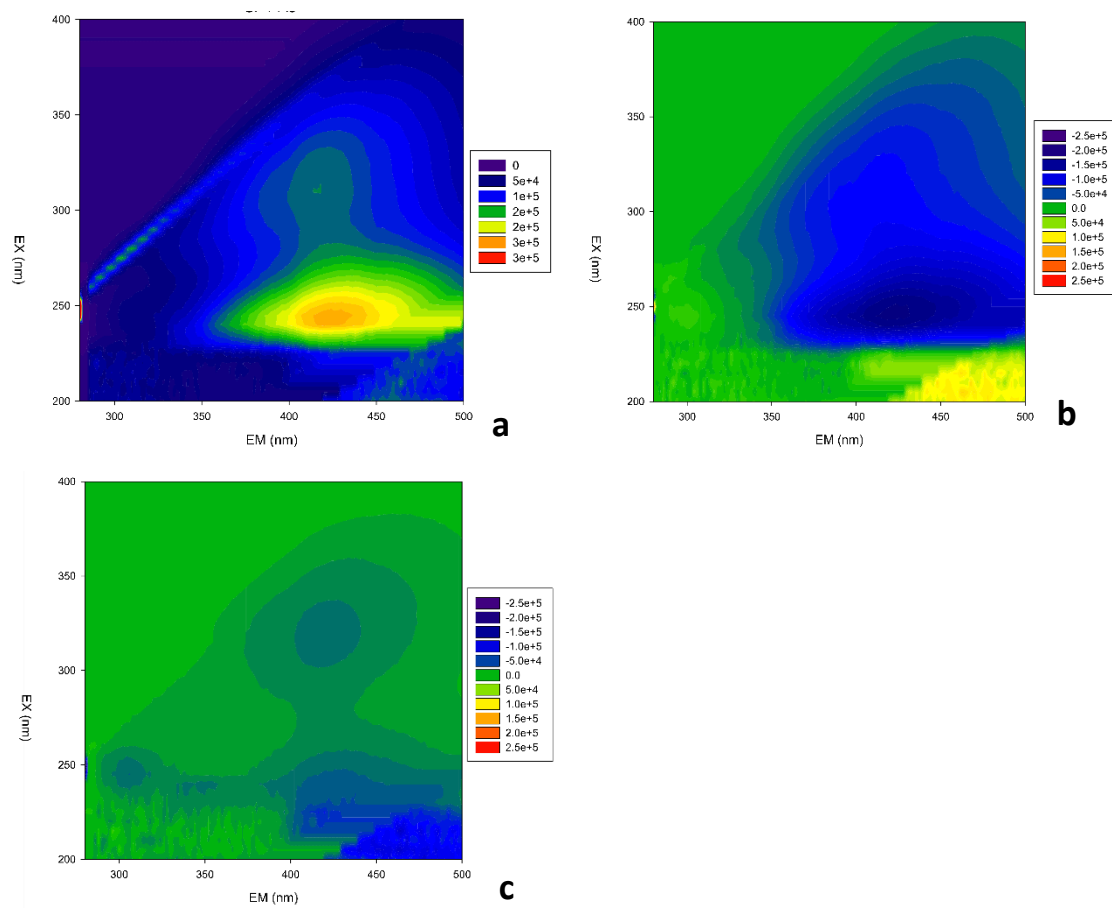


Figure C-2. FEEM of sample collected before AOP (a). Subtracted FEEM between post UV/H₂O₂ and inlet (b). Subtracted FEEM between post-GAC and post-UV/H₂O₂ (c). Characteristics of the samples: Metaldehyde inlet: 2.11 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; [H₂O₂] = 27 mg/L ; UV = 0.75 kWh/m^3 . The Rayleigh scatter has been corrected on the FEEM.

