

Department of Chemistry

**Formation of Adsorbable Organic Bromine
in Treated Drinking Waters**

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DECLARATION

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

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ABSTRACT

During chlorination of bromide-containing waters, significant concentrations of brominated disinfection by-products (Br-DBPs) form since bromine, which is formed from oxidation of bromide by chlorine, is a more reactive halogenation agent than chlorine in reaction with aquatic dissolved organic matter (DOM). Adsorbable organic bromine (AOBr) analysis offers the capacity to measure the total Br-DBPs in treated drinking waters. Since brominated organic compounds are known to be potentially of greater health concern than the corresponding chlorinated organic compounds, the measure of AOBr holds potential as a broad health impact indicator of the chemical water quality of disinfected waters.

Traditionally, halogenated DBPs have been measured as individual species (e.g. the trihalomethanes and haloacetic acids). Recent analytical developments have allowed the measurement of adsorbable organic halogen (AOX) as a bulk parameter of halogenated DBPs. The first adsorbable organic halogen (AOX) method measured all halogenated compounds (including AOBr) as a total of the organic halogenated compounds, expressed as a chlorine equivalent concentration. Since then the method has been further developed, modified, and optimised, and, with technological advancements in analytical instrumentation, ion chromatography (IC) has been used as the halide detection system, allowing separation of the halogens to measure adsorbable organic chlorine (AOCl), AOBr and adsorbable organic iodine (AOI). This halogen-specific AOX method consists of several analytical steps starting from the enrichment/adsorption of the organic halogen compounds onto activated carbon, followed by a nitrate wash of the activated carbon to remove inorganic contaminants. The next step is the combustion of the activated carbon with adsorbed organic halogenated compounds, and the collection of the resulting halide gases in an absorber solution. The final step involves halide detection by ion chromatography. Efforts have previously been made to optimise and validate the method in each step for better AOX measurement, including the use of different types of activated carbon and absorber solutions, and different oxygen flow rates for optimisation and model compounds for validation. The contribution of known individual halogenated DBPs to the total AOX has been assessed, however these individual halogenated DBPs

were found to constitute less than 50% of the total AOX. The remaining fraction may contain compounds which could potentially be of health concern.

This Thesis focuses on the formation of AOB_r in synthetic drinking waters during chlorination, commencing in Chapter 1 with a review of the formation of DBPs, including a brief description of the disinfectants commonly used in drinking water treatment and the precursors (both organic and inorganic) involved in DBP formation. The formation of halogen-specific AOX, particularly the formation of AOB_r, and the methods used to measure AOX concentration, as well as the role of bromide ion in the oxidative water system, are also described.

In Chapter 2, the further optimisation, validation and application to real waters of a halogen-specific AOX method, focusing on the measurement of AOB_r, is presented. Optimisation included trialling the application of a reducing agent (sodium sulfide) as the absorber solution as compared to ultrapure water, and studying the influence of repetition of gas line washes on the recovery of model compounds. The optimised halogen-specific AOX method was validated based on the recovery of model compounds covering a wide range of classes of DBPs and the recovery of total bromine (mass balance of bromine using concentrations of AOB_r and bromide after quenching). The validation of a halogen-specific AOX method based on the mass balance of total bromine, from the analysis of AOB_r and bromide, has not previously been reported. Ultrapure water was found to be preferable as an absorber solution compared to sodium sulfide solution, since very good recoveries (87 – 107 %) of selected model compounds were obtained with ultrapure water as compared to sodium sulfide solution (68 – 93 %) as the absorber solution. An increase in volume of the absorber solution from addition of the gas line washing solution had been previously identified. The influence of different gas line washing parameters on the total volume of the absorber solution, and thus the impact on the recoveries of the model compounds, was therefore assessed. The gas line washing parameters of 2 repetitions and the duration of the washing time being 1.0 sec produced optimum recoveries of selected model compounds, therefore these parameters were adopted for this halogen-specific AOX method. Very good recoveries of organic halogen from all model compounds were obtained, indicating high or complete conversion of all organic halogen in the model compound solution through to halide in the absorber

solution for IC analysis. Moreover, excellent recoveries of total bromine (mass balance of initial bromide compared to the concentrations of AOB_r and the sum of HOBr and bromide (measured as bromide after quenching)) were obtained from chlorination of synthetic waters containing standard DOM and bromide, demonstrating the validity of the halogen-specific AOX method for AOB_r measurement. The application of this method to real waters also successfully monitored the conversion of bromide to AOB_r from the raw water to the final chlorination stage in a groundwater treatment plant. A good recovery (104 %) of total bromine was observed from the post-filtration to the post-chlorination stage, providing further evidence for the validity of the AOB_r measurement using the halogen-specific AOX method to monitor the transformation of bromide in drinking water systems. This rigorous validation of the halogen-specific AOX method provides considerably increased confidence in AOX measurements.

In Chapter 3, mechanisms involved in the formation of AOB_r under typical drinking water treatment conditions were investigated. The influence of water quality parameters (i.e., bromide/bromine concentration, DOM type and concentration, chlorine concentration) on AOB_r formation was also investigated for synthetic waters. The impact of bromide recycling on AOB_r formation during chlorination of bromide-containing waters was also assessed. In order to elucidate the influence of bromine reactivity with reactive sites of DOM for AOB_r formation, synthetic waters containing standard DOM and bromide were treated with chlorine, and synthetic waters containing DOM only were treated directly with bromine (HOBr). In chlorination of synthetic waters containing DOM and bromide ($\text{Br}^- + \text{HOCl}$), AOB_r was formed through electrophilic substitution and addition at maximum levels, with ~90% of the initial bromide being converted into AOB_r. In bromination experiments (HOBr), on the other hand, only 27-40% of the added bromine was incorporated into DOM as AOB_r, while the majority of bromine (62-74%) was reduced to bromide through redox reactions (electron transfer) with DOM. The dominance of AOB_r formation in the chlorination experiments is likely due to bromide recycling. In this case, with the presence of chlorine in excess, the initial bromide was oxidised to bromine (HOBr), which could react with DOM through electrophilic substitution and addition reactions to produce AOB_r and through redox reactions to produce oxidised-DOM and bromide. This reduced bromide could then be re-oxidised to reform HOBr

by the chlorine in excess, and the reformed HOBr could then react with DOM reactive sites to produce more AOB_r, leading to a high conversion of initial bromide to AOB_r. Conversely, in direct bromination, electrophilic substitution and addition, and redox reactions (electron transfer), occur with the HOBr, with electron transfer being the dominant pathway, but the reduced bromide cannot be recycled since chlorine is absent and so no more AOB_r formation is possible.

The type of DOM influenced AOB_r formation in chlorination and bromination experiments, where DOM of high SUVA₂₅₄ value produced more AOB_r than DOM of low SUVA₂₅₄ value, indicating that bromine reacts quickly with aromatic structures in DOM. Formation of the regulated trihalomethane, bromoform, was found to not always represent the formation of the total measure of brominated organic compounds, AOB_r, indicating that bromoform is not a useful surrogate for brominated organic DBPs. Consideration of the incorporation of halogen-specific AOX into drinking water guidelines was therefore proposed.

In Chapter 4, competition between chlorine and bromine for reactive sites of DOM for the formation of AOCl and AOB_r, respectively, was studied. A pre-chlorination step for synthetic waters containing DOM was applied before the addition of bromine. Different pre-chlorination scenarios for synthetic waters (i.e. different pre-chlorination concentrations, different pre-chlorination times, pre-chlorination at a low and a high chlorine concentration followed by the addition of bromine/bromide (at fixed and different concentrations)) were also investigated. In these experiments, the pre-chlorination time was short and, with the higher chlorine concentration experiments, a chlorine residual remained when the bromine/bromide was added. There was strong competition between chlorine and bromine for reactive sites for halogenation, since AOCl and AOB_r concentrations both increased with increasing pre-chlorination concentration. It is well known that bromine reacts faster than chlorine with organic moieties. During pre-chlorination, it was expected that some of the DOM reactive sites would be consumed by reaction with chlorine, resulting in less DOM reactive sites available for electrophilic substitution and addition by the subsequently added bromine, thus reducing AOB_r formation with increasing pre-chlorination concentration. Interestingly, the pre-chlorination step did not limit AOB_r formation. In fact, it enhanced AOB_r formation, with almost 100 % Br-incorporation

observed with the addition of bromine to pre-chlorinated samples, while AOCl was found to decrease. A further experiment was conducted where the synthetic water was pre-chlorinated until all the chlorine was consumed (24 h), allowing optimum formation of AOCl, before addition of bromine at different concentrations. It was found that the AOB_r concentrations were consistently and increasingly higher with increasing HOBr concentrations, while the AOCl concentrations decreased.

Two reaction pathways were proposed to explain the phenomenon of AOCl decreasing in parallel with increasing HOBr concentrations. The first pathway was that HOBr not only reacted with DOM in substitution/addition reactions to form AOB_r, but also oxidised chlorinated DOM intermediates (AOCl), where the Cl substituent was removed in the oxidation process. The second pathway was that HOBr not only oxidised DOM, but also reacted with DOM in substitution/addition reactions to form AOB_r, including DOM already in the form of AOCl, where a bromine substituent replaced a chlorine substituent, converting some AOCl to AOB_r. It was also proposed that both hypothesised pathways may operate in the reaction mixture. A model compound experiment with hexachlorobenzene (HCB) treated with HOBr in excess, where the formation of bromoform was observed, provided some evidence for the second pathway. The second pathway was utilised for the empirical modelling undertaken in Chapter 5 to study and define the various pathways leading to AOB_r formation.

In Chapter 5, a conceptual kinetic model was proposed to better understand the multiple step reactions leading to AOB_r formation. Model calculations were performed with the Kintecus software to fit the experimental data obtained in Chapter 3 and Chapter 4. This is the first report of a comprehensive study using modelling software to simulate AOB_r formation from various reaction pathways. The fractions of reactive sites were determined based on reactions involved in the formation of AOB_r. DOM1 was assigned to the fraction of sites reacting with both HOBr and HOCl to form Br-DOM1 and Cl-DOM1, respectively, through electrophilic substitution and addition reactions. Cl-DOM1 was comprised of the intermediate products (chlorine-substituted functional groups) that may react further with HOBr, leading to replacement of chlorine to form additional Br-DOM1-replace. DOM2 was allocated for oxidation by HOBr to release bromide. DOM3 was

introduced as specific reactive sites reacting only with HOBr to form Br-DOM3 through electrophilic substitution and addition. Finally, DOM4 was added for oxidation by HOCl, a reaction which controls the concentration of chlorine in solution, with the HOCl remaining inducing bromide recycling and thus more AOBBr formation. Model calculations for AOBBr formation were a sum of Br-DOM1, Br-DOM1-replace, and Br-DOM3. A semi-empirical sensitivity analysis for the proposed rate constants and the values of the DOM fraction reactive sites determined by iterative adjustment was performed for their evaluation. Calculated AOBBr concentrations resulting from the model were in good agreement with the trends of experimental data for all experiments. Moreover, model calculations allowed a better understanding of the contribution of each reaction pathway to total AOBBr formation.

This Thesis highlights the utility of the halogen-specific AOX method for the study of AOBBr formation in disinfected drinking waters. The method has been successfully utilised to monitor the conversion of bromide to AOBBr during treatment processes (i.e. chlorination and pre-chlorination), providing a significantly more comprehensive understanding of the formation of brominated DBPs than traditional studies of individual DBP formation. Under these experimental conditions, AOBBr formed as a result of electrophilic substitution and addition reactions between bromine and DOM. Redox reactions between HOBr and DOM also occurred, reforming bromide which was measured at the conclusion of the reaction time. AOBBr was found to form at maximum concentration when bromide-containing waters were treated with a high concentration of chlorine. In this situation, the reformed bromide from the initial redox reaction was able to be re-oxidised to HOBr by the excess chlorine, and the reformed HOBr then reacted with DOM to produce more AOBBr, leading to the maximum concentration of AOBBr. The possibility of replacement of bromine for chlorine within chlorinated-DOM (AOCl), producing additional AOBBr and less AOCl, was introduced. While the requirement for effective control of pathogen risk means that it is critical to maintain disinfectant residuals in drinking water distribution systems, in some chlorinated drinking water distribution systems using source waters containing bromide, a high concentration pre-chlorination or final disinfection step could potentially lead, not only to the formation of high concentrations of brominated trihalomethanes, but to full conversion of bromide to AOBBr. High formation of AOBBr in treated drinking water is of significant interest

since the health risks of brominated organic compounds are generally higher than their chlorinated analogues. Hence, it is recommended that source waters containing high bromide concentrations be treated with advanced water treatment technologies (e.g. reverse osmosis) for bromide removal to minimise or mitigate AOB_r formation.

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LIST OF ABBREVIATIONS

AOBr	adsorbable organic bromine
AOCl	adsorbable organic chlorine
AOI	adsorbable organic iodine
AOS	adsorbable organic sulphur
AOX	adsorbable organic halogen
AQF	automatic quick furnace
AR	analytical reagent
Br-DBP	brominated disinfection by-product
CAR	carboxen
CH	chloral hydrate
Cl-DBP	chlorinated disinfection by-product
Da	Dalton
DBP	disinfection by-product
DOC	dissolved organic carbon
DOM	dissolved organic matter
DPD	<i>N,N</i> -diethyl- <i>p</i> -phenylenediamine
DVB	divinylbenzene
EPA	Environmental Protection Agent
GA	gas absorber
GAC	granular activated carbon
GC-MS	gas chromatography-mass spectrometry
GWTP	groundwater treatment plant
h	hour
HAA	haloacetic acid
HAN	haloacetonitrile
HCB	hexachlorobenzene
HK	haloketone
HNM	halonitromethane
HS	headspace
IC	ion chromatography
IHSS	international humic substances society

IS	internal standard
LOD	limit of detection
MCL	maximum contaminant limit
MeOH	methanol
min	minute
MQ	milliQ
MTBE	methyl <i>tert</i> -butyl ether
NOM	natural organic matter
NR-DOM	Nordic dissolved organic matter
PDMS	polydimethylsiloxane
PL-DOM	Pony Lake dissolved organic matter
SAT	soil aquifer treatment
SPME	solid-phase microextraction
SR-DOM	Suwannee River dissolved organic matter
SUVA	specific ultraviolet absorbance
SUVA ₂₅₄	specific ultraviolet absorbance at 254 nm
TBP	tribromophenol
TCP	trichlorophenol
THM	trihalomethane
TOC	total organic carbon
TOX	total organic halogen
US NCI	United States national cancer institute
UV	ultraviolet
UV-Vis	ultraviolet visible
WA	Western Australia
WCWA	Water Corporation Western Australia

LIST OF PUBLICATIONS AND PRESENTATIONS ARISING FROM THIS THESIS

Journal Articles

Some of the research presented in Chapter 3, 4, and 5 has been published in the journal *Environmental Science & Technology*.

Langsa, M., Heitz, A., Joll, C. A., von Gunten, U., Allard, S. (2017) Mechanistic Aspects of the Formation of Adsorbable Organic Bromine during Chlorination of Bromide-containing Synthetic Waters. *Environmental Science & Technology*, **51**(9), 5146-5155.

Some of the research presented in Chapter 2 has been accepted for publication in the 2017 Special Issue on “Disinfection By-Products in Drinking Water, Recycled Water and Wastewater: Formation, Detection, Toxicity and Health Effects” in the *Journal of Environmental Science*.

Langsa, M., Allard, S., Kristiana, I., Heitz, A., Joll, C. A., (2017) Halogen-Specific Total Organic Halogen Analysis: Assessment by Recovery of Total Bromine. *Journal of Environmental Science*, **58**, 340-348.

Oral Presentations

Markus Langsa, Cynthia Joll, Anna Heitz, Ina Kristiana, Sebastien Allard, Suzanne McDonald (2013) A Novel Technique to Measure DBPs in Drinking Water, *NOM5 Down Under, 5th IWA Specialist Conference on Natural Organic Matter Research*, Perth, 4th October 2013.

Markus Langsa, Sebastien Allard, Cynthia Joll, Anna Heitz, Urs von Gunten (2015) Influence of Dissolved Organic Matter on the Formation of Adsorbable Organic Bromine in Synthetic Waters, *NOM6 6th International Water Association (IWA)*

Specialist Conference on Natural Organic Matter in Water, Malmo, Sweden, 7-10th September 2015.

Markus Langsa, Sebastien Allard, Cynthia Joll, Anna Heitz, Urs von Gunten (2015) Formation of Adsorbable Organic Bromine in Synthetic Waters: A Mechanistic Study, *Micropol and Ecohazard 2016, 9th IWA Specialist Conference on Assessment and Control of Micropollutants and Hazardous Substances in Water*, Singapore, 22-25th November 2015.

Conference Poster Presentations

Markus Langsa, Sebastien Allard, Cynthia Joll, Anna Heitz, Urs von Gunten (2015) Mechanistic Study on the Formation of Adsorbable Organic Bromine in Synthetic Waters, *Gordon Research Conference on Drinking Water Disinfection By-Products*, South Hadley, Massachusetts, USA, 9-14th August 2015.

Chapter 1

INTRODUCTION

1.1 Aquatic Natural Organic Matter

Aquatic natural organic matter (NOM) is an operationally defined term that collectively describes water-borne organic materials that come from dead or living organisms (plants, animals, microorganisms), including their waste and degradation products (Chow et al., 1999). NOM occurs in rivers, lakes and groundwaters as a result of the degradation of terrestrial biomass through soil leaching and the decomposition of aquatic organisms (Bruchet and Rybacki, 1993). Moreover, Franchi and O'Melia (2003) reported that the quantity, character and properties of NOM in waters are different depending on the biogeochemical process involved in their surroundings such as age, climate, nature of the catchment, time of the year and the present concentration of NOM.

Researchers have characterised and classified NOM based on its organic functional characteristics for better understanding of this organic matter. Thurman and Malcolm (1981) reported that NOM contains a variety of different organic compounds, ranging from largely aliphatic to highly coloured aromatic components. Matilainen et al. (2011) reported that some of this organic matter is negatively charged. Furthermore, Owen et al. (1993) reported that NOM present in waters can also be classified into two components, hydrophobic and hydrophilic. The hydrophobic portion represents the organic materials that are rich in aromatic carbon, dominated by phenolic structures and also conjugated double bonds. Hydrophilic NOM, on the other hand, is reported to have a higher proportion of aliphatic carbon and nitrogenous functionality, such as carbohydrates, proteins, sugars and amino acids. Hydrophobic acids are reported to constitute the major fraction of aquatic NOM, accounting for more than half of the dissolved organic carbon (DOC) in water. DOC is operationally defined as the quantity of organic matter that passes through a 0.45 μm membrane filter (McDonald et al., 2004).

In aquatic ecosystems, DOC represents one of the largest active organic carbon reservoirs in the biosphere, with carbon equivalents almost equal to atmospheric CO_2 carbon (Amon and Benner, 1996). According to Aiken (1993), the source of DOC can be categorised as both allochthonous in which DOC is derived from the terrestrial watershed, and autochthonous, where DOC is entering to system from

biota growing in the water body. Degradation and leaching of organic detritus in the watershed lead to the production of DOC which is then transported to lakes *via* streams and shallow ground water flow. The chemical characteristics of the DOC, therefore, are influenced by the source materials, as well as by biogeochemical processes involved in carbon cycling of the system. These processes include the flow of organic carbon from the watershed to the system, carbon fixation by algae and aquatic plants, organic materials transformation and degradation by heterotrophic microbial activity, particulate organic material transport to the sediments, DOC remobilisation from the sediments, and photodegradation by UV light (Aiken, 1993).

DOC comprises humic and non-humic fractions: the humic fraction which accounts for approximately 50 % of the DOC (Owen et al., 1993) present in natural waters is described as organic substances that consist of polyelectrolytic organic acid with a wide range of molecular sizes, including in the macromolecular range (molecular weight estimated to range from 5000 to 100000 Da). The non-humic fraction is classified as known biomolecular classes of compounds, including lipids, carbohydrates, polysaccharides, amino acids, proteins, waxes and resins (McDonald et al., 2004). Aquatic humic acids and fulvic acids, the two main components of aquatic humic substances based on their solubility in water have been considered as the most important organic substances in terms of their chemical properties and implications for water treatment processes. Therefore, for the present research, the term NOM refers to both humic acids and fulvic acids. Despite the vast body of research that has been conducted on aquatic humic and fulvic acids, the chemical structure of this material is still largely unidentified. It is well accepted that the major functional groups are aliphatic and aromatic carboxylic acids, ketones, alcohols and phenols and several hypothetical structures have been proposed (Duan and Gregory, 2003; Leenheer, 2004; Schulten and Leinweber, 1996). One example of a hypothetical molecular structure of humic acid showing important functional groups is presented in Figure 1-1 (Duan and Gregory, 2003).

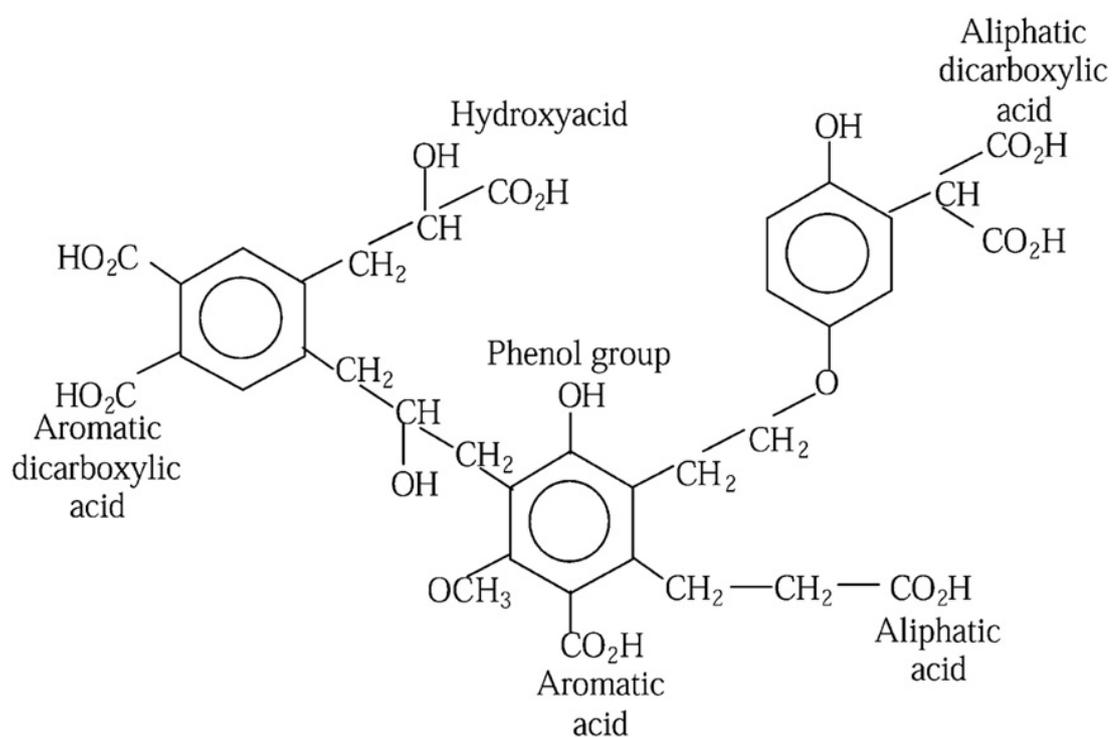


Figure 1-1: Hypothetical molecular structure of humic acid (adapted from (Duan and Gregory, 2003)).