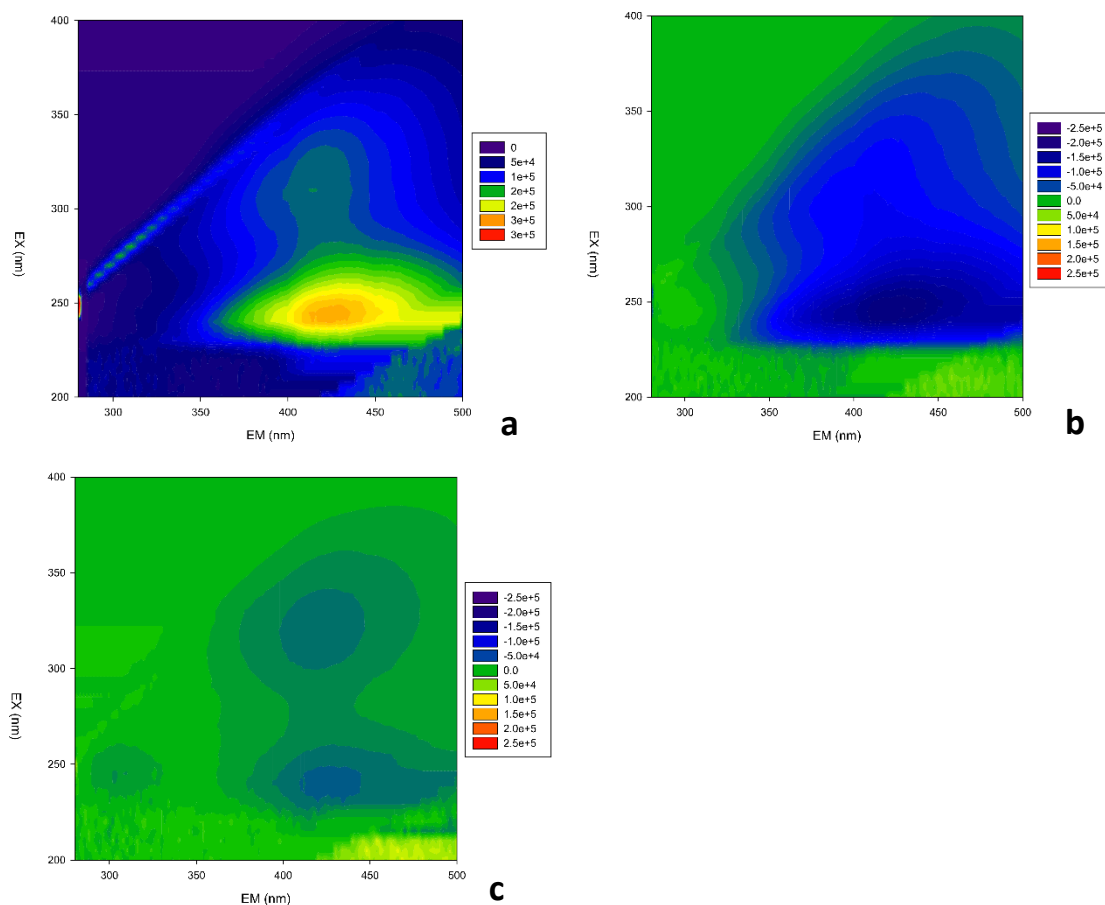


Figure C-3. FEEM of sample collected before AOP (a). Subtracted FEEM between post-UV/H₂O₂ and inlet (b). Subtracted FEEM between post-GAC and post-UV/H₂O₂ (c). Characteristics of the samples: Metaldehyde inlet: 0.53 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; [H₂O₂] = 28 mg/L ; UV = 0.75 kWh/m^3 . The Rayleigh scatter has been corrected on the FEEM.