The presence of NOM in natural waters has been of interest to researchers as it can create problems for drinking water quality and drinking water treatment processes (Jacangelo et al., 1995; Murray and Parsons, 2004). Aesthetic water quality problems have been reported due to colour and off tastes and odours of water containing high levels of NOM. Water treatment processes to remove high levels of NOM require high doses of coagulant and disinfectant which, in turn, result in an increase in sludge and formation of potentially toxic disinfection by-products (DBPs) (Jacangelo et al., 1995; Murray and Parsons, 2004; Semmens and Field, 1980). Promotion of biological growth in distribution systems is another problem associated with the presence of NOM in treated drinking waters (Jegatheesan et al., 2004). NOM can also increase concentrations of heavy metals and organic pollutants in raw water sources, through metal-NOM complexation and adsorption (Cabaniss, 2009; Liu et al., 2007; Schmitt et al., 2003).

The use of a molecular weight characterisation of the DOC present in a water sample as a “fingerprint” has been applied for potential treatment strategies. For example, Amy *et al.* (1988) suggested that a water source containing higher molecular weight humic acids should be treated with chemical coagulation instead of treating by activated carbon as large molecules are unable to be adsorbed into the smaller pores of the activated carbon. However, a water source with medium molecular weight material is more suitable with the activated carbon treatment. Low molecular weight fulvic acids which are very hydrophilic and therefore, cannot be removed by coagulation or adsorption can be more effectively treated using an oxidative technique (Matilainen *et al.*, 2011; Matilainen *et al.*, 2002; Matilainen *et al.*, 2010). The term NOM in this thesis refers to the total dissolved organic matter (DOM) in water derived from terrestrial and aquatic precursor materials.

1.2 Disinfection and Disinfection By-Products

In Australia and in many other developed countries, disinfection is the final phase of the drinking water treatment process. Disinfection inactivates pathogens in the product water before distribution to the customer. While the use of chemical disinfectants is effective in controlling microbial growth in finished water, as powerful oxidants, they also react with both organic and inorganic materials naturally present in source waters (rivers, lakes and ground waters) and in treated waters, forming disinfection by-products (DBPs).

In the 1970s it was discovered that chloroform, a trihalomethane (THM), was present in finished drinking water (Bellar *et al.*, 1974; Rook, 1974). Chloroform was later found to be an animal carcinogen by the US National Cancer Institute (NCI, 1976), raising concerns that disinfection as a water treatment technology may cause adverse health outcomes. Since that time, numerous studies have been conducted on a wide variety of research questions including: identification of other by-products arising from the disinfection of water (Adin *et al.*, 1991; Barrett *et al.*, 2000; Harrington *et al.*, 1996; Richardson *et al.*, 2003); defining of water quality and treatment characteristics that lead to the formation of THMs and other DBPs (Chowdhury *et al.*, 2009; Croué *et al.*, 2000; Diehl *et al.*, 2000); quantification of the occurrence and distribution of DBPs in finished drinking water (Krasner, 1999; Långvik and

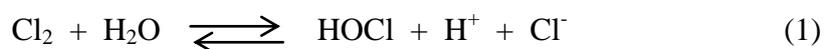
Holmbom, 1994; Richardson et al., 2007) and; development and assessment of technologies and treatment modifications for the control of DBPs (Baribeau et al., 2001; Jacangelo et al., 1995; Lykins et al., 1994).

To meet DBP regulations of a maximum contaminant limit (MCL) of total THMs permitted in finished drinking water set up by regulatory bodies (e.g., USEPA and European Union regulate the MCL of total THMs to 80 µg/L and 100 µg/L, respectively), drinking water utilities have developed alternative disinfectants to chlorine to minimise and control the formation of THMs and other regulated DBPs (Richardson, 2003; Symons et al., 1996). However several studies have shown (e.g. (Richardson et al., 2002; Richardson et al., 2003; Stevens et al., 1976; Wolfe et al., 1984) that different types and dosages of disinfectants produce different classes of DBPs. The following sections provide a more detailed description of the most common disinfectants used in disinfection of drinking water, namely chlorine, chloramine, and ozone, and their impact on the formation of DBPs in treated waters.

1.2.1 Chlorine as a Disinfectant

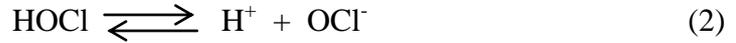
Chlorine has become a universal disinfectant used in water and wastewater treatment during the past century. While the main purpose of chlorine in water treatment is disinfection, because of its oxidising powers, it also has other useful purposes. As an oxidant, chlorine is used for destruction of taste and odour compounds, controlling the growth of bacteria and algae, removal of iron and manganese, reduction of hydrogen sulfide, and colour removal by “bleaching” of organic colour (White, 1999).

When chlorine gas is dissolved in water, a hydrolysis reaction occurs, producing hypochlorous acid (HOCl) as represented by the following equation (Cheremisinoff et al., 1981; Connick and Chia, 1959; Gordon et al., 1948; Morris, 1946; White, 1999):



Since the rate of the reaction is rapid (completed within a few seconds, equilibrium constant, $K = 4.48 \times 10^4$) at normal temperatures, it is well accepted that HOCl acts

as the disinfectant rather than chlorine gas itself (Gordon et al. (1948)). Hypochlorous acid undergoes a further reaction with water, ionisation, to form hypochlorite ions (OCl^-):



The equilibrium of this reversible process can be expressed as:

$$K = \frac{(\text{H}^+)(\text{OCl}^-)}{(\text{HOCl})} \quad (3)$$

Rearrangement of the ionisation constant equation gives,

$$\frac{K}{\text{H}^+} = \frac{(\text{OCl}^-)}{(\text{HOCl})} \quad (4)$$

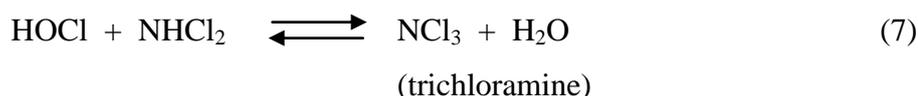
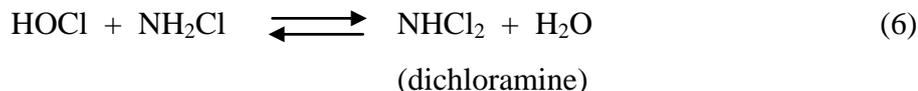
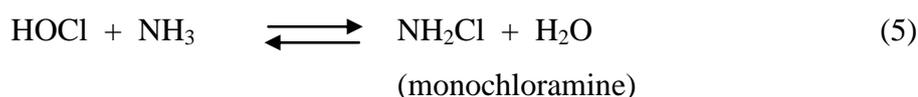
Thus, the relative concentrations of HOCl and its conjugate base, OCl^- , are dependent on pH, with increasing pH driving the equilibrium to the right, resulting in increasing concentrations of OCl^- (Gordon et al., 1948). Hypochlorous acid and hypochlorite ion, also known as free available chlorine, are strong oxidants indicated by their standard electrode potentials at 25°C (E°) of +1.49 V and +0.90 V, respectively (Glaze, 1990).

As already mentioned, early studies on the use of chlorine to treat waters containing NOM found that organic halogen compounds formed as a result of unwanted side reactions (Bellar et al., 1974; Rook, 1974). A survey conducted by USEPA of 80 selected cities across the USA reported by Symons et al. (1975) to measure the concentration of several organohalides in finished drinking water subjected to chlorination found that chloroform, bromodichloromethane, dibromochloromethane, and bromoform, all collectively termed trihalomethanes (THMs) were detected in the drinking water. It is now well recognised that chlorine produces the highest concentrations of halogenated DBPs, with THMs and haloacetic acids (HAAs) are the two largest classes of DBPs identified in the chlorinated water treatment plants.

Krasner, (1999) summarised the major DBPs identified as a result of chlorination: these include THMs, HAAs, haloacetonitriles (HANs), haloketones, haloaldehydes, and halophenols.

1.2.2 Chloramine as a Disinfectant

Chloramine is another disinfectant commonly used in the final disinfection of the treated water to control microbial growth and to reduce the formation of certain DBPs (Diehl et al., 2000; Kirmeyer et al., 2004; Wolfe et al., 1984). It forms when free chlorine reacts with ammonia in water. The presence of ammonia in water could be added as a part of the treatment process, or it may be naturally present in water, or as a result of agricultural or industrial discharges. Chloramine includes monochloramine, dichloramine, and trichloramine and produced in the process of chloramination, by the following reactions (Diehl et al., 2000; Wolfe et al., 1984):



For disinfection purposes, monochloramine is the desired chloramine species. The speciation is highly dependent upon pH, the ratio of chlorine to ammonia-nitrogen (expressed as $\text{Cl}_2:\text{NH}_3\text{-N}$), mixing dynamics and to lesser degree, temperature and contact time. The formation of monochloramine is completed within seconds at pH 6.5-9.0, at a 5:1 of $\text{Cl}_2:\text{NH}_3\text{-N}$ weight ratio and at 25 °C (Kirmeyer et al., 2004).

The standard electrode potentials (E°) of chloramine and dichloramine are +0.75 V and 0.79 V (Glaze, 1990), respectively which are lower than the standard potentials of free available chlorine, indicating that chloramines are less strong oxidants than chlorine. Although chloramines are less reactive than free chlorine especially when reacting with organic precursor materials such as NOM, their residual can be

maintained longer in the distribution system compared to free chlorine residual (Richardson, 1998). Moreover, they can reduce certain odour problems caused by chlorination but more importantly, they have been shown to produce lower concentrations of THMs (between 40 and 80 % lower than free chlorination) and HAAs (Kirmeyer et al., 2004).

Despite their advantages, there are several disadvantages associated with using inorganic chloramines as drinking water disinfectants (Kirmeyer et al., 2004; Wolfe et al., 1984). Free chlorine can preferentially react with a variety of organic nitrogen compounds ($R-NH_2$) to form organic chloramines. This reaction is faster than the reaction between chlorine and ammonia. For example, Jensen & Johnson (1989) found that peptides react with chlorine 2 to 3 times faster than ammonia, and it is likely that amino acids chlorinated 9 to 40 times faster. The fact that certain nitrogenous organic compounds react faster with chlorine than ammonia can result in the competition to form inorganic monochloramine, and therefore may reduce the effectiveness of monochloramine formation during chloramination. In addition, Bichsel and von Gunten (2000), found that water containing iodide treated with monochloramine produces iodinated DBPs which are classified as the most genotoxic and cytotoxic DBPs identified in finished drinking water (Richardson et al., 2008; Richardson et al., 2007).

1.2.3 Ozone as a Disinfectant

Ozone, the most powerful oxidant currently use in water treatment processes, has been widely used in drinking water treatment plants for more than a century. It was first applied at Oudshorn, Holland in 1893, and also other plants at Wiesbaden (1901) and Paderborn (1902) in Germany and later in Nice, France, in 1906. The first ozonation plant in the USA was installed in Whiting, Indiana, in 1941 (Cheremisinoff et al., 1981). As the strongest oxidant compared to the other common oxidants (E^0 at 25 °C = 2.07 V) (Glaze, 1990), ozone has been applied in drinking-water treatment for both disinfection and oxidation purposes (von Gunten, 2003a; White, 1999).

Ozone is unstable in water and its stability depends on water characteristics, particularly pH, NOM, temperature and alkalinity (Stahelin and Hoigne, 1985; von

Gunten, 2003a). Ozone decomposes in water through chain reactions involving the formation of OH free radicals as shown in the following reactions (Staehelin and Hoigne, 1985; von Gunten, 2003a):



While ozone is powerful for inactivating pathogenic microorganisms, formation of bromate (BrO_3^-), a potential carcinogenic compound formed in bromide-containing waters treated with ozone is the main drawback for the use of ozone as an oxidant (von Gunten, 2003b).

According to Camel and Bermond (1998), there are three purposes of using chemical disinfectants, namely pre-oxidation, intermediate oxidation and final disinfection in drinking treatment plant. The pre-ozonation step for raw drinking waters has been reported to effectively remove mineral compounds, colour, turbidity, suspended solids, bad taste and odour (Camel and Bermond, 1998; Nieminski and Evans, 1995). The aim of an intermediate step using ozone during water treatment is to degrade toxic micropollutants and remove DBPs precursor (Hart et al., 1995; Lambert et al., 1996; Meijers et al., 1995). Final disinfection using ozone will eliminate persistent pathogens and minimise the formation of halogenated DBPs (Camel and Bermond, 1998; Wolfe et al., 1989). However, ozone is short-lived and, therefore, water treated with ozone does not carry a significant disinfectant residual which makes it less desirable than chlorine or chloramine as a secondary disinfectant.

1.3 Disinfection By-Products Formation

The formation of DBPs can be summarised by the following equation (Krasner, 1999):



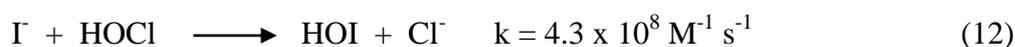
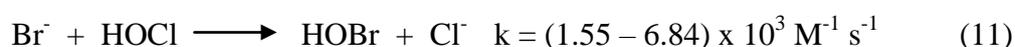
All chemical disinfectants (e.g. chlorine, monochloramine, ozone, and chlorine dioxide) are known to form various types of DBPs. DBP precursors include NOM, bromide and iodide which may be naturally present in water sources. Bromide and iodide present in natural waters can be rapidly oxidised by oxidants such as chlorine to produce hypobromous acid (HOBr) and hypoiodous acid (HOI), respectively, which can then react with NOM to form brominated and iodinated DBPs, in a similar way to chlorine (hypochlorous acid, HOCl) forming chlorinated DBPs. These DBPs may lead to potential adverse health effects (Hua et al., 2006). In fact, Plewa et al.(2004) reported that brominated DBPs are hundreds of times more toxic than their chlorinated analogues and iodinated DBPs are even more toxic than their brominated analogues. The extent of DBP formation depends on the dose and type of disinfectant, the nature and concentration of precursors, and various other water quality parameters, such as temperature and pH. The halogenated DBPs which can be individually identified include the trihalomethanes (THMs) and haloacetic acids (HAAs), the two most abundant classes of DBPs, as well as the haloacetonitriles (HANs), haloketones (HKs), halonitromethanes (HNMs), haloacetamides, halopyrroles and chloral hydrate (CH) (Chowdhury et al., 2009; Croué et al., 2000; Harrington et al., 1996; Richardson et al., 2007; Wu et al., 2000). To date, hundreds of halogenated DBPs have been identified (Richardson and Postigo, 2015), but they account for no more than about 50 % of the total organic halogen (TOX) concentration in finished drinking water, while the remaining 50 % of the halogenated organic material contributing to TOX has not been identified (Li et al., 2011b; Singer, 1994).

1.3.1 Inorganic DBP Precursors

Bromide and iodide ions are the common halide ions naturally occurring in source waters (Agus et al., 2009; Flury and Papritz, 1993; Heller-Grossman et al., 1999; Magazinovic et al., 2004). Both are present from either natural or anthropogenic processes (Agus et al., 2009; von Gunten and Hoigne, 1994). Naturally occurring bromide is usually detected in the range of 20 to 2000 $\mu\text{g L}^{-1}$ while iodide is found at much lower concentrations, generally varying between 0.4 and 100 $\mu\text{g L}^{-1}$ worldwide (Agus et al., 2009). High bromide and iodide levels can be detected in extreme environments (e.g. arid watersheds) where water is channelled from outside (e.g. irrigation) and evaporation is dominant thus resulting in the precipitation of salts in

the soil. Those salts containing bromide and iodide will be transported by agricultural runoff to the rivers. Locations that can also have high bromide and iodide levels include the groundwaters and surface waters of coastal cities impacted by saltwater intrusion or inland areas where the water bodies are impacted by natural salt deposits from ancient seas or oil-field brines (Richardson, 2003).

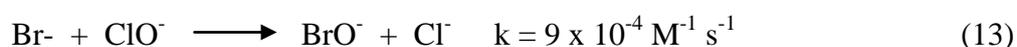
When bromide and iodide are in contact with chlorine during disinfection, they can be rapidly oxidised to hypobromous acid (HOBr) and hypoiodous acid (HOI), according to the following equations (Kumar and Margerum, 1987; Nagy et al., 1988):



HOBr and HOI are active oxidants that can react with NOM to form brominated and iodinated DBPs in a similar way as hypochlorous acid (HOCl) reacts with NOM. For reaction 12, oxidation of iodide with high chlorine concentration is preferred to form iodate which in turn minimises the formation of HOI leading to minimum formation of iodinated DBPs (Kristiana et al., 2009).

1.3.2 Chemistry of Bromide in Drinking Water Disinfection

Bromide-containing water treated with chlorine during the disinfection process leads to formation of hypobromous acid and hypobromite (HOBr/OBr⁻), as shown in equations (1) and (3).



Aqueous bromine (HOBr and OBr⁻) is reported to be more reactive and a better substituting agent (Heeb et al., 2014; Westerhoff et al., 2004) than chlorine (HOCl and OCl⁻) towards NOM to form brominated DBPs (Br-DBPs) through electrophilic substitution and addition (Criquet et al., 2015). Therefore, Br-DBPs will be the dominant product compared to their chlorinated analogues (Cl-DBPs) when bromide-containing waters are treated with chlorine. Bromine can also oxidise NOM and release bromide through electron transfer. The released bromide can create a Br-

recycling effect resulting in a very high formation of Br-DBPs where a significant proportion of the available bromide is eventually incorporated into organic brominated compounds. In this case, reduced bromine (measure as bromide) is re-oxidised to HOBr (or OBr-) in the presence of excess chlorine. The oxidised bromine then reacts further with remaining NOM in waters to form additional Br-DBPs. The role of bromide in oxidative water treatment was summarised by Heeb et al. (2014) as shown in Figure 1-2.

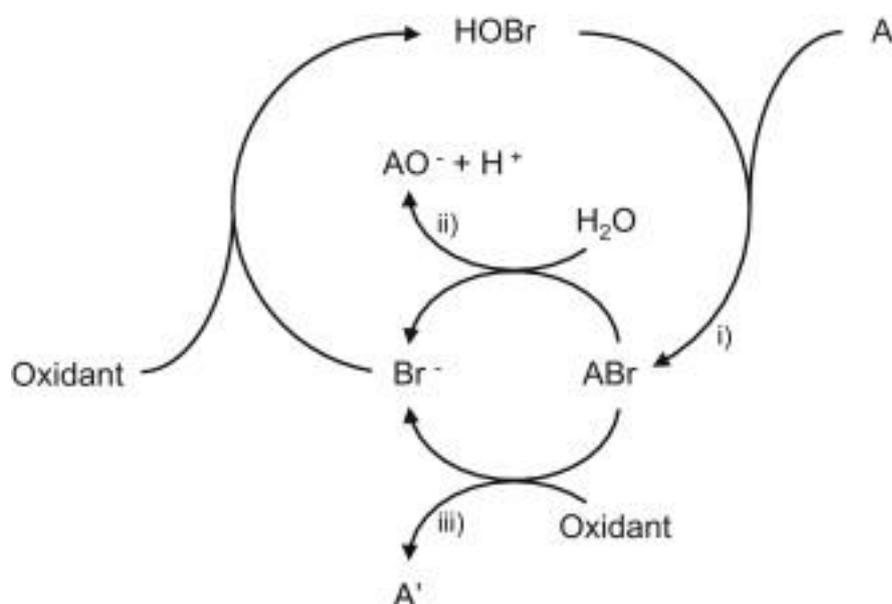


Figure 1-2: Role of bromide in the oxidation reactions in water treatment with A representing organic or inorganic reactants to form (i) brominated compounds (ABr), (ii) AO- through hydrolysis of ABr, or (iii) A' after further oxidation of ABr (Heeb et al., 2014).

1.4 Adsorbable Organic Halogen (AOX)

The term “adsorbable organic halogen (AOX)” is an operationally defined term used to describe the fraction of total organic halogen (TOX) which can be adsorbed onto activated carbon. Recent studies have aimed at improving the adsorption of TOX onto the activated carbon (Hua and Reckhow, 2006; Kristiana et al., 2015; Li et al., 2011a; Li et al., 2011b) but it is recognised that the recovery of organic halogens is not necessarily complete, and is in fact difficult to control and to ascertain. Therefore, the term AOX is usually used: AOX is a group parameter that has been

used to estimate the total organic-bound halogen in water (Hua and Reckhow, 2006). Since the AOX parameter is a reflection of the total concentration of organic-bound halogen, it has also been used as a bulk parameter to indicate the potential level of toxicity due organic DBPs in treated waters (Hua and Reckhow, 2006; Li et al., 2011b).

The formation of AOX in the disinfection of treated waters in the presence of organic and inorganic precursors is illustrated in Figure 1-3. The diagrammatic representation showing different mechanisms for production of AOX and the major DBPs formation during chlorination of bromide-containing water is illustrated in Figure 1-4.

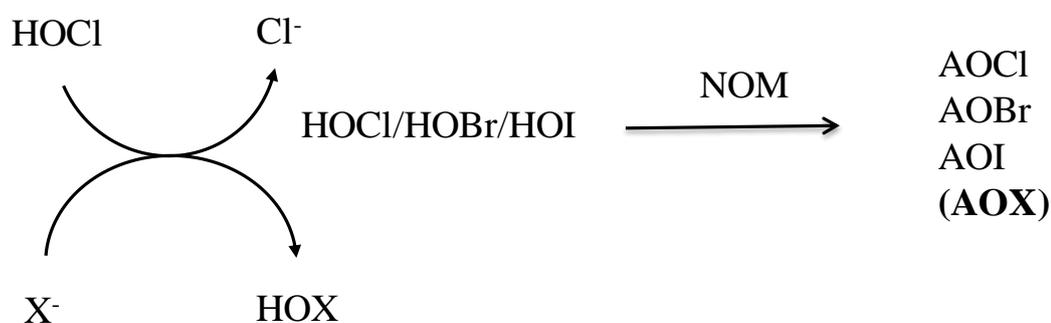


Figure 1-3: AOX formation expressed as its halogen species resulted from reaction between oxidised inorganic precursor ($X^- = \text{Br}^-, \text{I}^-$) by chlorine to form hypohalogenous acid with NOM.

As well as drinking water disinfection, AOX can come from a range of sources including anthropogenic pollution (Jekel and Roberts, 1980; Långvik and Holmbom, 1994), and as naturally occurring products from species such as algae, bacteria, lichens and fungi (Gribble, 1998; Řezanka and Dembitsky, 1999; Spinnler et al., 1994). In water reuse and soil aquifer treatment (SAT), chlorination before discharge has always been considered problematic due to the potential for formation of AOX material which is likely to resist biodegradation in the subsurface and have possible effects on human health (Drewes and Jekel, 1998). Similarly in wastewater processes, AOX as a measure for halogenated compounds is an important parameter for the characterization of industrial wastewaters. The discharge of AOX-containing

wastewaters often causes technical and financial problems for some specific industries. A potential source of AOX in wastewater is through application of chlorinous budget cleaners (e.g. chloramine T, chloramine BARS, sodium hypochlorite, chloric lime) (Baycan et al., 2007), bleaching of pulp or kraft mill effluents with chlorine-containing agents (Barton and Payne, 1999; Sjöström et al., 1985), and the use of different types of organohalogens in the plastics industries (Asplund et al., 1989).

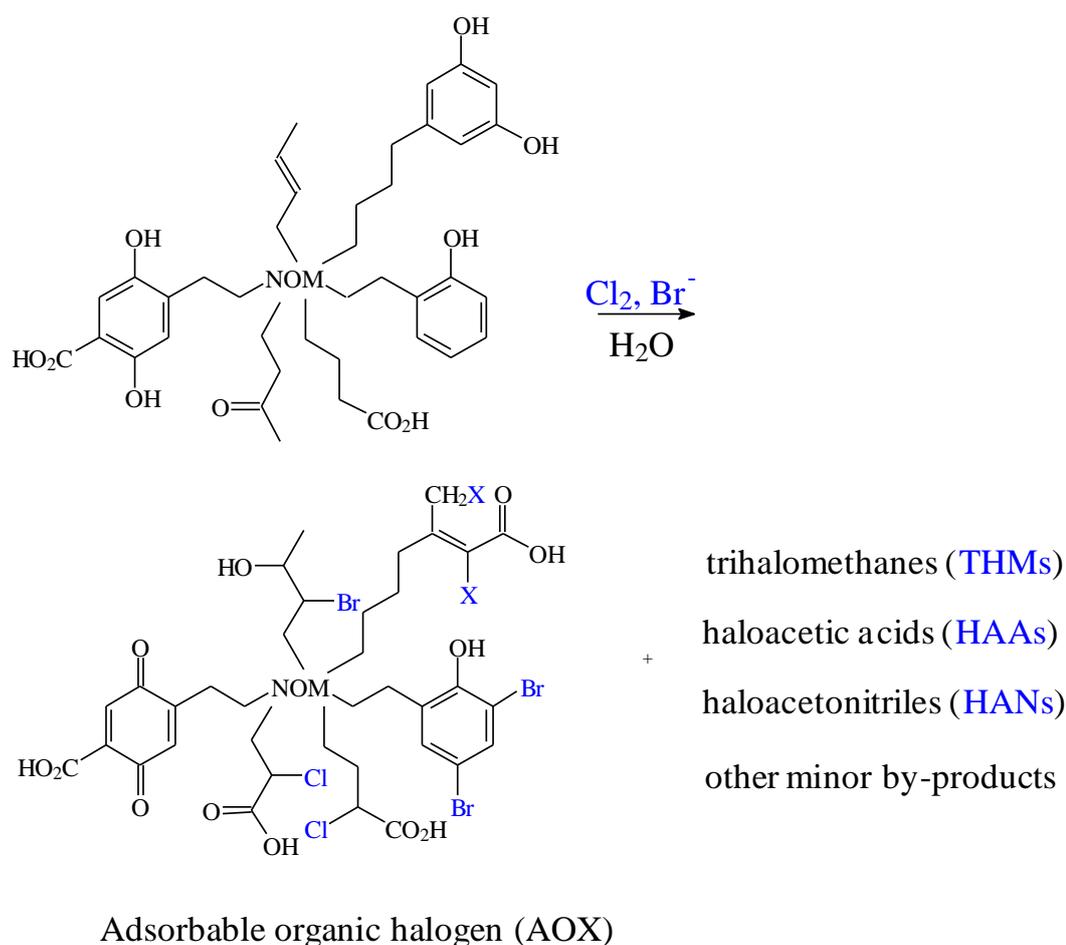


Figure 1-4: Proposed diagrammatic formation of AOX and major DBPs during chlorination of water containing NOM and bromide (adapted from (Kristiana, 2007).

A method for AOX analysis in water was originally developed by Kuhn in 1974 (Glaze et al., 1977; Kuhn and Sontheimer, 1973). This procedure involved adsorption of NOM onto activated carbon, followed by combustion of the activated carbon and

adsorbed material and, finally, microcoulometric titration of the formed halide. Since then, different variants of this method have been widely used to analyse organic halogens in chlorinated drinking water and industrially polluted water (Benabdallah El-Hadj et al., 2007; Drewes and Jekel, 1998; Hua and Reckhow, 2006; Jekel and Roberts, 1980; Li et al., 2002; Sjöström et al., 1985). The most up-to-date AOX analysis utilises ion chromatography (IC) for the detection of halogen-specific AOX (Kristiana et al., 2015; Li et al., 2011b). The basic principle of this method is the same as the conventional method in that it involves adsorption of organic halogen onto activated carbon, combustion of the activated carbon containing organic halogen, and absorption of halide gases after combustion. However, for the halide gas detection, IC is employed instead of microcoulometric titration. The AOX-IC method allows analysis of chloride, bromide and iodide generated from dissolution of the hydrogen halide gases in water, the gases being produced from the combustion of organic halogen adsorbed onto the activated carbon.

Substantial efforts have been made to validate halogen-specific AOX method for the accurate measurement of total halogenated DBPs in treated drinking waters (Brandt and Kettrup, 1987; Echigo et al., 2000; Hua and Reckhow, 2006; Kristiana et al., 2015; Oleksy-Frenzel et al., 2000). Moreover, a few studies have specifically investigated the influence of using activated carbon to adsorb halogenated organic compounds during the enrichment/adsorption process (Li et al., 2011a; Li et al., 2010; Li et al., 2011b). In adsorption process, the organic solutes of the sample are absorbed by activated carbon in the glass columns. However, while the purpose of using activated carbon is to enrich the organic halogen compounds from water samples, it has been reported that activated carbon can also act as a reductant (Li et al., 2010; Li et al., 2011b). Li *et al.* (2010) reported that up to 20 % of chlorinated Suwannee River fulvic acid was reduced to chloride by activated carbon. Further studies on the reducing effect of some brominated organic DBPs to inorganic bromide by activated carbon by Li et al. (2011b) revealed that around 10% of brominated Suwannee River fulvic acid was reduced to bromide. In their other study, Li et al. (2011a) reported that up to 10 % of polar brominated DBPs formed from chlorination of humic acid samples penetrated through the activated carbon. The reduction of some halogenated DBPs to inorganic halides during the adsorption by activated carbon can create certain systematic error for the halogen-specific AOX

measurement as the inorganic halides would be eliminated from activated carbon during rinsing with nitrate solution.

As a group parameter, AOX is especially useful in process control since it can be determined within a short time with relatively simple equipment. However, it has the disadvantage that it does not provide information concerning the multitude of specific organic substances present (Jekel and Roberts, 1980). Early AOX methods based on coulometric titration could not distinguish between the halogens, and therefore could not distinguish adsorbable organic chlorine (AOCl) from adsorbable organic bromine (AOBr) and iodine (AOI) (Hua and Reckhow, 2006). The determination of these three specific AOX species is vital for studies of disinfection of waters containing bromide and iodide, and, in particular, for toxicity studies, since TOI/AOI is likely to be more of a health concern than TOBr/AOBr, which is likely to be more problematic than TOCl/AOCl (Li et al., 2011b).

To date, hundreds of individual halogenated DBPs species have been reported in the literature (Richardson and Postigo, 2015). Many studies have attempted to correlate the contribution of these individual halogenated DBPs to total AOX concentration. However, the main focus of these studies (Hua et al., 2006; Kristiana et al., 2009; Richardson, 2003; Tan et al., 2016) has been only on selected brominated DBPs such as the regulated brominated trihalomethanes (THMs), brominated haloacetic acids (HAAs), and non-regulated brominated haloacetonitriles (HANs). They reported that the contribution of these brominated DBPs is less than 50% of AOBr (Hua et al., 2006; Kristiana et al., 2009; Richardson, 2003; Tan et al., 2016). The unknown fraction of AOBr particularly and AOX in general may also contain toxic compounds with potential health effects (Hua and Reckhow, 2008). It is difficult and impractical to measure individual halogenated compounds but halogen-specific AOX method offers an alternative approach by quantification of the total concentration of halogenated organic compounds. Halogen-specific AOX is particularly useful since it can provide information on the fates and reactivities of each halogen (i.e. Cl, Br, I). The next section provides further discussion on AOBr formation as the major theme of this Thesis.

1.4.1 Adsorbable Organic Bromine (AOBr)

Bromide-containing waters treated with chlorine will form bromine species (HOBr and OBr⁻) which may react with naturally present organic matter (in this section refers to DOM) in waters to form brominated DBPs, also known as AOBr. Therefore, AOBr represents total organic bromine produced during water treatment processes.

Bromine reacts with organic moieties from aquatic DOM in a similar manner to chlorine reactions. It can either react by electrophilic substitution and addition which lead to the formation of brominated DBPs in solution (equation 1) (Acero et al., 2005; Criquet et al., 2015; Westerhoff et al., 2004), or by electron transfer and release of bromide (oxidation-reduction reaction; equation 2) (Song et al., 1996).



The presence of these two halogenated oxidants (chlorine and bromine) in the water leads to competition for reactions with reactive sites of DOM to produce chlorinated DBPs, brominated DBPs or a mixture of both. Bromine has been reported to react faster with DOM than chlorine. For example, Westerhoff et al.,(2004) found that bromine rate constants for reaction with DOM extract are 10 times higher than the corresponding reaction with chlorine. Moreover, Heeb and others (Heeb et al., 2014) determined that the species-specific rate constant of a series of phenolate compounds, representative of DOM reactive moieties, with bromine are on average 3000 times higher than with chlorine. Therefore, with higher reactivity than chlorine, bromine can affect the yield/magnitude and species distribution of halogenated DBPs (Cowman and Singer, 1995; Hua and Reckhow, 2006; Richardson, 2003; Symons et al., 1993).

The formation of AOBr through electrophilic substitution and addition reactions is reported to vary depending on the types of disinfectants and the characteristics of organic precursor (i.e. aromaticity content). Westerhoff, et al. (1998) reported that about 10 % of bromine was incorporated into DOM as AOBr while the remaining bromine was reduced to bromide when bromide-containing waters were treated with

ozone. Further study by the same authors (Westerhoff et al., 2004) revealed that pre-ozonation of water containing DOM followed by the addition of bromine reduced the rate reaction of bromine and DOM but it did not influence the substitution efficiency of bromine with DOM. More bromine incorporated with DOM to form AOB_r was reported by Song et al. (1996). In their study, aqueous bromine was added directly into water containing DOM and reported Br-incorporation by 20 %. Moreover, Echigo and Minear (2006) reported that when aqueous bromine was mixed with a solution containing DOM extract, 80% of Br-incorporation was observed in 1 second of reaction time. A more recent study by Criquet et al. (2015) reported about 20 % of Br-incorporation for all selected DOM extracts with the exception for Pony Lake DOM extract (< 10 %). It is also reported that bromination of phenolic compounds at pH 8 resulted in almost 100% Br-incorporation. Finally, Tan et al. (2016) who studied the conversion of bromide in raw water through different treatment processes in the groundwater treatment plant reported that about 70 % of initial bromide was incorporated into DOM to form AOB_r after the final chlorination stage.

1.5. Scope of Study

The fact that brominated DBPs are potentially cytotoxic and genotoxic over a hundred times more than their chlorinated analogues has raised concerns about the maximum formation of these compounds in bromide-containing waters treated with disinfectants during drinking water treatment processes. Many of Western Australia's source waters have been reported to contain high levels of bromide (up to 8 mg L⁻¹) (Gruchlik et al., 2014). Conventional coagulation/flocculation treatment processes applied in drinking water treatment plants do not effectively remove bromide in waters (Kristiana et al., 2015; Tan et al., 2016), leading to significant formation of AOB_r after final chlorination in the treated waters. A large number of identified individual brominated DBPs have been reported in the literature while many remain unknown, making it not feasible to conduct toxicological, epidemiological, and occurrence studies for all of these compounds. The halogen-specific AOX method is able to distinguish between the group parameters of chlorinated DBPs (AOCl), brominated DBPs (AOB_r), and iodinated DBPs (AOI). As a bulk measurement of halogenated DBPs, the halogen-specific AOX method can be used to estimate the total organic halogens formed in treated drinking waters. This

information can be used to study the reactivities and fates of halides in water treated with oxidant disinfectants. It can also provide key information in studies of the potential toxicity levels of halogen-specific AOX in treated waters. The development, validation and application of a method to test for AOX is therefore a major focus of this Thesis.

In the present study, a previously published AOX method was further optimised and validated for better improvement of halogen-specific AOX measurement in treated waters (Kristiana et al., 2015). This method consisted of five steps: adsorption or enrichment of halogenated organic compounds from aqueous solution into activated carbon, nitrate washing to remove inorganic contaminants present within activated carbon after adsorption, combustion of the activated carbon containing halogenated organic compounds, absorption of halide gases produced after combustion with absorber solution, and detection of halides in the absorption solution. The optimisation of the analytical parameters included the impact of gas line wash and different types of absorber solutions. Validation of the optimised AOX method was performed based on the recoveries of model compounds covering different classes of DBPs and recoveries of total bromine (mass balance of AOB_r and bromide). The optimised and validated method for the measurement of AOB_r were then applied to real waters to monitor the conversion of bromide to AOB_r from the raw waters to the final disinfection stage in one of the groundwater treatment plants in Western Australia. AOB_r formation in synthetic waters under different disinfection scenarios was studied. The effect of Br-recycling on AOB_r formation was investigated. The pre-chlorination step showing the competition between chlorine and bromine to DOM reactive sites for halogenations was also studied. The most fundamental part of this study where bromine can substitute chlorine in Cl-intermediates was assessed. Finally, AOB_r formed in this study was then validated with a conceptual kinetic model.

This Thesis commences with a discussion on the halogen-specific AOX method optimisation, validation and application, given in Chapter 2. Chapters 3 and 4 describe AOB_r formation as effects of Br-recycling and pre-chlorination of DOM reactive sites before bromine addition to assess the competition between chlorine and bromine towards DOM, respectively. In Chapter 5 model calculations performed

using modelling software, Kintecus, were used to validate experimental observations on AOB_r formation as described in Chapters 3 and 4. Finally, Chapter 6 provides the overall conclusions reached from this study, as well as recommendations for further studies.

Chapter 2

ADSORBABLE ORGANIC HALOGEN METHOD DEVELOPMENT: VALIDATION AND APPLICATION TO REAL WATERS

Some of the research presented in Chapter 2 has been accepted for publication in the 2017 Special Issue on ‘Disinfection By-Products in Drinking Water, Recycled Water and Wastewater: Formation, Detection, Toxicity and Health Effects’ in the *Journal of Environmental Sciences*.

Langsa, M., Allard, S., Kristiana, I., Heitz, A., Joll, C.A. (2017) Halogen-Specific Total Organic Halogen Analysis: Assessment by Recovery of Total Bromine. *Journal of Environmental Sciences*, **58**, 340-348.

2.1 INTRODUCTION

In general, analytical methods used to identify and measure adsorbable organic halogen (AOX) in water systems involve adsorption of organic halogen onto activated carbon, combustion of the activated carbon, collection of hydrogen halide gases in an absorber solution and determination of halide ions. The AOX method was first introduced by Kuhn in 1974 (Glaze et al., 1977; Kuhn and Sontheimer, 1973), where detection of the halide ions was achieved by microcoulometric titration, with all halides measured together and expressed as a chlorine equivalent concentration. Since then, different variants of this method have been widely used to analyse organic halogen (expressed as a chlorine equivalent concentration) in chlorinated drinking water and industrially polluted water (Benabdallah El-Hadj et al., 2007; Drewes and Jekel, 1998; Hua and Reckhow, 2006; Jekel and Roberts, 1980; Li et al., 2002; Sjöström et al., 1985), and a method for the analysis of AOX is available in the Standard Methods for the Examination of Water and Wastewater (Eaton et al., 2005). As a bulk measurement of halogenated organic compounds, AOX is especially useful in process control since it can be determined within a short time with relatively simple equipment. However, it has the disadvantage that it does not provide information concerning the multitude of specific organic substances present (Jekel and Roberts, 1980). Most crucially, the bulk AOX measurement is incapable of differentiating between the halogens, and therefore the method cannot distinguish adsorbable organic chlorine (AOCl) from adsorbable organic bromine (AOBr) and iodine (AOI) (Hua and Reckhow, 2006). The determination of these three specific AOX species is vital for studies of disinfection of waters containing bromide and iodide, and, in particular, for toxicity studies, since AOI is likely to be of greater health concern than AOBr, which itself is likely to be more problematic than AOCl (Li et al., 2011b). Therefore, an analytical method which can differentiate between AOCl, AOBr and AOI is crucial in a variety of studies of disinfection by-products (DBPs).

Different methods of halide detection for halogen-specific AOX analysis have been developed using neutron activation (Lunde et al., 1975; Symons et al., 1987) and ion chromatography (IC) (Brandt and Kettrup, 1987; Hua and Reckhow, 2006; Li et al., 2011b; Oleksy-Frenzel et al., 2000). These two technologies have successfully

differentiated between AOCl, AOBr and AOI, however, IC is preferred for routine analysis due to the lower cost and more ready availability of the instrumentation (Hua and Reckhow, 2006). Utilising IC for halogen-specific AOX measurement enables the separation and individual quantification of chloride, bromide and iodide ions in the absorber solution.

There have been some differences in the reported methods for the analysis of halogen-specific AOX using IC in terms of combustion, types of absorbing solutions and the IC system. Brandt and Kettrup (1987) first reported the use of IC to separate between AOCl, AOBr and sulphur compounds (AOS) in water samples. In their method, the combustion temperature was set to 1050 °C and the combustion was conducted in the presence of oxygen at a flow rate of 300 mL min⁻¹. Hydrogen peroxide solution was chosen to collect the reaction gas (absorber solution) followed by off-line halide detection by IC. Aqueous solutions of model compounds containing chlorine and bromine were analysed to evaluate the performance of the method and recoveries of the model compounds varied from 3 to 109%. Chloramin-T, a biocide chemical, exhibited the lowest recovery, while the highest recovery was obtained for trichloroacetic acid (Brandt and Kettrup, 1987). The poor recovery of Chloramin-T is likely due to its decomposition in water to form hypochlorite, which would not be absorbed onto the activated carbon but rather oxidise the carbon surface (Potwora, 2009), forming chloride which would remain in the water phase and not be recovered in the AOX method. In addition, Oleksy-Frenzel *et al.* (2000) developed a method of differential AOX analysis which optimised the combustion conditions and the absorption system. The combustion temperature remained at 1050 °C but the oxygen flow was 150 mL min⁻¹. A sulphuric acid solution was used prior to the absorber for drying of the combustion gases to remove water vapour, followed by collection of the reaction gas in a sodium sulfide solution. Recoveries of model compounds containing chlorine, bromine and iodine were reported to range from 14 to 103% (Oleksy-Frenzel *et al.*, 2000). While the selection of model compounds by Brand and Kettrup (1987) focussed on halogenated non-phenolic based compounds, Oleksy-Frenzel *et al.* (2000) covered a wider range of halogenated compounds including iodinated X-ray contrast media. The lowest recoveries were found for chloro- and iodo-acetamide (14% and 37%, respectively), while the highest recovery corresponded to iodoacetic acid (103%) (Oleksy-Frenzel *et al.*, 2000). Echigo *et al.*

(2000) used a similar combustion system to the system described by Brandt and Kettrup (1987), except that MQ water was used as the absorber solution. The recovery of chlorinated and brominated model compounds ranged from 76 to 84%. Furthermore, Hua and Reckhow (2006), who developed a method for the analysis of halogen-specific AOX using a conventional Euroglass TOX analyser (similar to the combustion system reported by Oleksy-Frenzel et al. (2000)) and an off-line IC, reported high recoveries (92-104%) of model compounds containing chlorine, bromine and iodine. Finally, a more recent study from our laboratory (Kristiana et al., (2015) of a halogen-specific AOX method, using a state-of-the-art on-line AOX-IC system, validated the optimised method using model compounds and applied it to some real water samples. In this study, a comprehensive assessment of key analytical parameters for accurate measurement of halogen-specific AOX in waters was performed, including the use of different types of granular activated carbon, two different absorber solutions, and selected model compounds covering different classes of DBPs. The recoveries of selected compounds representing different classes of DBPs were all reported to be greater than 85% (Kristiana et al., 2015).

Since the application of the halogen-specific AOX method to measure the concentration of AOCl, AOBr and AOI in water samples involves a few different processes (namely adsorption of organic halogen compounds onto activated carbon, nitrate wash to remove inorganic contaminants from the activated carbon after adsorption, collection of reaction gases in an absorber solution after combustion of the activated carbon and adsorbed compounds, and detection of halide ions in the absorber solution by IC), the accuracy of the measurement depends on the performance of each process, constituting several analytical challenges. In the adsorption process, the organic solutes of the sample are adsorbed onto activated carbon in small glass columns. Previous studies applied different types of activated carbon for the enrichment of organic halogen compounds on the activated carbon. Brandt and Kettrup (1987) used sugar activated carbon (ZAK, Merck, FRG), Oleksy-Frenzel et al. (2000) chose Mitsubishi's activated carbon (Japan), and Hua and Reckhow (2006) selected CPI and Calgon activated carbon. Kristiana et al. (2015) tested different commercially available activated carbons, including Acticarb GC1200N, Filtrasorb[®], Carbon 437, Carboxen[™]572, CPI International, Darco[®], Ecologix, and Mitsubishi, for release of inorganic contaminants before and after the

nitrate wash. It was found that CPI International and Darco[®] were the two types of activated carbon which released the minimum amount of inorganic contaminants (Kristiana et al., 2015).