C.2 FEEM of samples from the O₃/H₂O₂ - UV/H₂O₂ AOP

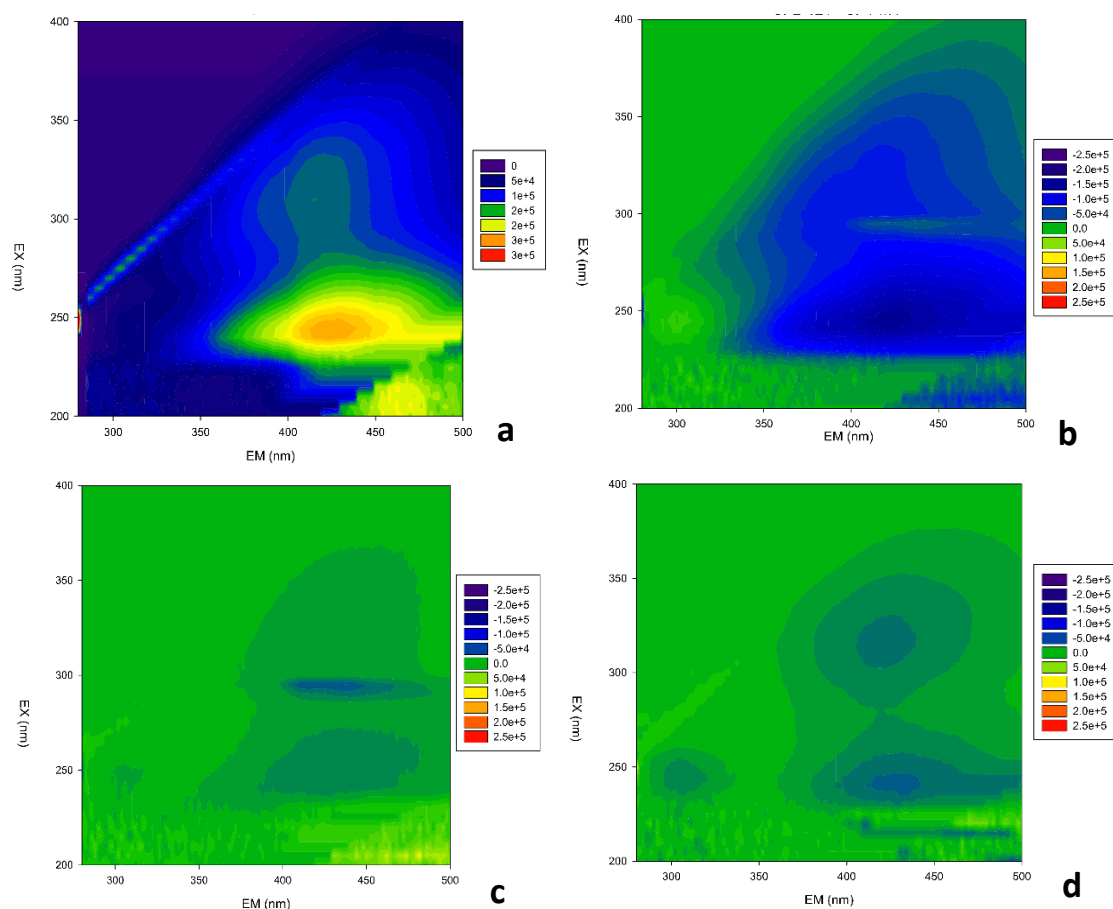


Figure C-4. FEEM of sample collected before AOP (a). Subtracted FEEM between post-O₃/H₂O₂ and inlet (b). Subtracted FEEM between post-UV/H₂O₂ and post-O₃/H₂O₂ (c). Subtracted FEEM between post-GAC and post-UV/H₂O₂ (d). Characteristics of the samples: Metaldehyde inlet: 0.80 µg/L; flow rate: 2.5 m³/h; [H₂O₂] = 24 mg/L; [O₃] = 6.2 mg/L; UV = 0.83 kWh/m³. The Rayleigh scatter has been corrected on the FEEM.