For the enrichment process, AOX preparators equipped with burette and pump to control the flow rate of the water samples passing through the activated carbon are used. Oleksy-Frenzel (2000) used an adsorption unit EFU 1000 (Thermo Instrument GmbH, Germany) equipped with three channels for water sampling with a sample flow rate of 3 mL min⁻¹. Brandt and Kettrup (1987) used a Gilson peristaltic pump Model Minipuls 2 (Abimed GmbH, Dusseldorf, FRG) for the enrichment process, with a flow rate of 2.5 mL min⁻¹. Hua and Reckhow (2006) used a filtration unit EFU 1700 (Euroglas B. V., Delft, Netherlands) with the flow rate of the filtration was 3 mL min⁻¹. In the previous study by Kristiana et al. (2015), the AOX module model TXA03 (Mitsubishi, Japan) contained two automatic burettes for sampling (3 mL min⁻¹ sampling flow rate) and one automatic burette for washing. The three adsorption units/modules (Brandt and Kettrup, 1987; Hua and Reckhow, 2006; Kristiana et al., 2015; Oleksy-Frenzel et al., 2000) were all similarly designed with two mini glass columns filled with activated carbon which were installed in the column holder in series, as shown in Figure 2.1.

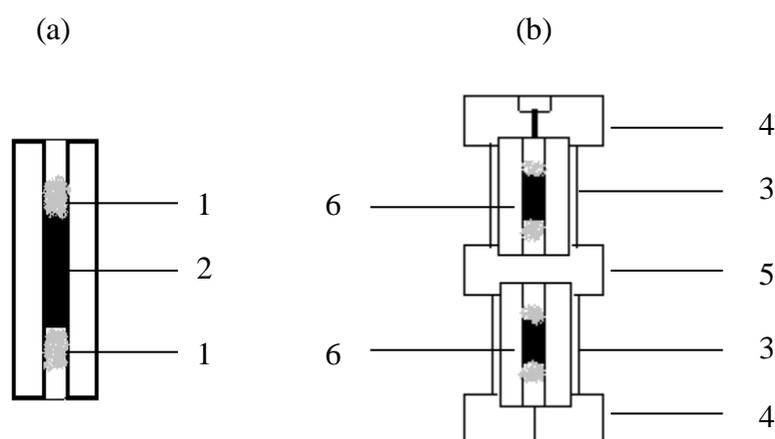


Figure 2-1: (a) Glass mini-column packed with activated carbon; (b) two glass mini-columns in series. 1: ceramic wool, 2: activated carbon, 3: column holder, 4: locking screw, 5: connector screw, 6: glass column.

While the purpose of using activated carbon is to extract the organic halogen compounds from the water samples, it has been reported that activated carbon can also act as a reductant (Li et al., 2010; Li et al., 2011b). Li et al. (2010) reported that up to 20% of the chlorine incorporated into chlorinated Suwannee River fulvic acid was reduced to chloride by the activated carbon used in the AOX analysis. Further studies on the reduction of some brominated organic DBPs to inorganic bromide by activated carbon during AOX analysis by Li et al. (2011b) revealed that around 10% of the bromine incorporated into brominated Suwannee River fulvic acid was reduced to bromide. The potential reduction of some halogenated DBPs to inorganic halides during adsorption on activated carbon could create certain systematic errors for the halogen-specific AOX measurement as the produced inorganic halides would be removed from the activated carbon during the subsequent rinsing step with nitrate solution. Kristiana et al. (2015) investigated the CPI International activated carbon in terms of acting as a reducing agent (and producing halide ions in the activated carbon columns) and potential breakthrough of AOX. With careful examination of the effluent collected after adsorption of a halophenol mixture (2,4,6-trichlorophenol, 2,4,6-tribromophenol, and 2-iodophenol; up to $1000 \mu\text{g L}^{-1}$ each) with two activated carbon columns in series, it was found that there was no breakthrough of analytes. In addition, each halophenol standard, measured as AOC_l, AOB_r and AOI, respectively,

was almost fully recovered (Kristiana et al., 2015). This indicates that two activated carbon columns in series effectively adsorbed all of the halophenol standards, without reduction to the halides, thus diminishing the possibility of errors in the adsorption process.

2.1.1 Scope of Study

The objectives of the work described in this Chapter were to further optimise the method previously developed in our laboratory for halogen-specific AOX analysis (Kristiana et al., 2015). Although the instrumental parameter settings had been fully optimised, there were still some analytical parameters that remained un-optimised which may contribute to better AOX measurement. Therefore, the first part of the optimisation work involved the investigation of different gas line washing times on the recovery of model compounds, followed by the use of a different absorber solution containing a reducing agent for comparison with MQ water as the absorber solution to collect the hydrogen halide gases after combustion. The final objective was to validate the performance of the AOX method in treated drinking water based on the recoveries of a selection of organic halogen model compounds. Another approach for halogen-specific AOX method validation, particularly for the measurement of AOB_r, was based on determining the mass balance of bromine species after chlorination of solutions containing DOM and bromide. Finally, application of the optimised halogen-specific AOX method on real waters was conducted. This is the first comprehensive report of halogen-specific AOX method validation involving the recovery of total bromine (mass balance of the concentrations of AOB_r and bromide after disinfection compared to the initial bromide concentration).

2.2. EXPERIMENTAL

2.2.1 Chemicals and Reagents

All inorganic reagents, organic solvents and organic compounds were of analytical grade purity or higher, and were used without further purification.

2.2.2 Purified Laboratory Water

Laboratory water used in this study was treated in several steps to obtain water of sufficiently high purity to meet the requirements of this study. Tap water was firstly treated by passing it through an Ibis[®] reverse osmosis system which involved filtration through a 5 µm pre-filter, followed by an activated charcoal filter and two mixed-bed ion exchange purification packs in series, and then a reverse osmosis membrane. The permeate water was stored in a 60 L polypropylene tank. Water from the storage tank was fed to a Purelab Ultra Analytic purification system (Elga, UK) which produced high purity water with a conductivity of 18.2 mΩ and a dissolved organic carbon concentration range of 50-100 µgC L⁻¹. This high purity water is referred to as MilliQ (MQ) water in this Thesis.

2.2.3 Cleaning Procedures

All non-volumetric glassware was rinsed with deionised water (3x) and annealed overnight at 550 °C prior to use. All volumetric glassware was rinsed with MQ water (5x) and further rinsed with the solvent to be used. All syringes were flushed with appropriate solvent (5x) prior to use.

2.2.4 Halogen-Specific AOX Analysis

2.2.4.1 Preparation of Standard Solutions

A mixed halophenol standard solution, as used in the Standard Method (Eaton et al., 2005) and in the AQF-100 Mitsubishi combustion module manual, was prepared. This solution contained 2,4,6-trichlorophenol, 2,4,6-tribromophenol and 2-iodophenol (Sigma-Aldrich Australia; purity ≥ 98%). A stock solution (50 mL; 2 g L⁻¹ of the respective halogen) was prepared in methanol. A working solution of halophenols (100 mg L⁻¹) was prepared by dilution of the stock solution in methanol. Aliquots of the working solution were further diluted into MQ water to achieve working standard solutions ranging in concentration from 0 – 1000 µg L⁻¹.

For calibration of the IC system, aqueous individual stock solutions (1000 mg L⁻¹) of the three anions (chloride, bromide and iodide) were prepared from reagent grade potassium salts (Sigma-Aldrich, Australia). These stock solutions were then diluted with MQ water to make working standard solutions with concentrations varying from 10 to 1000 µg L⁻¹.

2.2.4.2 Sample Isolation and Enrichment on Activated Carbon

Standard solutions and water samples (50 mL) were acidified to pH 2 with nitric acid (analytical grade, 70% HNO₃) and passed through two activated carbon microcolumns in series using a Mitsubishi TOX Sample Preparator (Model TX-3AA; Mitsubishi, Japan) (Part 1, Figure 2.2). The activated carbon columns were then washed with aqueous nitrate solution (5 mL, 5 g L⁻¹) to remove inorganic halides. The activated carbon from the two microcolumns was manually transferred to a sample boat and placed in the automatic solid sampler unit (Part 2, Figure 2-2).

2.2.4.3 Combustion of Activated Carbon and Adsorbed Species, and Collection of Hydrogen Halide Gases

The activated carbon onto which the halogenated organic compounds were adsorbed was combusted (1000 °C) with the use of an automatic quick furnace (AQF-100; Mitsubishi, Japan) (Part 3, Figure 2.2). The hydrogen halide gases formed from combustion were collected in a gas absorption unit containing MQ water that was automatically dispensed from a reservoir (GA-100; Mitsubishi, Japan) (Part 4, Figure 2.2). In a separate experiment, another aqueous absorbing solution containing approximately 0.5 g L⁻¹ Na₂S was also trialled in order to compare the effectiveness of the collection of halide gases. A water supply unit (WS-100; Mitsubishi, Japan) was used to supply argon gas (flow rate 150 mL min⁻¹) and water to the inner pyrolysis tube, the latter promoting the condensation of gases and improved recovery after combustion. The Ar/O₂ and O₂ gas flow rates through the furnace were 200 and 400 mL min⁻¹, respectively. A small amount of water (a total of 3.12 mL over two washes for 1.0 sec) was passed through the gas lines leading into the gas absorption tube to ensure all halide gases were collected, before the sample was automatically injected into an ion chromatography (IC) system (ICS-3000, Dionex, Sunnyvale, CA, USA) (Part 5, Figure 2.2).

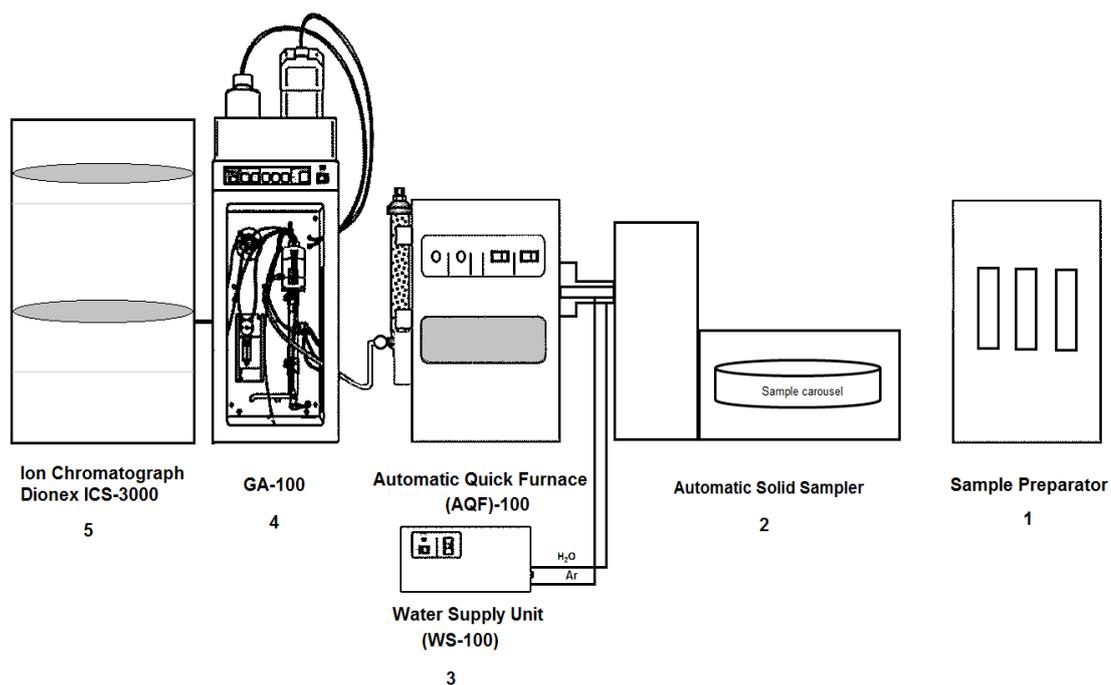


Figure 2-2: Schematic Diagram of Automatic Quick Furnace (AQF-100) with online Ion Chromatography and off-line Sample Preparator (after (Kristiana et al., 2015)).

2.2.4.4 Analysis of Absorber Solution by Ion Chromatography

The concentrations of halogen-specific AOX (i.e. AOCl, AOBr and AOI) in the sample were measured as chloride, bromide and iodide, respectively, in the absorber solution using the IC system (ICS-3000, Dionex, Sunnyvale, CA, USA).

Separation of halide ions was conducted using an IonPac® AS19 ion chromatography column (4 x 250 mm) with an IonPac® AG19 (4 x 50 mm) guard column (Dionex®). Dionex ICS3000 VWD Conductivity Detector was applied for halide detection. The mobile phase (9 mM potassium hydroxide solution) was generated using an eluent generator, and the system was operated at a flow rate of 1.0 mL min⁻¹. The injection volume loop was 100 µL. The quantification limit was 3 µg L⁻¹ for chloride, 2 µg L⁻¹ for bromide, and 1 µg L⁻¹ for iodide. All MQ water required for the operation of the IC system was replaced daily.

2.2.5 Halogen-Specific AOX Method Optimisation

2.2.5.1 Variation of Absorber Solution

An aqueous solution of the reducing agent, sodium sulfide (Na_2S) (reagent grade, Sigma-Aldrich, Australia) (500 mg L^{-1}), was prepared. The performance of the Na_2S solution as an absorber solution was compared to MQ water by assessing the recovery of selected model compounds.

2.2.5.2 Washing of the Gas Line

The effect of different parameter settings for washing of the gas line (number of washes and duration of washes) on the concentration factor was determined. The concentration factor allows calculation of the recovery of model compounds and determination of AOX concentrations in samples in the halogen-specific AOX analysis. The total volume of the absorber solution (MQ water) was measured by weight (five replicates).

2.2.6 Recovery of the Halogen-Specific AOX Method

Model organic compounds (26) containing chlorine, bromine and/or iodine, representing some major classes of DBPs, were selected to validate the optimised halogen-specific AOX method. The model compounds included haloacetic acids (HAAs), haloacetonitriles (HANs), chlorophenols, bromophenols and halogenated benzenes. A stock solution of each organic halogen compound was prepared at a concentration of 100 mg L^{-1} in methanol. Final working solutions ($100 \text{ } \mu\text{g L}^{-1}$ in MQ water; 250 mL) were then prepared. All stock solutions were kept at $-15 \text{ }^\circ\text{C}$ to avoid degradation. Aliquots (50 mL) of the final working solutions were analysed through the full halogen-specific AOX method. Details of the selected model compounds are provided in Table 2.1.

The measured concentration of halogen in the model compounds in the sample solution (final working solution) was calculated as follows:

$$\text{Measured concentration of halogen in sample solution } (\mu\text{g/L}) = \frac{\left(\frac{\text{Peak Area}}{\text{Slope of Calibration Curve}} \right)}{\left(\frac{\text{Sample Volume}}{\text{Volume of Absorber Solution}} \right)} \quad (1)$$

where peak area was determined from the IC signal of the corresponding halide, and the slope was determined from the IC calibration curve. The sample volume/volume of absorbing solution represents the concentration factor (enrichment factor) in the sample preparation steps.

The recovery of halogen in the model compounds through the halogen-specific AOX method was calculated as follows:

$$\text{Recovery of halogen in model compounds} = \frac{\text{measured concentration of halogen in sample solution } (\mu\text{g/L})}{\text{known concentration of halogen in sample solution } (\mu\text{g/L})} \times 100\% \quad (2)$$

where the measured concentration of halogen in the sample solution was determined from Equation (1).

Table 2-1: Model compounds used for validation of the halogen-specific AOX method.

Compound*	Purity (%)	Number of halogen atoms		
		Chlorine	Bromine	Iodine
Chloroacetic acid	99	1		
Dichloroacetic acid	99.9	2		
Chlorodibromoacetic acid	94.6	1	2	
Trichloroacetic acid	99	3		
Bromoacetic acid	99		1	
Bromochloroacetic acid	99.9	1	1	
Bromodichloroacetic acid	99.9	2	1	
Dibromoacetic acid	98.7		2	
Bromoacetonitrile	97		1	
Dibromoacetonitrile	>90		2	
Chloroacetonitrile	99	1		
Dichloroacetonitrile	98	2		
Bromochloroacetonitrile	NA	1	1	
Trichloroacetonitrile	98	3		
2-Chlorophenol	>99	1		
4-Chlorophenol	>99	1		
2,6-Dichlorophenol	99	2		
2,4,6-Trichlorophenol	98	3		
Pentachlorophenol	97	5		
4-Bromophenol	99		1	
2,4-Dibromophenol	95		2	
2,4,6-Tribromophenol	99		3	
Bromobenzene	>99.5		1	
1,2-Dichlorobenzene	99	2		
1,4-Dibromobenzene	98		2	
2-Iodophenol	98			1

* Purchased from Sigma-Aldrich (Castle Hill, NSW, Australia), except for dibromoacetonitrile (Supelco) and bromochloroacetonitrile (Accustandard Inc. New Haven, CT, USA).

2.2.7 Measurement of Halogen-Specific AOX during Halogenation of a DOM Extract

2.2.7.1 Measurement of Chlorine Equivalent Concentration

Standardisation of the stock aqueous NaOCl solution (analytical grade, available Cl₂=11%, Sigma-Aldrich, Australia) was performed by preparing a diluted stock solution (2000x dilution) and measuring the UV absorbance of this diluted solution at 292 nm ($\epsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$) (Morris, 1966) using a CARY 60 UV-VIS Agilent Technologies spectrophotometer. A calibration curve of chlorine concentrations

versus absorbance was prepared by analysis of chlorine solutions of known concentrations (0 – 30 μM ; prepared by dilution of the standardised stock aqueous NaOCl solution). The chlorine equivalent residuals were analysed using the *N,N*-diethylphenylene-1,4-diamine (DPD) colorimetric method.

2.2.7.2 Preparation of Bromide Solution

A stock aqueous bromide solution (1 g L^{-1} ; 12.5 mM) was prepared from the reagent grade potassium salt ($\geq 99\%$, Sigma-Aldrich, Australia).

2.2.7.3 Measurement of Bromide Ion

Bromide was measured with an ion-chromatography (ICS-3000 Dionex, Sunnyvale, CA, USA) with an AG9H/AS9H column and a 9 mM Na_2CO_3 eluent with a flow rate of 1 mL min^{-1} . Injection volume loop was 100 μL . The quantification limit was 2.8 (± 0.9) $\mu\text{g L}^{-1}$.

2.2.7.4 Preparation of DOM Extract Solutions

The aromatic rich dissolved organic matter (DOM) extract, Suwannee River (SR; catalogue number: 2R101N; International Humic Substances Society), was selected for the halogenation of a DOM extract experiments. A SR-DOM stock solution (100 mgC L^{-1}) was prepared by dissolving the SR extract powder in MQ water and filtration through a 0.45 μm membrane filter. A series of SR-DOM working solutions (approximately 1 to 8 mgC L^{-1}) were prepared and their DOC concentrations determined by the UV/persulfate oxidation method using a Shimadzu TOC- V_{ws} Total Organic Carbon Analyser.

2.2.7.5 Preparation of Quenching Solution

A stock aqueous sulphite solution (1.3 g L^{-1} ; 10 mM) was prepared from the reagent grade sodium salt ($\geq 98\%$, Sigma-Aldrich, Australia).

2.2.7.6 Halogenation of DOM Extract Solutions

An aqueous solution (2 L) containing SR-DOM (4 mgC L^{-1}) and bromide (500 $\mu\text{g L}^{-1}$, 6.26 μM) was prepared from the respective stock solutions. The pH of the solution was maintained constant at pH 8 using 1 mM phosphate buffer. The DOM extract solution was treated with chlorine (75 μM , $\sim 5.3 \text{ mgCl}_2 \text{ L}^{-1}$) for contact times

of 10, 15, 30, 45, 60 min and 24 h. The residual oxidant (sum of HOCl and HOBr, expressed as a free chlorine equivalent concentration in mg L^{-1}) in each sample was measured by the *N,N*-diethyl-phenylene-1,4-diamine (DPD) colorimetric method (Eaton et al., 2005) and followed over time. The oxidant residual was quenched with sodium sulphite solution (10% excess) prior to analysis of halogen-specific AOX and bromide ion (Salhi and Von Gunten, 1999). The recovery of bromine in these experiments, measured as the sum of AOB_r and residual bromide concentrations compared to the initial bromide concentration, was monitored.

2.2.8 Measurement of Halogen-Specific AOX in a Drinking Water Treatment Plant

Water samples from several sampling points in a drinking water groundwater treatment plant (GWTP) in Perth, Western Australia, were collected for real-world application of the halogen-specific AOX measurement. The water treatment process is comprised of pre-chlorination, coagulation (alum)/flocculation (polyacrylamide polyelectrolyte), filtration, fluoridation, pH adjustment and chlorination for disinfection. Free chlorine equivalent concentrations of the water samples were measured at the sampling locations using a portable pocket colorimeter (HACH, Loveland, CO, USA; DPD). For water samples to be analysed for AOX, any chlorine equivalent residual remaining in the water samples was quenched immediately with aqueous sodium sulphite solution. Samples were collected in clean amber glass bottles. During transport from the plant to the laboratory, the water samples were cooled. In the laboratory, the samples were filtered through a 0.45 μm membrane filter and stored at 4 °C prior to analysis for bromide, dissolved organic carbon, halogen-specific AOX.

2.3. RESULTS AND DISCUSSION

2.3.1 Further Optimisation of the Halogen-Specific AOX Method

The halogen-specific AOX method using the AQF-IC instrumentation has been previously optimised and validated (Kristiana et al., 2015). A summary of the optimised parameters previously published by Kristiana et al. (2015) is presented in Table 2.2.

The halogen-specific AOX analysis is a measurement of the individual total organic halogen adsorbed from the sample onto the activated carbon. This analytical method involves several steps starting with sample adsorption, followed by the online processes for sample combustion, halide gas absorption and IC detection. Overall, the optimised parameters presented in Table 2.2 (Kristiana et al., 2015) cover all steps involved in the halogen-specific AOX analysis. A short summary of these optimised parameters reported by Kristiana et al. (2015) follows. For the adsorption of organohalogen compounds, activated carbon (100-200 mesh size) made by CPI International was found to perform the best. Nitric acid solution (5 mL) was sufficient to remove inorganic compounds from the activated carbon after the sample had been passed through it. Complete combustion of organohalogen compounds adsorbed on the activated carbon was achieved at 1000 °C in 10 min. MQ water was the optimum absorber solution, with the optimised absorption time being 1 min. Finally, for the halide ion detection by IC, an IonPac® AS19 column was chosen, with the IC run time being 30 min.

Table 2-2: Summary of optimised parameters for the analysis of halogen-specific AOX using the AQF-IC system (Kristiana et al., 2015).