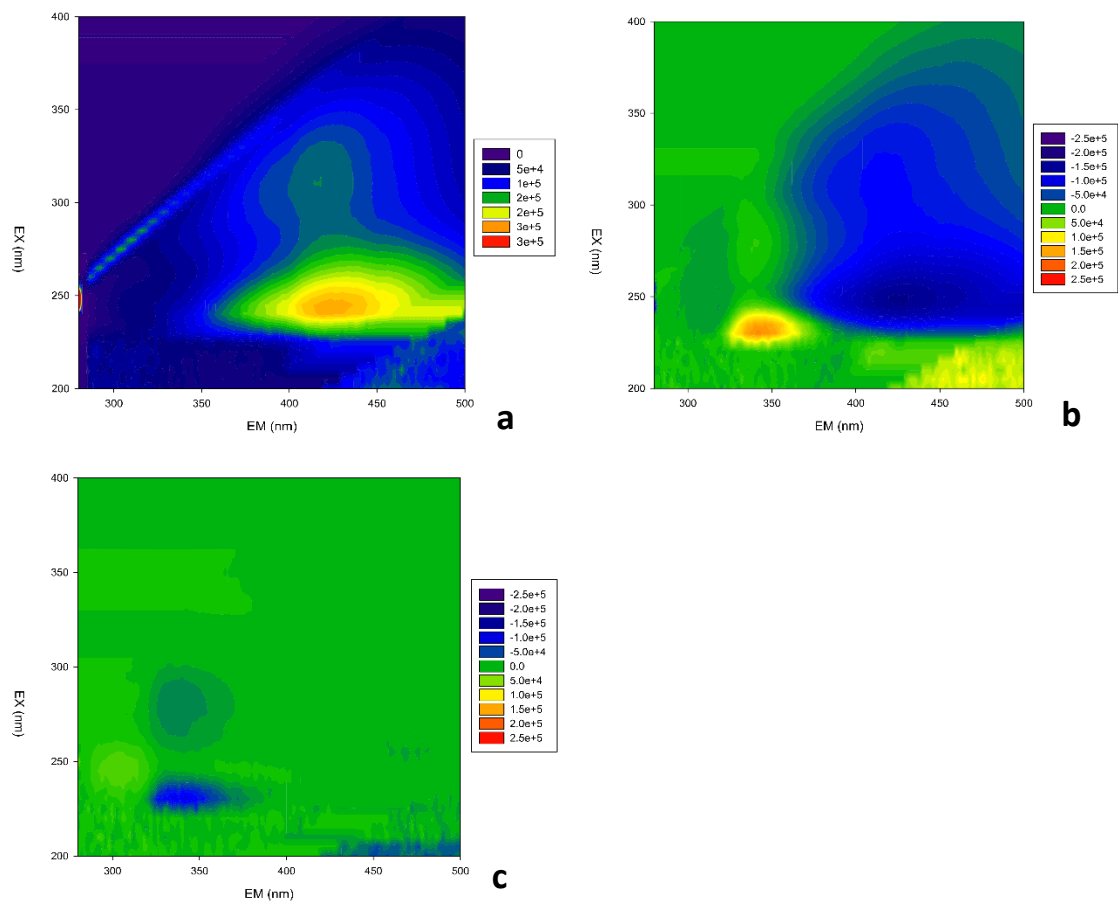


Figure C-5. FEEM of sample collected before AOP (a). Subtracted FEEM between post- O_3/H_2O_2 and pre-AOP (b). Subtracted FEEM between post-UV/ H_2O_2 and post- O_3/H_2O_2 (c). Characteristics of the samples: Metaldehyde inlet: $2.11 \mu\text{g/L}$; flow rate: $2.5 \text{ m}^3/\text{h}$; $[H_2O_2] = 24 \text{ mg/L}$; $[O_3] = 7.4 \text{ mg/L}$; UV = 0.56 kWh/m^3 . The Rayleigh scatter has been corrected on the FEEM.

Appendix D HPSEC chromatograms of samples collected between each stage of the AOPs

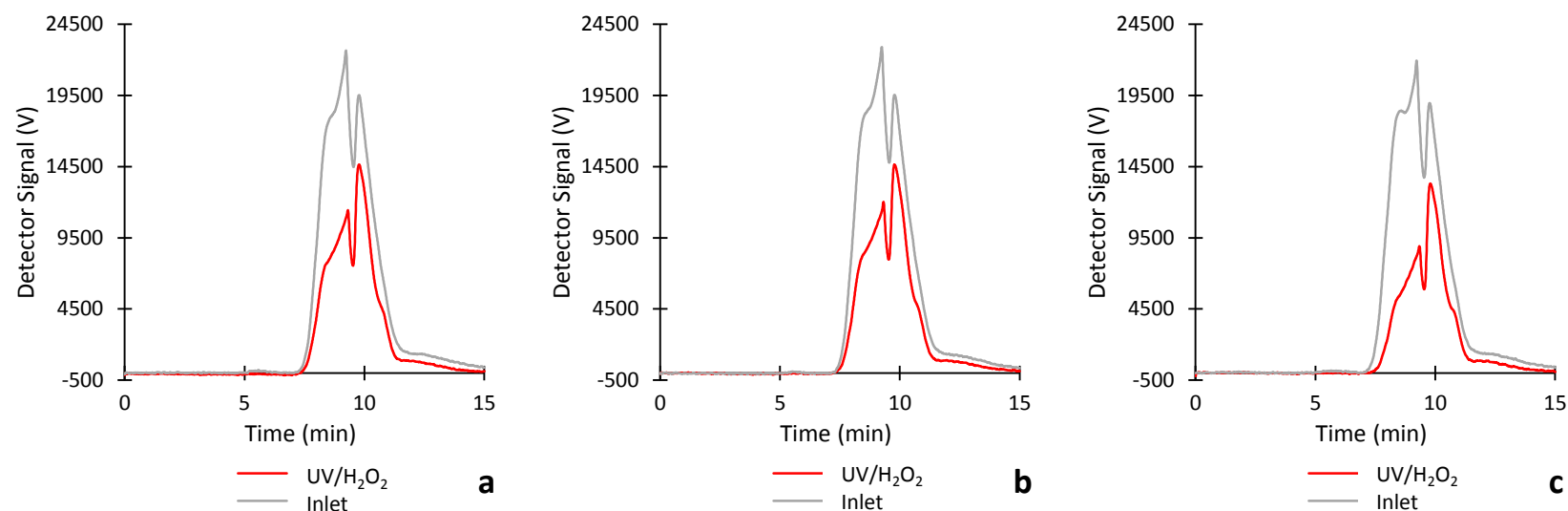


Figure D-1. HPSEC chromatograms of samples collected before and after the UV/H₂O₂ AOP having the following characteristics:

(a) Metaldehyde inlet: 2.14 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; $[\text{H}_2\text{O}_2] = 30 \text{ mg/L}$; UV = 0.50 kWh/m^3 .