AOX Process	Parameter	Optimum Conditions and Values	
Sample Preparation	Sample pH	pH 2	
	Sample volume	50 mL	
Sample Adsorption	Type of activated carbon	CPI International	
	Washing solution for inorganic removal	Aqueous sodium nitrate solution ($5 \text{ g L}^{-1} \text{ NO}_3^-$)	
	Volume of washing solution	5 mL	
	Sample breakthrough	Below detection	
Sample Combustion	Combustion temperature	1000 °C	
	Combustion time	10 min	
	Gas flow	Ar/O ₂ : 200 mL min ⁻¹ O ₂ : 400 mL min ⁻¹	
HX Gas Absorption	Absorber solution	MQ water	
	Volume of absorber solution	5 mL	
	Absorption time	60 sec	
	Gas line wash	2 washes each at 1 s	
Ion Chromatography (IC) Analysis	IC column	IonPac® AS19	
	IC run time	30 min	
	Flow rate	1 mL min ⁻¹	
	Eluent gradient		0 – 8 min: 5 mM NaOH
			8 – 18 min: 30 mM NaOH
			18 – 23 min: 100 mM NaOH
		23 – 30 min: 1 mM NaOH	

The gas absorber (GA-100) unit is a part of the AQF-IC system that receives the reaction gas containing hydrogen halides (HX) from the combustion unit. The hydrogen halide gases dissolve in the MQ water in the absorber and the halide ions (X⁻) are separated and detected by IC. The absorber solution volume was optimised to be 5 mL. A key to understanding the halogen-specific AOX method was the realisation that the plug of water used to rinse the gas line from the combustion unit to the absorber unit just prior to injection of the absorber solution into the IC added 3.347 mL of water to the total volume of absorber solution (Kristiana et al., 2015). The purpose of washing the gas line is to ensure that there is no carryover between the samples. This 67 % increase in volume of the absorber solution affects the concentration factor in the calculation of the measured halogen-specific AOX concentration (Equation 1, Section 2.2.6), and therefore the recovery of the model

compounds. Taking this increased volume of absorber solution into account resulted in recoveries of studied model compounds being 85 (± 0.4) – 126 (± 20) % (Kristiana et al., 2015).

While many parameters for the halogen-specific AOX method were fully optimised, there were still several additional parameters which could be optimised, possibly contributing further to improved halogen-specific AOX analysis. Therefore, the first objective of this study was to further optimise these parameters of the halogen-specific AOX method using the AQF-IC instrumentation. To prepare a calibration curve for quantification of the AOCl, AOBr and AOI concentrations in unknown samples (Equation 1, Section 2.2.6), halophenol standard solutions containing 2,4,6-trichlorophenol, 2,4,6-tribromophenol, and 2-iodophenol, respectively, were used. The choice of halophenol standards was based on their use in the Standard Methods (Eaton et al., 2005) and the AQF instruction manual. Therefore, for the optimised method assessment experiments, halophenol standards were also used.

2.3.1.1 Effect of Different Absorber Solutions

The use of an aqueous sodium sulfide solution as an absorber solution was recommended by Oleksy-Frenzel et al. (2000) since they proposed that oxyhalogen species may be formed along with hydrogen halides during the combustion step and sodium sulphide can reduce these oxyhalogen species to halide ions. However, since Oleksy-Frenzel et al. (2000) only used aqueous sodium sulphide solution as an absorber solution and did not compare this to the simpler option of MQ water, it was important to compare the use of both of these absorber solutions in the current halogen-specific AOX method using the AQF-IC instrumentation. The recoveries of the mixed halophenol standards and other model compounds when MQ water and aqueous sodium sulphide solution (0.5 g L^{-1}) were separately used as the absorber solutions are presented in Figure 2-3.

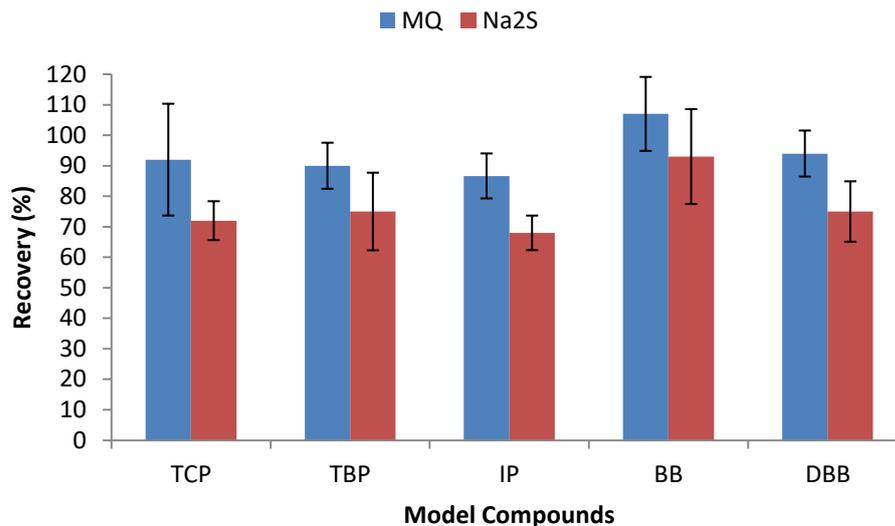


Figure 2-3: The effect of different absorber solutions (MQ water and aqueous sodium sulfide solution) on the recovery of selected model compounds. TCP: 2,4,6-trichlorophenol; TBP: 2,4,6-tribromophenol; IP: 2-iodophenol; BB: bromobenzene; DBB: 1,4-dibromobenzene (concentration of each halophenol in the sample was $100 \mu\text{g L}^{-1}$).

It is apparent from the data presented in Figure 2-3 that use of MQ water, rather than aqueous sodium sulfide solution, results in higher recoveries for all of the selected model compounds. The recoveries of the three individual halophenol standards with the use of MQ water were 87 – 107 %, while only 68 – 93 % of these compounds were found to be recovered with the use of aqueous sodium sulfide solution. For the bromobenzenes, the recoveries were again higher with the use of MQ water than with the use of aqueous sodium sulfide solution. Calibration studies showed negligible difference between the use of MQ water and sodium sulfide solution as the solvent for analysis (results not shown). The higher recoveries from the use of MQ water in the absorber indicate that formation of oxyhalogen species in the combustion process was not significant and that sodium sulfide solution in the absorber was not necessary, in contrast to the hypothesis of Oleksy-Frenzel et al. (2000). Oleksy-Frenzel et al. (2000) used a different set of model compounds (4-chloro-, 4-bromo-, and 4-iodo-phenol), which were essentially fully recovered, to verify their method using sodium sulfide solution in the absorber; however, their recoveries of a wider range of halogenated organic compounds were very variable (14 – 103 %) and the recovery of the only compound present in both studies, 1,4-

dibromobenzene, was 49 % (Oleksy-Frenzel et al. (2000)) compared to 77 % using sodium sulfide as the absorber solution and 94 % using MQ water as the absorber solution in the current study. Thus, the current study has shown that MQ water is superior to sodium sulfide as the absorber solution and therefore MQ water was chosen as the solvent for the absorber solution in this analytical method.

2.3.1.2 Effect of Gas Line Washing Time

Following on from the work of Kristiana et al. (2015) in identifying the increase in volume of the absorber solution from addition of the gas line washing solution, the influence of different gas line washing parameters to the total volume of the absorber solution, and thus the impact on the recoveries of the model compounds, was assessed. The volume of absorber solution dispensed from the GA-100 unit to the gas absorber tube was set constant at 5 mL. The AQF-100 system program has a setting range for the number of gas line washes from 0 to 99, with the duration of washing time being varied from 0.1 to 2.0 sec. In these experiments, the number of washes and the time for each wash was varied. One or two washes, for 0.1, 0.5 or 1.0 sec, were selected, as the maximum capacity of the gas absorber tube is only 10 mL. The results are presented in Table 2.3.

Table 2-3: The impact of the number and repetitions of gas line washing on recoveries of selected model compounds.

Gas Line Washing		Final Absorber Volume (mL)	Concentration Factor ^{*)}	Recovery of Model Compounds (%)		
Number of Washes	Time (sec)			TCP	TBP	IP
1x	0.1	5.37±0.15	9.31	78±2	80±3	84±4
1x	0.5	5.96±0.08	8.39	89±1	92±4	86±2
1x	1.0	6.71±0.18	7.45	89±4	91±1	87±4
2x	0.1	5.60±0.00	8.93	88±6	90±3	86±4
2x	0.5	6.82±0.15	7.33	88±1	89±1	84±2
2x	1.0	8.12±0.13	6.16	91±6	91±4	85±1

^{*)} Volume of sample (50 mL) divided by final absorber volume; TCP: 2,4,6-trichlorophenol; TBP: 2,4,6-tribromophenol; IP: 2-iodophenol (concentration of each halophenol in the sample was 100 µg L⁻¹).

Increasing the number of washes and the time of washing consistently increased the total absorber volume, as expected. The minimum washing volume (0.37 mL) was added with one wash for 0.1 sec, where the total absorber solution volume was 5.37 mL. This increase in the total absorber volume by 7.4% resulted in the highest concentration factor (9.31) of AOX from the samples to the absorber solution. Increasing the time of washing to 0.5 and 1.0 sec resulted in the total volume of the absorber solution being 0.96 mL and 1.71 mL, respectively.

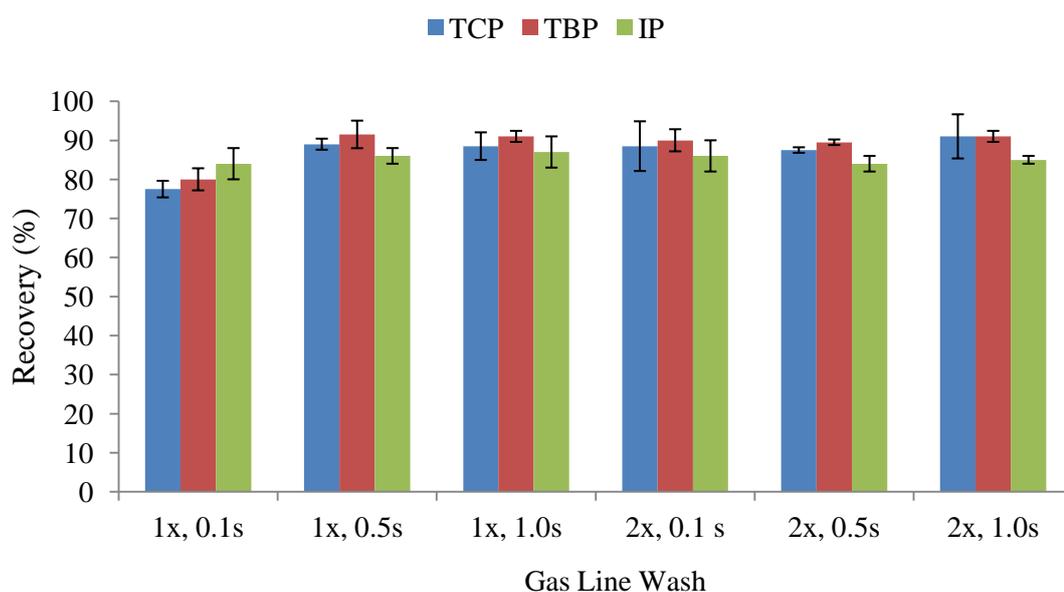


Figure 2-4: Recoveries of model compounds when different numbers of washes for different lengths of time in the gas line between the combustion unit and the absorber unit were used. TCP: 2,4,6-trichlorophenol, TBP: 2,4,6-tribromophenol, IP: 2-iodophenol (concentration of each halophenol in the sample was $100 \mu\text{g L}^{-1}$).

Regarding the impact of the gas line setting parameters on the recoveries of the model compounds, there was no significant difference in the recoveries of the model compounds with the exception of the smallest volume increase experiment (one wash for 0.5 sec) (Figure 2-4). At this setting value, the recovery of TCP was less than 80 %, while TBP exhibited a recovery of 80 %. Most likely, under these conditions, not all of the halides remaining in the gas line were washed into the absorber solution, resulting in an incomplete recovery. The remaining settings produced similar recoveries of the halophenol standards, but the two washes at 1.0 sec each setting was found to produce the optimum recoveries of the chlorinated and

brominated halophenol standards. TCP and TBP were recovered identically (91 %), while IP exhibited a recovery of 85 %. Therefore, the gas line setting parameters of two washes for 1.0 sec each were selected for this halogen-specific AOX method.

2.3.2 Further Validation of the Halogen-Specific AOX Method

2.3.2.1 Recoveries of Organic Halogen in Model Compounds

Recoveries of organic halogen in model compounds have been widely reported as AOX method validation approaches (e.g. (Brandt and Kettrup, 1987; Kristiana et al., 2015; Oleksy-Frenzel et al., 2000)), where several halogenated organic compounds are selected for validation of the optimised method. In the current study, the recoveries of organic halogen from a wide range of halogenated organic compounds, representing major classes of DBPs, were investigated based on the optimised method. The trihalomethanes (THMs) were not studied as the recoveries from this class of DBPs have been previously reported (e.g. ten THMs studied by (Kristiana et al., 2015)).

The recoveries of organic halogen from 26 model compounds using the halogen-specific AOX method, along with their pK_a , molecular weight, and octanol/water partition coefficient ($\log K_{ow}$), are presented in Table 2.4. Very good recoveries of organic halogen from all model compounds were obtained, indicating high or complete conversion of all organic halogen in the model compound solution through to halide in the absorber solution for IC analysis. The recoveries ranged from 78 % to 135% for organochlorine compounds, with only monochloroacetic acid found to be recovered less than 80 % (78 %). For organobromine compounds, the range of recoveries was slightly better than the organochlorine compounds, being 83 to 118 %, with most of the organobromine model compounds exhibiting recoveries around 100 %. 2-Iodophenol represented the only organoiodine compound and its recovery was 85 %.

Since the recoveries were consistently high across all chemical classes studied, functional groups did not appear to affect the recoveries achievable in the halogen-specific AOX method. The recoveries were also consistently high across different molecular weight, pK_a , and $\log K_{ow}$ values. Likewise in several previous studies, there has been no observable significant trend between molecular weight and

recovery of AOX from model compounds (e.g. (Brandt and Kettrup, 1987; Kristiana et al., 2015; Oleksy-Frenzel et al., 2000; Reckhow et al., 1990).

Table 2-4: Physical and chemical properties of selected model compounds, as well as their recoveries through the optimised halogen-specific AOX method.

No.	Compound	MW (g mol ⁻¹)	log K _{ow}	pK _a	Recovery (%)		
					AOCl	AOBr	AOI
	Haloacetic Acids						
1	Chloroacetic acid	94.5	0.34	2.86	78±6		
2	Dichloroacetic acid	128.9	0.52	1.35	110±12		
3	Chlorodibromoacetic acid	252.3	1.62		80±10	97±2	
4	Trichloroacetic acid	163.4	1.44	0.66	85±4		
5	Bromoacetic acid	138.9	0.43	2.86		95±4	
6	Bromochloroacetic acid	173.4	0.61		94±4	111±4	
7	Bromodichloroacetic acid	207.8	1.53		87±6	92±8	
8	Dibromoacetic acid	217.9	0.70			95±6	
	Haloacetonitriles						
9	Bromoacetonitrile	120.0	0.20			108±2	
10	Dibromoacetonitrile	198.8				107±6	
11	Chloroacetonitrile	75.0	0.11		80±8		
12	Dichloroacetonitrile	109.9			105±4		
13	Bromochloroacetonitrile	154.4			135±15	118±10	
14	Trichloroacetonitrile	144.4			115±10		
	Chlorophenols						
15	2-Chlorophenol	128.6	2.16	8.3	101±6		
16	4-Chlorophenol	128.6	2.16	9.2	89±4		
17	2,6-Dichlorophenol	163.0	2.80	7.7	93±8		
18	2,4,6-Trichlorophenol ^{*)}	197.5	3.58	6.25	91±5		
19	Pentachlorophenol	266.3	4.74		82±12		
	Bromophenols						
20	4-Bromophenol	173.0	3.40			99±2	
21	2,4-Dibromophenol	251.9	3.29	7.71		83±6	
22	2,4,6-Tribromophenol ^{*)}	330.8	4.18	5.97		91±2	
	Iodophenol						
23	2-iodophenol ^{*)}	220.0	2.68	8.41			85±1
	Halogenated benzenes						
23	Bromobenzene	157.0	2.88			109±6	
24	1,2-Dichlorobenzene	147.0	3.28		94±4		
25	1,4-Dibromobenzene	235.9	3.77			98±2	

*) Halophenol standards

While the recoveries of 1,2-dichlorobenzene and 1,4-dibromobenzene were 94 and 98 %, respectively, in the current study, Brandt and Kettrup (1987) and Oleksy-Frenzel et al. (2000) both reported low recoveries (<49%) for these benzenes. The excellent recovery observed currently for 1,4-dibromobenzene was consistent with the recovery (93 %) for this compound reported by Kristiana et al. (2015). The recoveries of the dihalobenzenes obtained from the current study were > 94 %, indicating that the CPI activated carbon may offer superior adsorption of the dihalobenzenes compared to the Mitsubishi activated carbon and “Sugar Activated Carbon” used by Oleksy-Frenzel et al. (2000) and Brandt and Kettrup (1987), respectively.

In terms of the recoveries of the HAAs, Oleksy-Frenzel et al. (2000) reported a low recovery of 2-chloroacetic acid (35 %) and proposed that this compound did not fully adsorb onto the activated carbon. They suggested that molecular weight could affect the recoveries of the HAAs, since HAAs with increasing molecular weight had increasing recoveries (83 % recovery for trichloroacetic acid). The excellent recoveries of the HAAs in the current study (> 80 %, Table 2.4) are in contrast to the findings of Oleksy-Frenzel et al. (2000) and suggest superior adsorption of these model compounds onto the CPI activated carbon. In our study, CPI activated carbon was chosen due to its minimal or low release of AOX contamination compared to the activated carbon used by Oleksy-Frenzel et al. (2000) (Mitsubishi) as reported by Kristiana et al. (2015). The very good recoveries of model compounds achieved in our study indicate that CPI activated carbon appears to offer the added benefit of an improved enrichment process of AOX from halogen-containing waters.

In conclusion, this model compound study across a wide range of functional groups and molecular weights, including the three types of organohalogen compounds (organochlorine, organobromine and organoiodine), demonstrates very good method performance in terms of recovery of organic halogen in the halogen-specific AOX method.

2.3.2.2. Measurement of Halogen-Specific AOX during Halogenation of DOM Extract Solutions: Accuracy of AOB_r Method

To study the performance of the halogen-specific AOX method in a practical application, an aqueous standard DOM extract (Suwannee River DOM; 4 mgC L⁻¹) was treated with chlorine (75 μM, ~ 5 mg Cl₂ L⁻¹) in the presence of bromide ion (6.26 μM, 500 μg L⁻¹) at pH 8, and the formation of halogen-specific AOX and the total amount of bromine and bromide (measured as bromide after quenching any oxidant residual) was measured over 1 h.

Figure 2-5 shows the AOCl and AOB_r formation, resulting from reaction of chlorine and bromine with the SR-DOM reactive sites, over time, as well as the reduced bromine measured as bromide after quenching, and the total bromine, calculated as the sum of AOB_r and bromide. It is apparent that only 13 % of the added chlorine (75 μM) was incorporated into SR-DOM and measured as AOCl (10 μM) in the first 5 min of experimental time. Chlorine continued to be incorporated into SR-DOM, albeit more slowly, for the remainder of the experimental period (18 % Cl- incorporation, 13.3 μM, after 1 h). In contrast, 83 % of the initial bromide was incorporated into SR-DOM to form AOB_r (5 μM) in the first 5 min and maximum bromide incorporation (88 %, 5.3 μM) was reached after 15 min. The formation of AOB_r and AOCl appears to be nearly complete after the reaction time of 60 min, even though the free chlorine equivalent residual was 33 μM at this time, indicating that nearly all reactive sites within the SR-DOM had been consumed. Interestingly, not all of the initial bromide was converted into AOB_r, with 0.8 μM remaining as bromine or bromide at the conclusion of the experiment. This remaining bromine/bromide indicates that there was a strong competition between halogens (HOCl and HOBr) with reactive sites for halogenation (formation of AOCl and AOB_r, respectively) through electrophilic substitution and addition, however these halogens are also reduced via electron transfer (redox) reactions with DOM, releasing chloride and bromide, respectively. Further explanations for these processes are given below and in Chapter 3.

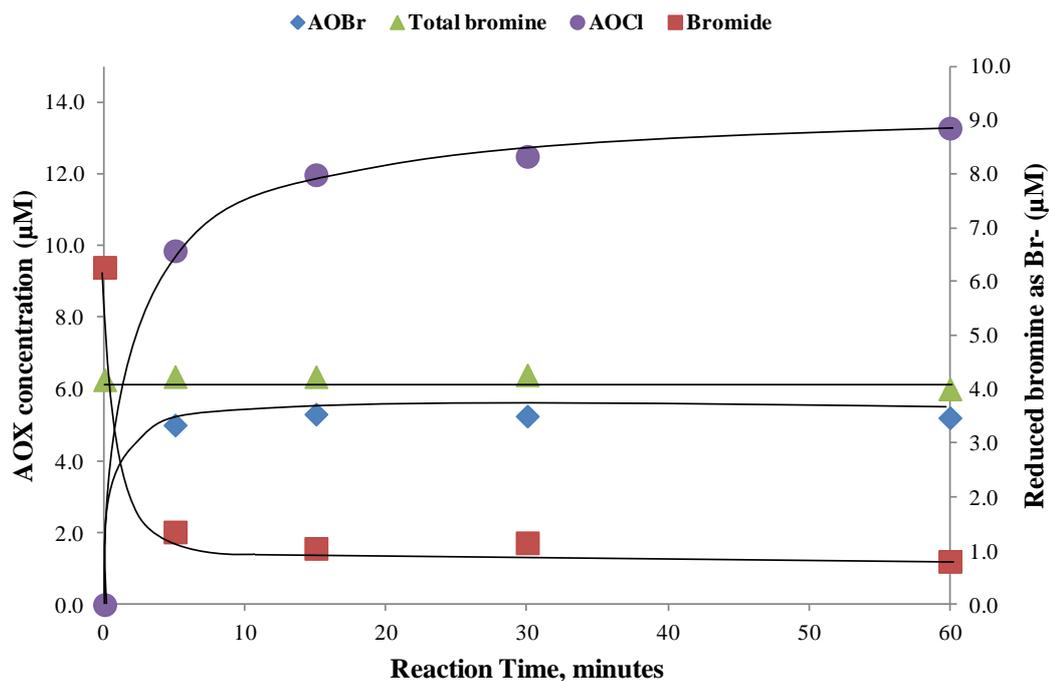


Figure 2-5: Concentrations of halogen-specific AOX (AOCl and AOBBr) and the inorganic bromine species (measured as bromide after quenching the oxidant residual) over time. Experimental conditions: SR-DOM (4 mgC L^{-1}), bromide ($500 \text{ } \mu\text{g L}^{-1}$, $6.26 \text{ } \mu\text{M}$), phosphate buffer (1.0 mM), $\text{pH} = 8$, chlorine ($75 \text{ } \mu\text{M}$, $\sim 5 \text{ mg Cl}_2 \text{ L}^{-1}$), Na_2SO_3 (10 % excess based on chlorine equivalent residual) for quenching. The “green triangles” represent the total bromine measured in the system at the sampling times, being the sum of measured AOBBr and bromide. Lines are shown to guide the eyes.