(b) Metaldehyde inlet: 2.11 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; $[\text{H}_2\text{O}_2] = 29 \text{ mg/L}$; UV = 0.50 kWh/m^3 .

(c) Metaldehyde inlet: 0.53 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; $[\text{H}_2\text{O}_2] = 36 \text{ mg/L}$; UV = 0.75 kWh/m^3 .

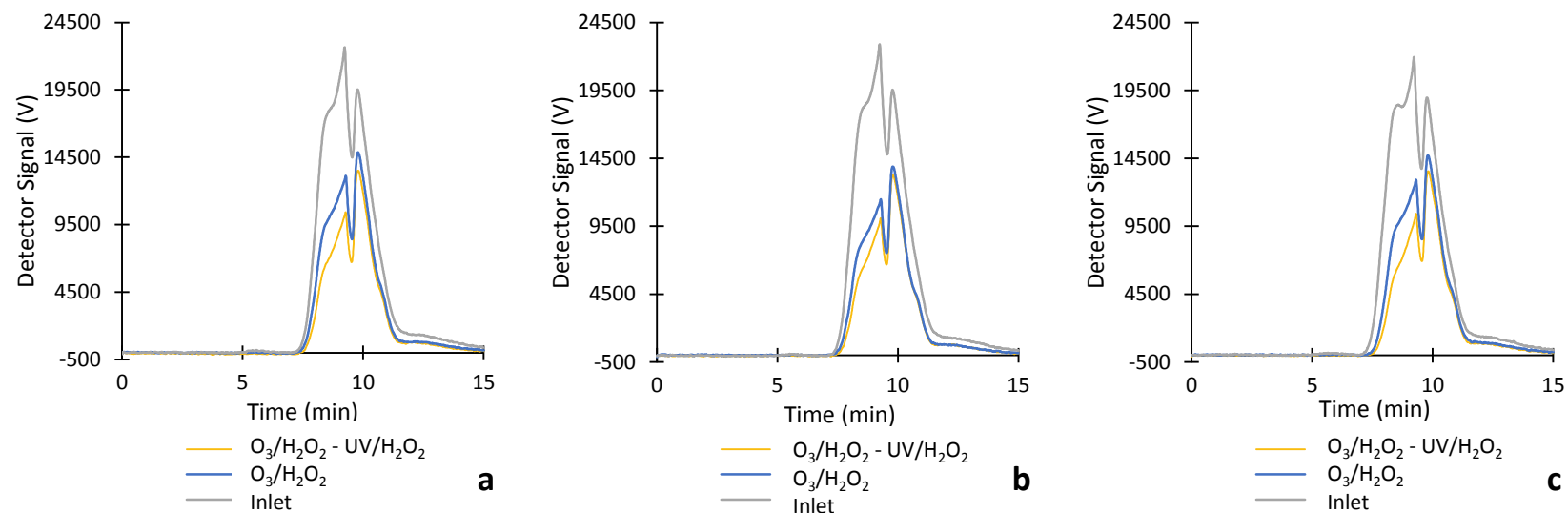


Figure D-2. HPSEC chromatograms of samples collected before and after the O_3/H_2O_2 - UV/ H_2O_2 AOP, and between its two sub-processes, having the following characteristics:

- (a) Metaldehyde inlet: 2.14 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; $[H_2O_2] = 14 \text{ mg/L}$; $[O_3] = 3.4 \text{ mg/L}$; UV = 0.56 kWh/m^3 .**
- (b) Metaldehyde inlet: 2.04 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; $[H_2O_2] = 17 \text{ mg/L}$; $[O_3] = 4.2 \text{ mg/L}$; UV = 0.55 kWh/m^3 .**
- (c) Metaldehyde inlet: 0.53 $\mu\text{g/L}$; flow rate: 2.5 m^3/h ; $[H_2O_2] = 13 \text{ mg/L}$; $[O_3] = 3.5 \text{ mg/L}$; UV = 0.77 kWh/m^3 .**