Bromide-containing waters when treated with chlorine will result in the rapid formation of hypobromous acid (HOBr) and hypobromite (OBr^-) (for simplicity, the term bromine will be used for the sum of HOBr and OBr^-). The produced bromine then reacts with organic moieties in the water, analogous to chlorine. Both AOCl and AOBBr form through electrophilic substitution and addition reactions of chlorine and bromine, respectively, with various functional groups in DOM. At the same time, chlorine and bromine can oxidise other reactive sites in DOM and be reduced in the process to chloride and bromide, respectively, via electron transfer (redox) reactions (the reactions between DOM and halogens are discussed in detail in Chapter 3). This reduced bromide can then be re-oxidised with the excess of chlorine present to

reform bromine which can then react further with reactive sites in DOM to form additional AOB_r (or oxidised species via electron transfer). This process is termed “bromide recycling”. At the end of the experimental time in Figure 2-5 (60 min), the bromide available to participate in the bromide recycling process is indicated by the bromide concentration (after quenching the oxidant residual). Reactivity of bromine, formed either from oxidation of bromide or direct aqueous bromine, towards DOM reactive sites was found to be varied. For instance, AOB_r formation through electrophilic substitution and addition is more dominant when bromide containing waters are treated with HOCl, while oxidation reactions appeared to be the dominant processes when synthetic waters containing DOM were treated directly with aqueous bromine (discussed in more detail in Chapter 3). In the current experiment, the high percentage of bromide incorporation (83 %), even after only 5 min of reaction time, suggests fast reaction of bromine with reactive sites in DOM. Moreover, bromide recycling plays a significant role for AOB_r formation, since reduced bromide is re-oxidised to form bromine for further AOB_r formation.

To evaluate the recovery of the initial bromide, as AOB_r or bromine or bromide, the total bromine represented by these three species was calculated (Figure 2-5). The recovery of the initial bromide was excellent at all times over the 1 h period, giving an excellent mass balance of bromine in the system. This result indicates that the halogen-specific AOB_r method provides an accurate measure of the AOB_r formed in the system. This is the first report of the use of a mass balance approach for halogen-specific AOX method validation. The high recovery of the initial bromide in this approach is consistent with the very good recoveries of model compounds (Section 2.3.2.1) demonstrated for the halogen-specific AOX method.

2.3.1 Application of Method: Measurement of Halogen-Specific AOX in a Drinking Water Treatment Plant

The optimised halogen-specific AOX method was applied to study the formation of halogen-specific AOX (AOCl and AOB_r) in a Western Australian drinking water groundwater treatment plant (GWTP1). GWTP1 uses a conventional water treatment process consisting of pre-chlorination followed by alum and polyelectrolyte addition, clarification, filtration, and final disinfection with chlorine. Three samples were collected through the plant to determine the impact of different treatment processes

on the formation and distribution of halogen-specific AOX. Figure 2-6 shows a schematic of the GWTP1 process and the concentrations of various water quality parameters at the three sampling points. The first sampling point was located at the GWTP1 raw water inlet, while the other two samples were collected after filtration and final chlorination. It should be noted that the GWTP1 inlet receives raw water from a variety of bores which extract water from different aquifers which contain water of variable quality. The bore combination varies depending on water demand, resulting in frequently changing water characteristics of the raw water. Some historical concentrations of bromide and DOM in the raw water for GWTP1 are presented in Table 2.5 (WCWA, 2009). The large variation in raw water quality at GWTP1 is illustrated by the wide variation in the minimum and maximum concentrations of bromide and DOM shown in Table 2.5. Table 2.5 also provides the concentration of bromide and DOM in raw water collected on the 28th May 2012 for the current study.

Table 2-5: Averages and ranges of some water quality characteristics of the raw groundwater blends at GWTP1 over a time period of approximately 3 years (2006-2009) (WCWA, 2009), and the concentrations of these water quality parameters on 28 May 2012.

Water sample	Raw water			
	Min	Max	Average	28 May 2012
DOM concentration (mgC L ⁻¹)	5.6	25.1	9.6	9.4
Bromide concentration (µg L ⁻¹)	420	1020	760	1350

It is apparent from Table 2.5 that the DOM concentration of the raw water sample collected for the current study (28 May 2012) was similar to the average historical average concentration, while the bromide concentration was almost double that measured for the historical average concentration. This is likely due to the input to GWTP1 of a new bore into a deep aquifer, where the water contains lower concentrations of DOM but much higher concentrations of bromide than the shallow aquifer, commencing in December 2009. The DOM concentration was observed to decrease (by 37 %) after the coagulation/flocculation stage and to decrease by a further 21 % after the post-chlorination stage, for a total 58 % reduction across the treatment plant (Figure 2-6).

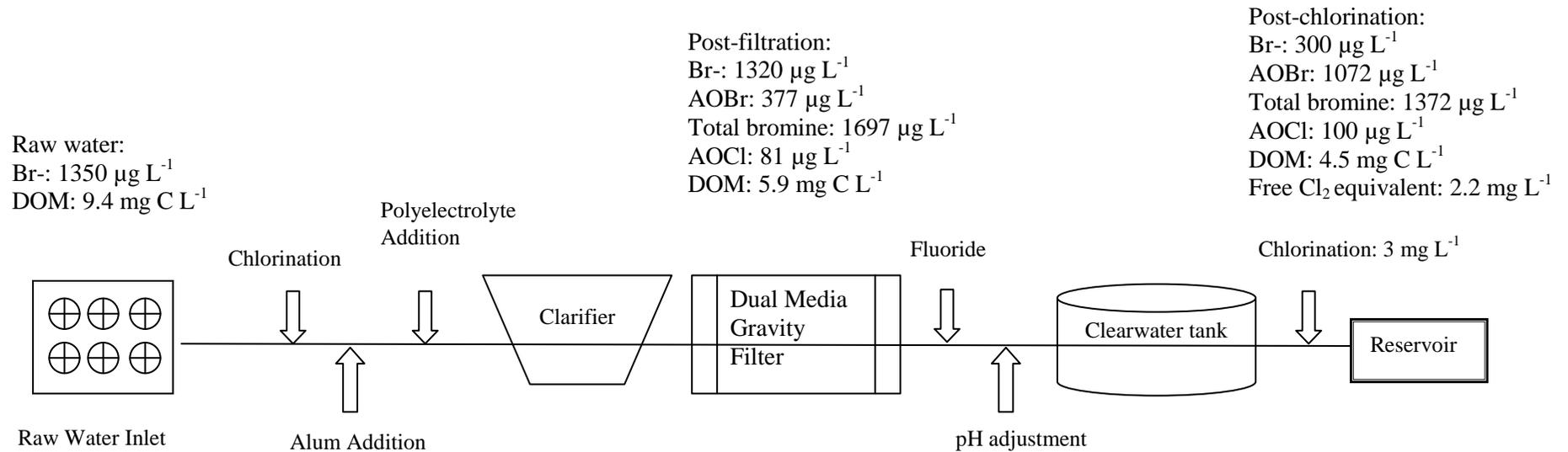


Figure 2-6: Schematic of the treatment processes in the groundwater treatment plant. Concentrations of bromide, dissolved organic matter, halogen-specific AOX, total bromine (calculated as the sum of bromide and AOB concentrations) and free chlorine equivalents at the three sampling points are shown.

In the post-filtration sample, approximately 28 % of initial bromide ($1350 \mu\text{g L}^{-1}$, $16.9 \mu\text{M}$) was converted to AOB_r ($377 \mu\text{g L}^{-1}$, $4.7 \mu\text{M}$), while 98 % of remaining bromide or bromine (i.e. 71 % of the initial bromide) was detected as bromide after quenching (Figures 2-6 and 2-7a). The AOB_r formed through chlorine (pre-chlorination addition) oxidising the bromide to bromine and the bromine undergoing electrophilic addition or substitution with reactive functional groups in the DOM. The total bromine recovered in the post-filtration sample ($1697 \mu\text{g L}^{-1}$; $21.2 \mu\text{M}$) was 25 % higher than the initial bromide concentration in the raw water inlet. This is likely to be due to a recent change in bore combination decreasing the bromide concentration in the collected raw water compared to the water part-way through treatment in the post-filtration stage. AOCl was also detected at a concentration of $80.9 \mu\text{g L}^{-1}$ ($2.3 \mu\text{M}$) in the post-filtration sample (Figures 2-6 and 2-7b), indicating that some chlorine added in the pre-chlorination step reacted with DOM moieties to form chlorinated organic compounds (measured as AOCl).

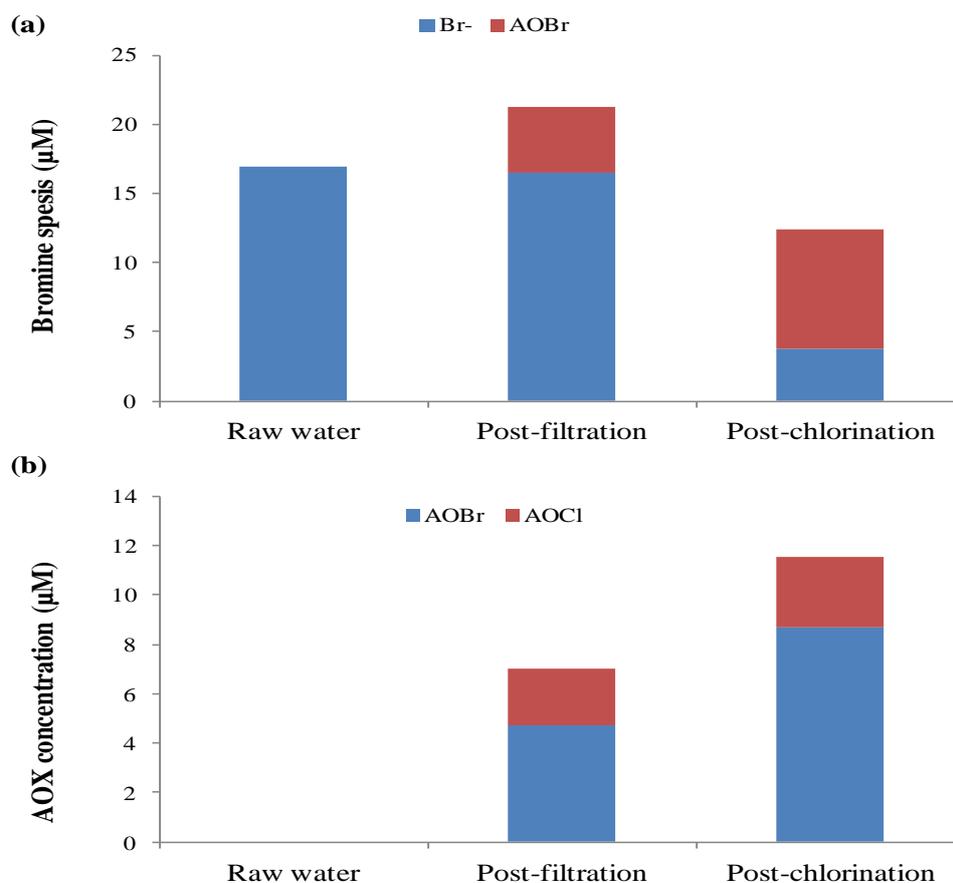


Figure 2-7: Halogen-specific AOX formation showing (a) conversion of bromide to AOB_r and (b) AOCl vs AOB_r through the water treatment train at GWTP1.

Final disinfection with chlorine ($3 \text{ mgCl}_2 \text{ L}^{-1}$) resulted in more AOB_r formation, with 53% of bromide measured in the post-filtration sample being incorporated into DOM to form AOB_r ($695 \text{ } \mu\text{g L}^{-1}$, $8.7 \text{ } \mu\text{M}$). Taking into account the AOB_r already present in the post-filtration sample ($377 \text{ } \mu\text{g L}^{-1}$, $4.7 \text{ } \mu\text{M}$), the total AOB_r concentration formed in the post-chlorination stage was $1072 \text{ } \mu\text{g L}^{-1}$ ($13.4 \text{ } \mu\text{M}$, Figures 2-6 and 2-7a). In contrast, only 2 % of the added chlorine ($3 \text{ mgCl}_2 \text{ L}^{-1}$) was incorporated into the remaining organic material to form AOCl ($19 \text{ } \mu\text{g L}^{-1}$, $0.5 \text{ } \mu\text{M}$, Figures 2-6 and 2-7b). The lower chlorine incorporation into DOM compared to high bromine incorporation, from both raw water to post-filtration water and post-filtration water to post-chlorination water, despite the lower concentration of bromine than chlorine, indicates that bromine is more reactive and faster to react than chlorine towards DOM reactive sites for electrophilic addition and substitution. Therefore, bromine is a better substitution/addition agent for halogenation compared to chlorine. A chlorine equivalent residual was still detected ($2.2 \text{ mg Cl}_2 \text{ L}^{-1}$) in the post-chlorination sample and residual bromide ($300 \text{ } \mu\text{g L}^{-1}$, $3.8 \text{ } \mu\text{M}$) was measured after quenching the chlorine equivalent residual. The total bromine, as a sum of AOB_r and bromide, in the post-chlorination sample was $1370 \text{ } \mu\text{g L}^{-1}$ ($17.1 \text{ } \mu\text{M}$), indicating a likely good recovery of bromine (75 %) from the post-filtration sample to the post-chlorination sample and a likely excellent recovery of bromine from the raw water sample to the post-chlorination sample, noting again the possible variability in water quality through the treatment process due to changing bore combinations.

Overall, from all sampling points, AOB_r was found to be the dominant product of halogen-specific AOX compared to AOCl (Figures 2-6 and 2-7b). Moreover, the formation of AOB_r after the final chlorination treatment compared to the post-filtration sample increased significantly from $4.7 \text{ } \mu\text{M}$ ($377 \text{ } \mu\text{g L}^{-1}$) to $13.4 \text{ } \mu\text{M}$ ($1072 \text{ } \mu\text{g L}^{-1}$) while AOCl increased slightly from $2.3 \text{ } \mu\text{M}$ ($81 \text{ } \mu\text{g L}^{-1}$) to $2.8 \text{ } \mu\text{M}$ ($100 \text{ } \mu\text{g L}^{-1}$). The dominance of AOB_r over AOCl, despite the lower concentration of bromine than chlorine, again shows the faster reactivity of bromine with DOM compared to chlorine. By comparing the formation of AOB_r in the last treatment (post-chlorination) with the initial bromide concentration in the raw water inlet, there was about 79 % bromide conversion into AOB_r, along with the excellent mass balance of total bromine across the plant.

These good to excellent mass balances of bromine following the flow and transformation of bromide from the raw water through the treatment process again support the validity of the halogen-specific AOX method, especially for AOB_r measurement in drinking water systems. Health risks related to the formation of brominated organic compounds (AOB_r) compared to their chlorinated analogues (AOCl) in treated drinking waters are of public health concern. Brominated DBPs (AOB_r) have been found to be of greater health concern than their chlorinated analogues (Richardson et al., 2008; Yang et al., 2014). In our laboratory and other laboratories, it has been shown that the concentrations of halogen-specific AOX correlate well with the toxicity of halogenated DBPs in water samples (e.g. (Neale et al., 2012; Savitz et al., 2006; Yang et al., 2014). The halogen-specific AOX method provides an important tool to monitor and better understand the formation of halogenated organic compounds, in particular the potentially more problematic brominated organic compounds, in drinking water systems.

2.3. CONCLUSIONS

Further optimisation of the instrumental conditions of the gas absorber module of the AQF-IC system, including comparison of an alternative absorber solution and different gas line washing parameters, resulted in a fully optimised method recovery for the analysis of halogen-specific AOX in water samples. The optimised method was applied to a wide range of halogenated organic compounds, representing major classes of DBPs and a variety of functional group types and molecular weights. Very good recoveries of organic halogen (as AOCl, AOBr and AOI) from all model compounds were achieved, indicating very good method performance in converting organic halogen in the model compound solution through to halide in the IC detector.

The application of this analytical method to study the formation of AOBr upon chlorination of an aqueous solution of a standard DOM extract and bromide was successful in monitoring the conversion of bromide to AOBr through electrophilic substitution and addition reactions. The bromine remaining in the solution was measured as bromide by quenching the oxidant residual. The recovery of the initial bromide as the total measured bromine (sum of AOBr and bromide) was excellent over the 1 h reaction period, indicating that the halogen-specific AOBr method provided an accurate measure of the AOBr formed in the solution. Studies of the flow and transformation of bromide in a groundwater treatment plant with a very high concentration of bromide and DOC in the inlet water showed good bromine recovery (mass balance of AOBr and bromide concentrations compared to initial bromide concentration), supporting the validity of the halogen-specific AOX method, especially for AOBr measurement in drinking water systems.

Due to the potential health impacts of brominated organic compounds (AOBr) in drinking waters, minimisation of AOBr in drinking water treatment plants and distribution systems is essential. The halogen-specific AOX method provides an important tool to monitor and better understand the formation and fate of halogenated organic compounds, in particular the potentially more problematic AOBr, in drinking water systems. The halogen-specific AOX method provides comprehensive information about the overall incorporation of halogen into organic compounds, rather than the incorporation of halogen into a few small individual DBP

molecules (e.g. THMs and HAAs), as are currently monitored and regulated. These specific DBPs have been reported to contribute only 50 % of total AOX formed in drinking waters ((Richardson, 2003). It is recommended that drinking water utilities consider inclusion of halogen-specific AOX analysis in their monitoring regimes. Further studies of halogen-specific AOX formation in drinking water systems as related to health impacts (e.g. epidemiological studies) would allow governments and health regulators to consider developing new guideline values for AOX concentrations in drinking waters.

Some of the research presented in Chapter 3, 4, and 5 has been published in the journal of *Environmental Science & Technology*. Reproduced in part with permission (Appendix 1) from **ENVIRONMENTAL SCIENCE & TECHNOLOGY**. Copyright 2017 American Chemical Society.

Langsa, M., Heitz, A., Joll, C. A., von Gunten, U., Allard, S. (2017) Mechanistic Aspects of the Formation of Adsorbable Organic Bromine during Chlorination of Bromide-containing Synthetic Waters. *Environmental Science & Technology*, **51**(9), 5146-5155.
<http://pubs.acs.org/doi/abs/10.1021/acs.est.7b00691>

Chapter 3

MECHANISTIC STUDY OF THE FORMATION OF ADSORBABLE ORGANIC BROMINE IN SYNTHETIC WATERS: ROLE OF BROMIDE RECYCLING DURING CHLORINATION

3.1 INTRODUCTION

Dissolved organic matter (DOM) is the main precursor of disinfection by-products (DBPs) formation upon disinfection during drinking water treatment. Additionally, inorganic compounds (e.g. bromide) are another class of DBPs precursors that play a significant role in the formation of halogenated DBPs.

During drinking water treatment, disinfection is mainly applied to inactivate microorganisms, which among other steps is important to provide safe drinking water (Gordon et al., 1948; Rosario-Ortiz et al., 2016; Sedlak and von Gunten, 2011). The main chemical disinfectant used for drinking water is chlorine ($\text{HOCl} + \text{ClO}^-$). It is usually employed as a pre-treatment to prevent the spread of waterborne pathogens and/or as a final disinfectant to provide a disinfectant residual to the consumer's tap (Rosario-Ortiz et al., 2016; Sedlak and von Gunten, 2011). Chlorine is applied at much higher concentration than the ubiquitously occurring bromide (concentration ranging from $10 \mu\text{g L}^{-1}$ to $2000 \mu\text{g L}^{-1}$ worldwide) (Agus et al., 2009; D'alessandro et al., 2008; Flury and Papritz, 1993; Heller-Grossman et al., 1999; Magazinovic et al., 2004).

In Australia, particularly in Western Australia, bromide levels are relatively high in many water sources (up to 2 mg L^{-1}) compared to other worldwide locations (average concentration in US $\sim 100 \mu\text{g L}^{-1}$) (Gruchlik et al., 2014; Magazinovic et al., 2004). Br-containing waters at high levels could potentially lead to high formation of Br-DBPs during chlorination of treated drinking waters.

When bromide is in contact with chlorine, it is quickly oxidised to form hypobromous acid/hypobromite ion (HOBr/OBr^-) with a second order rate constant ($k_{\text{HOCl,Br}^-}$) of $1550 \text{ M}^{-1}\text{s}^{-1}$, (Kumar and Margerum, 1987) which may react further with DOM to produce brominated DBPs. Bromine was found to react in a similar way to chlorine in treated drinking waters (Nokes et al., 1999). Moreover, bromine is more reactive and a better halogenation agent than chlorine towards organic moieties (Glaze et al., 1993; Heeb et al., 2014; Westerhoff et al., 2004; Westerhoff et al., 1998).

Even though, bromine can form Br-DBPs by electrophilic substitution and addition, it can also react by electron transfer, leading to oxidation reactions and release of bromide in solution (Acero et al., 2005; Criquet et al., 2015). The released bromide can then be reoxidised to bromine if chlorine is in excess and has another chance to react with DOM or for oxidation reaction.

The role of bromide acting as a catalyst in oxidative water treatment has been previously studied. Criquet et al. (2015) reported that reaction of bromine and the selected DOM samples (Suwannee River (humic and fulvic acid), Nordic, Leonardite, and Eliot soil) led to only 20 % of Br-incorporation in DOM reactive sites as Br-DBPs through electrophilic aromatic substitution and addition reactions. It is of note that in their studies, Criquet et al. (2015) used a large excess ($\geq 50:1$) of DOM to bromine. The low Br-incorporation indicates that the electron transfer process is likely to be the dominant pathway resulting in the reduction of bromine to bromide. Therefore, bromide is a catalyst in oxidation reaction since it could be recycled by the excess oxidant. Moreover, in their previous study, Criquet et al. (2012) reported that the oxidation of iodide to iodate during chlorination was catalysed by the presence of bromide. Haag et al. (1984) found that ammonia was oxidised faster with the presence of bromide during ozonation. Similarly, the presence of bromide was reported to enhance the oxidation of manganese (II) during chlorination (Allard et al., 2013) and the formation of N-nitrosodimethylamine (NDMA) from dimethylsulfoxide-containing waters during ozonation (von Gunten et al., 2010). Bromide recycling takes place until full consumption of the oxidant or until full bromide incorporation to DOM.

As stated before bromide is also a better halogenating agent. In line with this finding, a more recent work by Allard et al. (2015) revealed that the presence of bromide and iodide in treated drinking waters with chlorine may increase the formation of more toxic compounds (brominated I-THMs). Bromide was found to be responsible for a shift from chlorinated I-THMs (e.g. CHCl_2I) to brominated I-THMs (e.g. CHBr_2I) and an increased iodine incorporation in THMs (Allard et al., 2015). Although removing pathogens is the main objective in drinking water oxidative treatment due to their immediate health risk compared to exposure to chemicals, the potential health risks associated with DBPs must also be equally considered. Therefore, it is

crucial to understand the mechanisms leading to the formation of brominated organic compounds and to control their occurrence in distribution systems.

3.1.1 Scope of Study

This study focused on investigating the mechanisms involved in the formation of brominated organic compounds (AOBr) under typical drinking water conditions using the halogen-specific AOX method. The influence of water quality parameters (i.e. bromide concentration, DOM type and concentration, chlorine concentration) on AOBr formation was investigated using synthetic waters. To avoid bromide recycling and better understand the direct reactivity of bromine towards DOM reactive sites, bromination experiments (HOBr), where only bromine was added into the synthetic waters, were performed for comparison with the chlorination experiments ($\text{Br}^- + \text{HOCl}$).

3.2 EXPERIMENTAL

3.2.1 Chemicals and Reagents

Inorganic salts, organic solvents and organic compounds used in this study were all of analytical grade purity. Analytical grade sodium hypochlorite solution (11 %, Sigma-Aldrich Australia) was used to prepare chlorine solutions. Reagents used for the measurement of chlorine residual concentrations were also of analytical grade purity.

High purity water was prepared as described in Section 2.2.2.

3.2.2 Dissolved Organic Matter (DOM) Samples

Three DOM extracts, namely Suwannee River (SR-DOM), Nordic Reservoir (NR-DOM) and Pony Lake (PL-DOM), were purchased from the International Humic Substances Society (IHSS). SR-DOM and NR-DOM extracts are allochthonous and are derived from the decomposition of the vegetation and leachate from soils, respectively. PL-DOM fulvic acid is autochthonous and was isolated from a purely microbially based aquatic ecosystem in Antarctica. The details of the DOM samples are given in Table 3-1.

Table 3-1: Details of DOM samples used in the present study

Designated name	Catalogue number	Location	Fraction type	SUVA ₂₅₄ (L/mgC m)
SR-DOM	2R101N	Suwannee River, Georgia, USA	DOM	4.85
NR-DOM	1R108N	Nordic Reservoir, Skarnes, Norway	DOM	4.45
PL-DOM	1R109F	Pony Lake, Antarctica	Fulvic acid	3.06

Each DOM stock solution (100 mgC L⁻¹) was prepared by dissolving the DOM extract in MQ water, followed by filtration through 0.45 µm polyethersulfone membrane filters (Pall Life Science, Michigan, USA). The actual DOM stock solution concentration was determined by the UV/persulfate oxidation method using a Shimadzu TOC-Vws Total Organic Carbon Analyser. The DOM solutions were stored at 4 °C to avoid any analyte degradation. A series of DOM working solutions, covering the concentrations in the range from 1 to 8 mgC L⁻¹, was then prepared.

3.2.3 Preparation of Bromide Solution

Preparation of bromide solution was conducted as described in Section 2.2.7.3.

3.2.4 Preparation of Oxidant Solutions

Standardisation of the purchased aqueous NaOCl solution (11 %) was performed by direct UV measurement at 292 nm using a CARY 60 UV-VIS Agilent Technologies spectrophotometer. A calibration covering the chlorine concentration range of 5 – 50 µM was conducted by UV spectroscopy using the *N,N*-diethylphenylene-1,4-diamine (DPD) colorimetric method at 515 nm (Eaton et al., 2005). A chlorine stock solution (10 mM, ~710 mgCl₂ L⁻¹) was prepared by diluting the purchased chlorine solution in MQ water. This chlorine stock solution was used to produce the bromine stock solution and as an oxidant for the synthetic waters.

A bromine stock solution (500 µM) was produced by mixing chlorine stock solution with a slight stoichiometric excess (5 %) of bromide (Allard et al., 2013). The solution was vigorously stirred for at least 15 min to allow complete oxidation of

bromide to bromine. The concentration of the bromine stock solution was standardised as BrO^- (pH 11) by measurement of the UV absorbance at 329 nm ($\epsilon_{329} \text{ nm} = 332 \text{ M}^{-1} \text{ cm}^{-1}$) (Criquet et al., 2012). The oxidant residual measured as the sum of bromine and chlorine but recorded as chlorine equivalents was analysed using the DPD colorimetric method at 515 nm.

3.2.5 Preparation of Quenching Solution

Preparation of quenching solution for the disinfected waters was conducted as describe in Section 2.2.7.5

3.2.6 Halogen-Specific AOX Analysis

Halogen-specific AOX analysis of the water samples was conducted as described in Section 2.2.4.

3.2.7 Measurement of Bromide Ion

Measurement of bromide ion of the water samples was conducted as described in Section 2.2.7.3

3.2.8 Analysis of THMs

The regulated THMs (chloroform, bromodichloromethane, chlorodibromomethane, and bromoform) were extracted from water samples using a solid-phase microextraction (SPME) fibre (SUPELCO, divinylbenzene (DVB)/carboxen (CAR)/polydimethylsiloxane (PDMS)) in the headspace mode and analysed using gas chromatography with mass spectrometric detection (HS SPME-GC-MS). The GC-MS system was a Hewlett Packard 6890N GC interfaced to a Hewlett Packard 5975 Network Mass Selective Detector. Separation of the THMs was conducted using a 30 m x 0.25 mm ID ZB-5 (Phenomenex) column with a film thickness of 1 μm .

For calibration of the THMs, CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3 were mixed together in methanol to achieve a stock standard solution containing 2 g L^{-1} of each compound. A working solution (10 mg L^{-1}) was prepared by dilution in MeOH. A series of standard solutions covering the concentrations of THMs produced in the water samples ($5, 10, 20, 50, \text{ and } 100 \mu\text{g L}^{-1}$) were prepared by injecting aliquots of

the working standard solution into 10 mL of MQ water in 20 mL vials. Internal standard solution (1,2-dibromopropane in methanol (10 μL , 50 mg L^{-1})) and salt (sodium sulphate (1.67 g)) were added to each vial.

For THM analysis, 10 mL of water sample was transferred to a 20 mL vial, followed by the addition of internal standard solution and salt, as per the calibration. The SPME fibre was injected into the headspace of the vial to extract the analytes, while the vial was shaken for 15 min at 50 $^{\circ}\text{C}$. The analytes were then desorbed from the fibre in the injector port of the GC at 240 $^{\circ}\text{C}$ for 5 min. All samples, including blank samples, were analysed in duplicate. The limits of detection (LODs) for each analyte were calculated using the EPA Method Detection Limit method (US-EPA 2004) by using the standard deviation of replicate analyses ($n = 3$) of the mixed standard solution of 10 $\mu\text{g L}^{-1}$. The average LODs for CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3 were 0.3 $\mu\text{g L}^{-1}$ (2.6 nM), 0.2 $\mu\text{g L}^{-1}$ (1.2 nM), 0.4 $\mu\text{g L}^{-1}$ (1.9 nM), and 0.5 $\mu\text{g L}^{-1}$ (2.1 nM), respectively.

3.2.9 Synthetic Drinking Water Experimental Procedures

3.2.9.1 Chlorine Equivalent Residual Measurements

The chlorine equivalent residual measurements of the water samples were measured as detailed in Section 2.2.7.1.

3.2.9.2 Kinetic Study

A preliminary experiment to investigate the kinetics of AOBr formation was carried out with SR-DOM and PL-DOM. SR-DOM and PL-DOM were chosen since they have different aromatic content. Synthetic waters containing SR-DOM or PL-DOM (4 mgC L^{-1}) and bromide (as KBr; 6.26 μM ; 500 $\mu\text{g L}^{-1}$) were prepared in MQ water. Phosphate buffer (1 mM) was used to maintain pH 8. Phosphate buffer was used instead of carbonate buffer since the carbonate buffer capacity is not high enough in our pH range and because of the equilibrium of carbonate with atmospheric CO_2 associated with potential pH changes. The buffered DOM solutions were treated with aqueous HOCl solution to achieve a concentration of 75 μM ($\sim 5 \text{ mgCl}_2 \text{ L}^{-1}$). A high chlorine concentration was selected to ensure that all bromide was oxidised to bromine. For each synthetic water, samples were collected at various reaction times (5, 15, 30, and 60 min) for halogen-specific AOX and bromide analysis. The

concentration of AOB_r formed in 1 h was close to the concentration of AOB_r formed in 24 h. Therefore, for all AOB_r formation studies, a reaction time of 1 h was selected.

3.2.9.3 Effect of DOM Character and Concentration on AOB_r Formation Experiments

A series of synthetic waters containing either SR-DOM, NR-DOM or PL-DOM (4 mgC L⁻¹) and bromide (as KBr; 6.26 μM, 500 mg L⁻¹), with phosphate buffer (1 mM) added to maintain the pH at 8, were prepared in MQ water. To study the impact of DOM concentration, similar solutions were prepared with SR-DOM concentrations ranging from 1 to 8 mgC L⁻¹. Chlorine solution was added to the buffered DOM solutions to achieve concentrations of 30, 50, 75, and 140 μM Cl₂ for 1, 2, 4, and 8 mgC L⁻¹ of SR-DOM, respectively. The solutions were left for a reaction time of 1 h. At the end of the reaction period, the oxidant residual was measured by the DPD method (Section 2.2.7.1). The oxidant residuals were quenched immediately using aqueous sodium sulfite solution (Section 2.2.7.5) (10 % molar excess calculated based on oxidant residual) and the samples stored at 4 °C prior to analysis. The effect of sodium sulfite on the stability of AOX was tested in a separate set of experiments by quenching SR-DOM samples which had been treated with chlorine in the presence of bromide with sodium sulphite. High concentrations of sodium sulphite (i.e. 10x higher than the initial chlorine concentration) were found to decrease the AOX concentration, while when sodium sulphite was in only a slight excess (i.e. 10 % molar excess based on the oxidant residual), the AOX concentration was not affected. Therefore, a 10 % molar excess of sodium sulphite based on the oxidant residual was used to quench the samples. The samples were analysed for halogen-specific AOX, bromide, and THMs within 24 h.

3.2.9.4 Effect of Different Bromide Concentration on AOB_r Formation Experiments

Synthetic waters were prepared by addition of SR-DOM (4 mgC L⁻¹) and bromide to achieve a variety of concentrations ranging from 1.0 to 6.26 μM (80 – 500 μg L⁻¹). The pH of the solution was maintained at 8 by phosphate buffer (1 mM). Chlorination was performed by addition of chlorine to achieve an initial concentration of 75 μM in the synthetic waters and allowing the mixtures to react for

1 h. At the end of the reaction period, the oxidant residual was measured by the DPD method (Section 2.2.7.1). The oxidant residuals were quenched immediately using aqueous sodium sulfite solution (Section 2.2.7.4) (10% molar excess calculated based on oxidant residual) and the samples stored at 4 °C prior to analysis. The samples were analysed for halogen-specific AOX, bromide, and THMs within 24 h.

3.2.9.5 Effect of Different Chlorine Concentrations on AOBr Formation Experiments

A set of synthetic waters containing SR-DOM (4 mgC L⁻¹) and bromide (6.26 µM; 500 µg L⁻¹) were prepared in MQ water, and buffered to pH 8 with phosphate buffer (1 mM). Chlorine was added to these synthetic waters to achieve different initial concentrations (15, 30, 45, 60, 75, and 90 µM) and the reactions allowed to proceed for two different reaction times (1 h and 24 h).

At the end of the reaction period, the oxidant residual was measured by the DPD method (Section 2.2.7.1). The oxidant residuals were quenched immediately using aqueous sodium sulfite solution (Section 2.2.7.4) (10 % molar excess calculated based on oxidant residual) and the samples stored at 4 °C prior to analysis. The samples were analysed for halogen-specific AOX, bromide, and THMs within 24 h.

3.3 RESULTS AND DISCUSSION

3.3.1 AOBr Formation: Kinetic Study

A solution of Suwannee River DOM (4 mgC L⁻¹) in the presence of bromide (6.26 µM; 500 mg L⁻¹) was treated with chlorine (75 µM) and the evolution of inorganic bromine species (HOBr + Br⁻: measured together as bromide after quenching the oxidant residual) and AOBr are presented in Figure 3-1. Bromate was not detected in this experiment which is consistent with other previous studies (e.g. Heeb et al., 2014; Liu et al., 2012) where the formation of bromate was found to be insignificant during chlorination of bromide-containing solution. As expected, bromine, formed from oxidation of bromide by HOCl, reacted quickly with SR DOM to form AOBr which is consistent with other published studies (Nokes et al., 1999; Westerhoff et al., 2004). About 83 % of bromine was incorporated into DOM as AOBr in the first 5 min. Bromine incorporation reached a maximum of 88 % after 15 min. The decay of

inorganic bromine species was inversely correlated to the formation of AOB_r, with 23 % of the initial bromide remaining after 5 min and 13 % after 1 h. The bromine loss by volatilisation was negligible, as confirmed by the mass balance of measured bromine species (AOB_r and HOBr/Br⁻) ranging from 96 to 102 %. The evolution of inorganic bromine species and AOB_r for the corresponding experiment with Pony Lake (PL) DOM is presented in Figure 3-2. A slightly lower Br-incorporation was observed for PL-DOM compared to SR-DOM for reaction times less than 1 h, probably due to the lower aromatic content of PL-DOM, indicated by its lower SUVA₂₅₄ value. However, at a reaction time of 1 h, both DOM samples exhibited similar % Br-incorporation. This will be discussed in more detail in the following section.

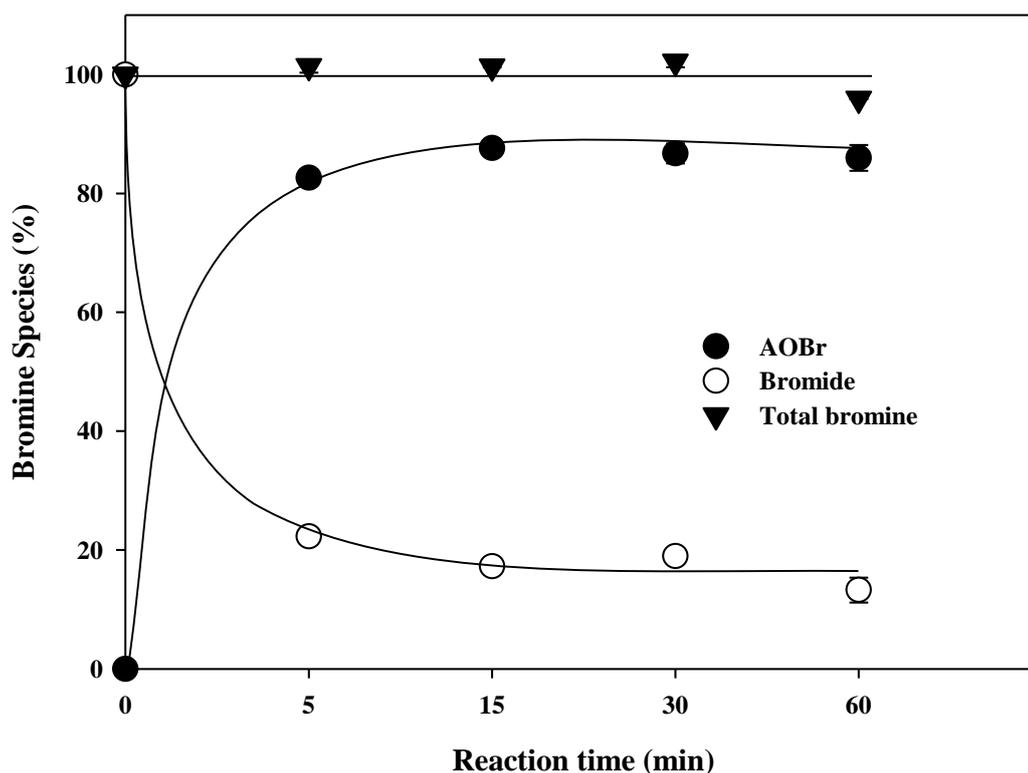


Figure 3-1: AOB_r concentrations expressed as Br-incorporation (%) (calculated from AOB_r concentration (μM) divided by initial bromide concentration (μM), multiplied by 100 %) and the inorganic bromine species measured as bromide after quenching during chlorination of Suwannee River (SR) DOM. The “black triangles”

represent the total bromine measured in the system at the sampling times, being the sum of measured AOBr and bromide. Experimental conditions: SR-DOM (4 mgC L^{-1}), bromide ($6.26 \text{ } \mu\text{M}$, $500 \text{ } \mu\text{g L}^{-1}$), phosphate buffer (1 mM), $\text{pH} = 8$, chlorine ($75 \text{ } \mu\text{M}$, $\sim 5 \text{ mg L}^{-1}$); Na_2SO_3 solution (10% molar excess based on chlorine equivalent residual) for quenching. Lines are shown to guide the eye.

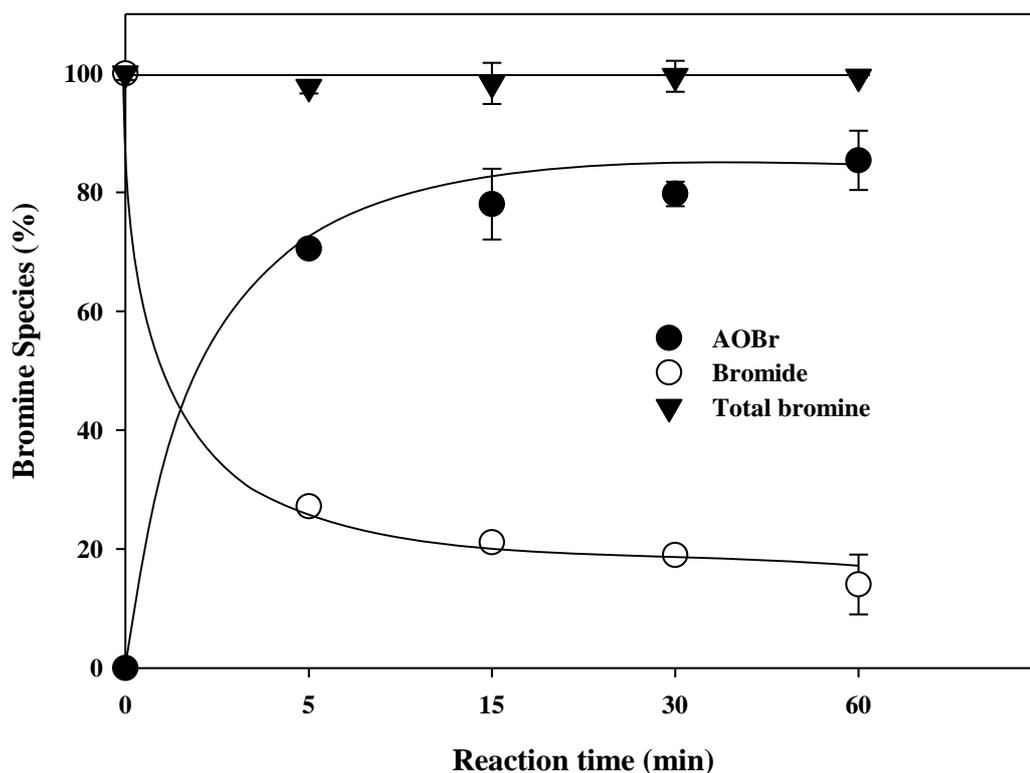


Figure 3-2: AOBr concentrations expressed as Br-incorporation (%) and the inorganic bromine species measured as bromide after quenching during chlorination of Pony Lake (PL) DOM. The “black triangles” represent the total bromine measured in the system at the sampling times, being the sum of measured AOBr and bromide. Experimental conditions: PL-DOM (4 mgC L^{-1}), bromide ($6.26 \text{ } \mu\text{M}$, 500 mg L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, chlorine ($75 \text{ } \mu\text{M}$, $\sim 5 \text{ mg L}^{-1}$); Na_2SO_3 solution (10% molar excess based on chlorine equivalent residual) for quenching. Lines are shown to guide the eye.

In terms of the reactions which occurred in these experiments, when HOCl was added to the solution, it reacted not only with DOM but it also oxidised bromide to

HOBr ($k = 1550 \text{ M}^{-1} \text{ s}^{-1}$) (Kumar and Margerum, 1987) (Equation (1)). HOBr then reacted with DOM organic moieties via electrophilic substitution and addition to form AOBBr as shown in equation (2) (Bousher et al., 1986; Song et al., 1996)



Simultaneously, HOCl and HOBr oxidised electron-rich fractions of DOM. The hypohalous acids were therefore reduced, resulting in a release of bromide (equation 3) and chloride (Equation 4) in solution (Criquet et al., 2015; Song et al., 1996).



The bromide released in solution was re-oxidised by the excess HOCl and formed more HOBr which reacted again with DOM moieties to form more AOBBr. This reoxidation of bromide to HOBr, after HOBr undertaking an initial redox reaction with DOM and in the presence of excess HOCl, is termed ‘bromide recycling’ (Criquet et al., 2015). The extent to which HOBr reacts with DOM reactive sites either to produce AOBBr via electrophilic substitution and addition or to produce oxidised DOM and release bromide depends on the composition and distribution of the organic functional groups and carbon bonding in DOM (Nokes et al., 1999).

In order to better understand the different mechanisms involved in this complex system, experiments where HOCl was added to synthetic waters containing DOM and bromide were compared to bromination experiments where HOBr was added directly to synthetic waters.

3.3.2 Effect of Water Matrix Constituents and Impact of Bromide Recycling on AOBBr Formation: Bromination (HOBr) vs Chlorination ($\text{Br}^- + \text{HOCl}$)

To elucidate the impact of bromide recycling on AOBBr formation, experiments where HOBr was added to synthetic waters to achieve initial concentrations of 1.0 – 6.26 μM were conducted in parallel with experiments where excess chlorine was added to synthetic waters containing bromide (1.0 – 6.26 μM) to achieve initial

concentrations of 30–140 μM . AOB_r (presented as % Br-incorporation), the sum of HOBr and bromide (measured as bromide after quenching), bromoform formation, and chlorine equivalent residual for chlorination ($\text{Br}^- + \text{HOCl}$) and bromination (HOBr) of different types of DOM, different concentrations of SR-DOM, and different concentrations of HOBr/ Br^- are given in Figures 3-3, 3-4, and 3-5, respectively.

As shown in Figures 3-3a, 3-4a, and 3-5a, AOB_r formation (as % Br-incorporation) was much higher in chlorination ($\text{Br}^- + \text{HOCl}$, grey bars) than bromination (HOBr, black bars). The maximum % Br-incorporation obtained in chlorination experiments reached 98 % (Figure 3a – 5a, grey bars), while in bromination experiments, the maximum % Br-incorporation was only 42 % of the initial bromide concentration (Figure 3a – 5a, black bars). Conversely, as illustrated in Figures 3-3b, 3-4b, and 3-5b, the sum of HOBr and bromide concentration reached up to a maximum of 72 % in the bromination experiments (Figure 3.3b – 3.5b, black bars) compared to only 18 % in the chlorination (Figure 3-3b – 3-5b, grey bars). As an illustrative example, for the bromination of PL DOM in Figure 3-3b, 74 % of the initial bromine was recovered as the sum of HOBr and bromide, measured as bromide after quenching, with 27 % of the initial bromine recovered as AOB_r (% Br-incorporation). This indicates that the redox reaction of HOBr with DOM is the dominant pathway in the bromination experiments, with oxidised DOM and bromide being formed, without opportunity for bromide recycling because HOCl is not present. The formation of AOB_r is only a minor reaction pathway in these experiments. For the corresponding chlorination of PLDOM experiment (Figure 3-3b), only 13 % of the initial bromide was recovered as the sum of HOBr and bromide, measured as bromide after quenching, with 87 % of the initial bromine recovered as AOB_r (% Br-incorporation). In this case, excess chlorine is available (Figure 3-3d) to recycle the bromide produced from HOBr oxidation of DOM to HOBr again, allowing further formation of AOB_r and a much lower sum of HOBr and bromide at the conclusion of the experiment, i.e. bromide recycling is a key factor in AOB_r formation.

3.3.2.1 Influence of DOM Type

Figure 3-3 presents AOB_r formation expressed as % Br-incorporation (a), the sum of HOBr and bromide measured as bromide after quenching (b), bromoform formation

(c), and chlorine equivalent residual (d) for bromination and chlorination of different types of DOM. SR-DOM and NR-DOM produced more AOB_r compared to PL-DOM in the bromination experiments (HOBr) (Figure 3-3a). For SR-DOM and NR-DOM, % Br-incorporation values of 38 % and 42 %, respectively, were achieved, while the corresponding value for PL-DOM was only 27 %. The relative % Br-incorporation values are consistent with the SUVA₂₅₄ values for the DOM samples. The SR-DOM and NR-DOM extracts had higher SUVA₂₅₄ values (4.45 and 4.85, respectively) than PL-DOM (3.06), indicating SR-DOM and NR-DOM contained more aromatic moieties, which are known to be reactive with halogen (Reckhow et al., 1990), than PL-DOM. The current results are also in agreement with various studies showing that high SUVA₂₅₄ DOM are more reactive with oxidants than low SUVA₂₅₄ DOM (Peters et al., 1980; Reckhow et al., 1990).

Conversely, in the bromination experiments, the sum of HOBr and bromide, predominantly representing bromide released in solution from oxidation of DOM, increased with increasing SUVA₂₅₄ values, with 73 % recovery of the initial bromide for PL-DOM compared to 65 % and 62 % for SR-DOM and NR-DOM, respectively (Figure 3-3b). For the chlorination (Br⁻+HOCl) experiments, no significant differences could be observed in AOB_r formation even though the % Br-incorporation for SR-DOM and NR-DOM was slightly higher (93 and 90 %, respectively) than for PL-DOM (87 %). Since bromide is recycled with the presence of excess chlorine residual (Figure 3-3d), HOBr reacts with DOM moieties until almost complete bromine incorporation in DOM (Figure 3-3a). Figure 3-3d also shows that the chlorine residual concentrations in the chlorination experiments were in the order of SR-DOM > NR-DOM > PL-DOM, similar to the order of % Br-incorporation (Figure 3-3a). Higher Br-incorporation in chlorination experiments than in bromination indicates the significant contribution of bromide recycling in AOB_r formation. Bromide recycling leads to an increase in Br-incorporation of 55, 47, and 60 % for SR-DOM, NR-DOM, and PL-DOM, respectively (Figure 3-3a).

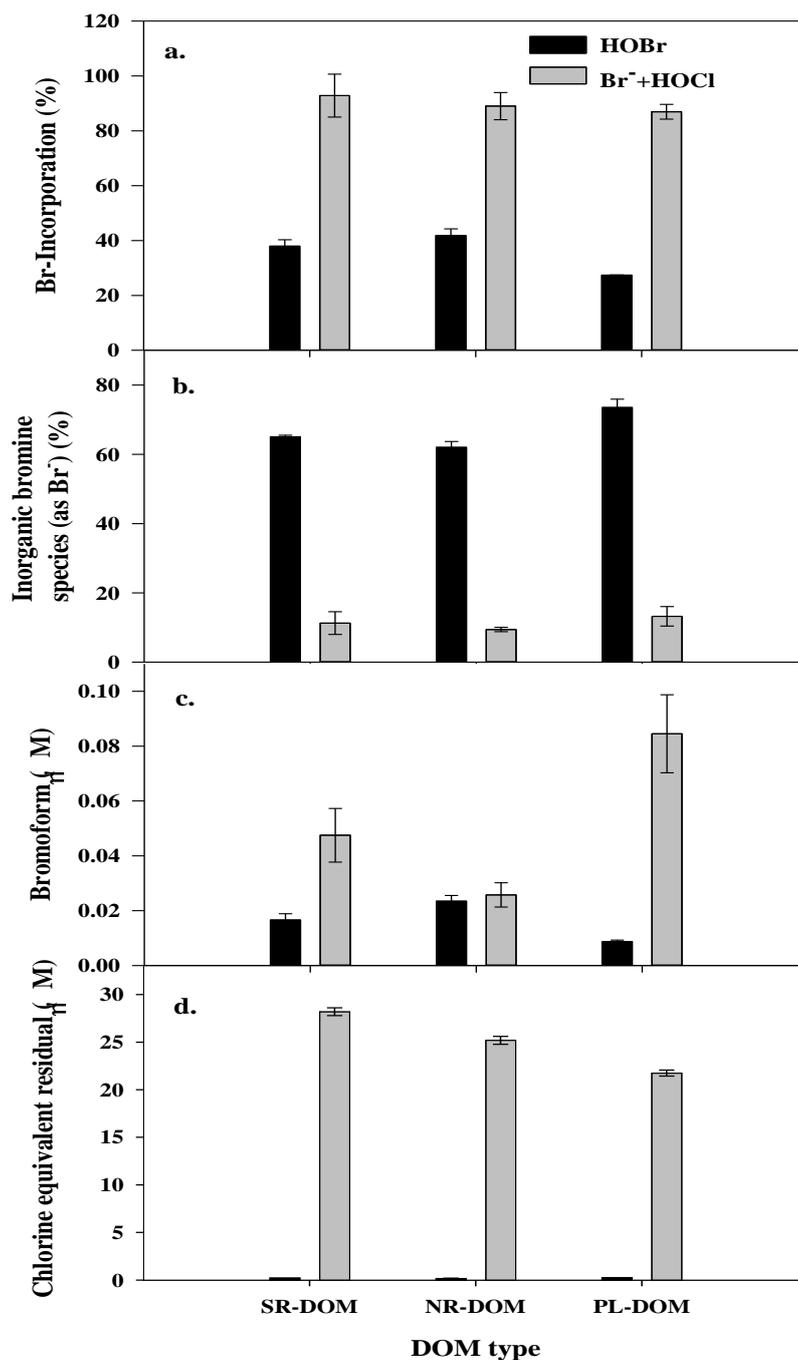


Figure 3-3: Comparison between bromination (HOBr) and chlorination (Br⁻+HOCl) in terms of AOB formation presented as % Br-Incorporation (a), the inorganic bromine species measured as bromide after quenching (b), bromoform formation (c), and chlorine equivalent residual (d) measured after 1 h experimental time for different types of DOM. Experimental conditions: DOM types (SR, NR, PL) (4 mgC L⁻¹); phosphate buffer (1 mM), pH = 8; for bromination: [HOBr] = 6.26 μM, for chlorination: [Br⁻] = 6.26 μM, [HOCl] = 75 μM; Na₂SO₃ solution (10 % molar excess based on chlorine equivalent residual) was used to quench the reactions.

Bromoform formation followed a similar trend to AOB_r for the bromination experiments (Figure 3-3c). As expected based on SUVA₂₅₄ values, the SR-DOM and NR-DOM extracts produced more bromoform (17 nM and 23 nM, respectively) than PL-DOM (9 nM) (Figure 3-3c). In this case, bromoform could be used as a surrogate for AOB_r formation. In contrast to bromination, since bromide was recycled during chlorination experiments, PL-DOM produced more bromoform (84 nM) than SR-DOM and NR-DOM (47 nM and 26 nM, respectively) in the chlorination experiments (Figure 3-3c). As reflected by its low SUVA₂₅₄ value, PL-DOM has a limited number of reactive sites compared to SR-DOM and NR-DOM. Each reactive site requires three bromine atoms to attach in order to produce bromoform. PL-DOM, containing less reactive sites, was more susceptible to reach triple bromination resulting in bromoform formation. SR- and NR-DOM, on the other hand, contain high concentrations of reactive sites, allowing bromine to react with many sites leading to single or double bromination, and therefore less bromoform production. Furthermore, SR-DOM and NR-DOM consumed chlorine equivalents more rapidly than PL-DOM. Therefore, in the chlorination experiments, less chlorine was available to form HOBr and thus lower concentrations of bromoform were formed. During the chlorination experiments, different trend was observed between bromoform and AOB_r, indicating that during drinking water treatment, where a chlorine residual is mandatory, bromoform can't be used as a surrogate for the overall formation of brominated organic compounds (i.e. AOB_r). If only regulated DBPs are used as a primary parameter, the formation of brominated organic compounds may be underestimated.

3.3.2.2 Influence of DOM Concentration

The effect of different SR-DOM concentrations on AOB_r formation was studied in similar chlorination and bromination experiments (Figure 3-4). The % Br-incorporation in the bromination experiments slightly and continuously increased with increasing DOM concentration from 28 to 39 % for 1 and 8 mgC L⁻¹, respectively (Figure 3-4a, black bars). Conversely, the bromide concentration decreased from 72 to 63 % for 1 mgC L⁻¹ and 8 mgC L⁻¹, respectively (Figure 3-4b). Increasing the SR-DOM concentration increases the number of reactive sites available for electrophilic substitution and addition reactions and therefore the formation of AOB_r. However, even for 8 mgC L⁻¹ of SR-DOM, oxidation of DOM

was still the dominant pathway and, since bromide recycling was not possible, the AOB_r concentrations (as % Br-incorporation) were relatively low. For the chlorination experiments, increasing the concentration of SR-DOM from 1 to 2 mgC L⁻¹ increased AOB_r formation by around 20 % from 71 to 90 %. Further increases in DOC to 4 mgC L⁻¹ and 8 mgC L⁻¹ resulted in only slight increases in Br-incorporation to 93 and 95 %, respectively (Figure 3-4a, grey bars). In the chlorination experiments, where excess chlorine was present (Figure 3-4d), bromide recycling occurred, with bromide formed during HOBr oxidation of DOM being reoxidised by chlorine to HOBr, leading to much higher % Br-incorporation. When the SR-DOM concentration was 1 mgC L⁻¹, the bromine appears to have been in excess compared to the concentration of reactive sites, resulting in only 71 % Br-incorporation. However, increasing the SR-DOM concentration to 2 mgC L⁻¹ appeared to allow most of the bromine to be incorporated into the DOM. Therefore, increasing the DOM concentration further to 4 and 8 mgC L⁻¹ did not significantly influence AOB_r formation since almost all the HOBr could be incorporated into DOM when the DOM concentration was 2 mgC L⁻¹. Br-recycling in chlorination increased Br-incorporation by 43 % at the lowest SR-DOM concentration (1 mgC L⁻¹). Moreover, increasing the SR-DOM concentration to 2–8 mgC L⁻¹ led to an increase in Br-incorporation of around 57 % because of the bromide recycling effect.

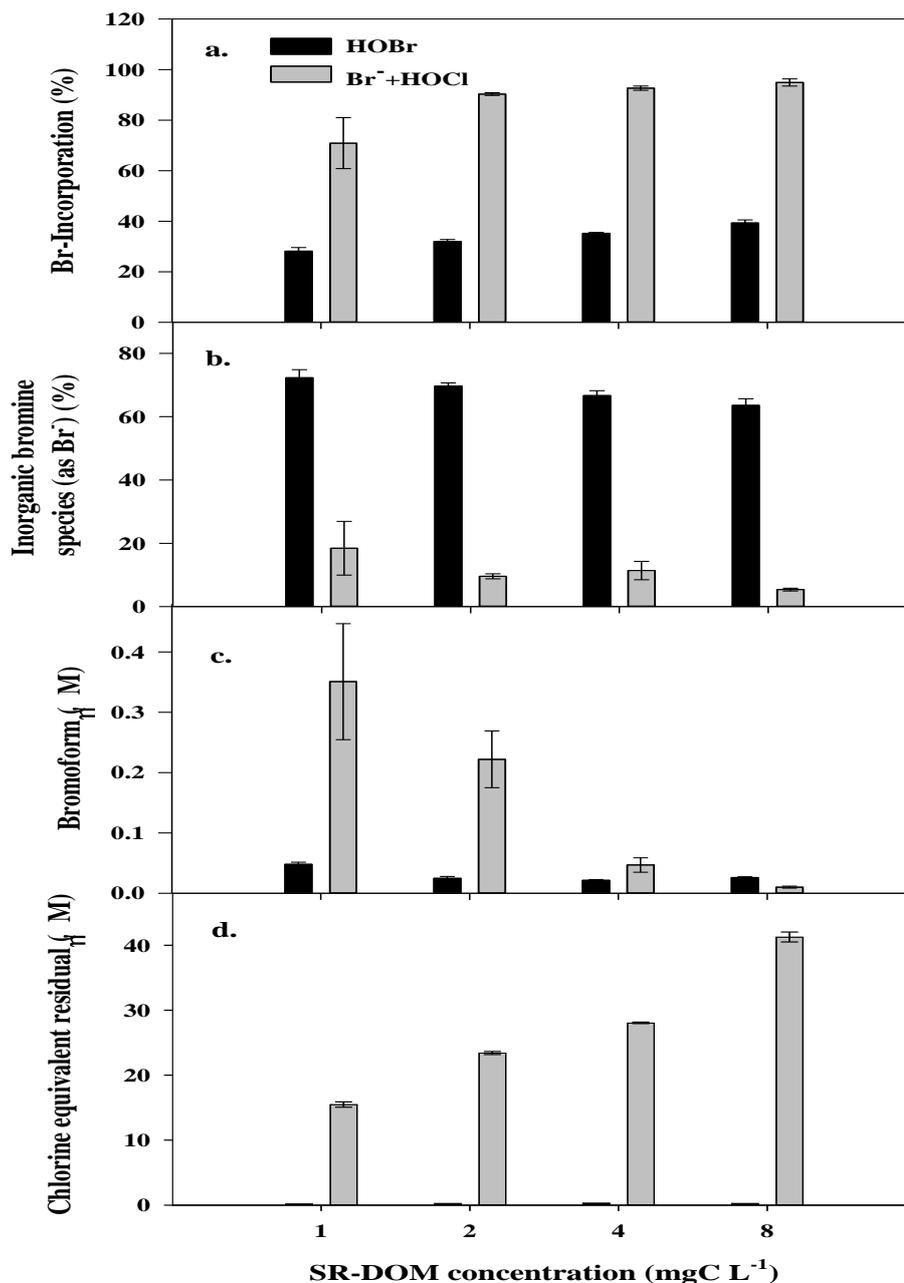


Figure 3-4: Comparison between bromination (HOBr) and chlorination (Br⁻+HOCl) in terms of AOB formation presented as % Br-Incorporation (a), the inorganic bromine species measured as bromide after quenching (b), bromoform formation (c), and chlorine equivalent residual (d) measured after 1 h experimental time for different SR-DOM concentrations. Experimental conditions: SR-DOM (1, 2, 4 and 8 mgC L⁻¹); phosphate buffer (1 mM), pH = 8; for bromination: [HOBr] = 6.26 μM; for chlorination: [Br⁻] = 6.26 μM, [HOCl] = 30, 50, 75 and 140 μM for 1, 2, 4 and 8 mgC L⁻¹ of SR-DOM, respectively; Na₂SO₃ solution (10 % molar excess based on chlorine equivalent residual) was used to quench the reactions.

For bromoform formation, no clear trend could be observed in the bromination experiments (Figure 3-4c). For 1 mgC L⁻¹, the concentration of bromoform was higher than for the higher DOC concentrations. As discussed above, for 1 mgC L⁻¹, the number of reactive sites appears to have been limited. Therefore, each reactive site may potentially undergo multiple halogenation, ultimately forming bromoform. For 2, 4 and 8 mgC L⁻¹, no significant differences were observed in bromoform concentrations since an excess of reactive sites was present and therefore bromine was evenly distributed across reactive sites. For the chlorination experiments, increasing the SR-DOM concentration decreased the bromoform concentration from 351 nM (at 1 mgC L⁻¹) to 10 nM (at 8 mgC L⁻¹) (Figure 3-4c). Increasing the SR-DOM concentration increases the number of reactive sites available for halogenation. Therefore, bromine can be widely distributed among reactive sites resulting in a reduced bromoform formation at high DOM concentrations. These outcomes are particularly significant for the water industry, where DBP regulations and guidelines focus on the trihalomethanes as indicator compounds for halogenated organic compounds, but the current study indicates that bromoform concentrations do not well reflect the bulk formation of brominated organic compounds (i.e. AOB_r).

3.3.2.3 Influence of Bromide/Bromine Concentration

The effect of the initial inorganic bromine concentration (HOBr or bromide) on AOB_r formation is presented in Figure 3-5. Increasing HOBr concentrations in bromination experiments increased the concentration of AOB_r but did not affect the fraction of bromine which formed AOB_r as the % Br-incorporation remained unchanged (37 to 39 %) (Figure 3-5a, black bars). Oxidation of DOM was still the dominant reaction in bromination, because more than 60% of the initial HOBr was reduced to bromide (Figure 3-5b). This indicates that even for the highest HOBr concentration, the concentration of reactive sites was not limiting the formation of AOB_r. The same proportion of bromine reacted through electrophilic substitution and addition for all HOBr concentrations. The same behaviour was observed for the chlorination experiments, where bromide was incorporated at a higher but similar yield (93 to 98 %) for all bromide concentrations. Again, the high yield of formation of AOB_r in these chlorination experiments is due to the effect of bromide recycling (supported by the presence of an oxidant residual as presented in Figure 3-5d) which contributes to an increase of % Br-incorporation of more than 50 %.

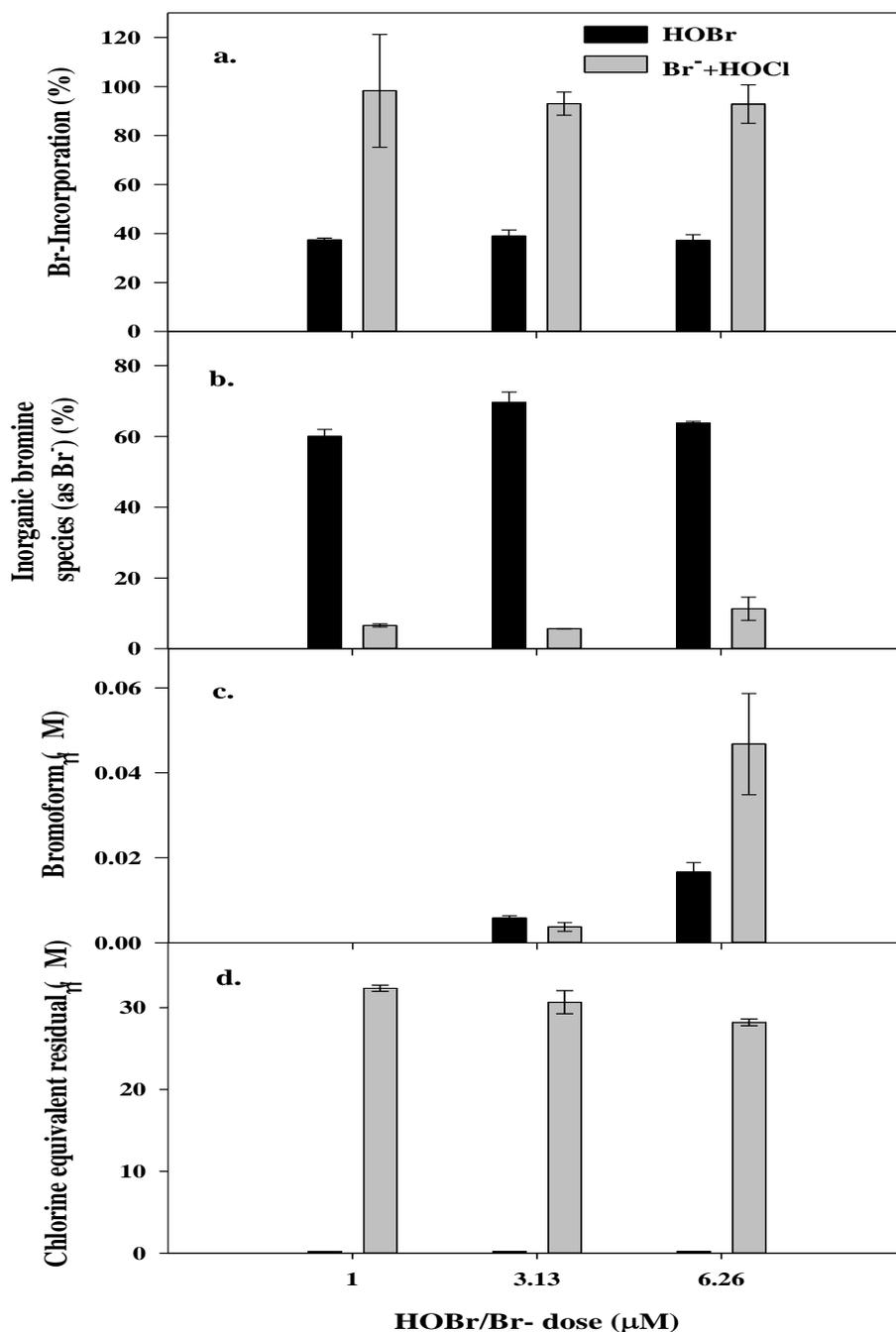


Figure 3-5: Comparison between bromination (HOBr) and chlorination (Br⁻+HOCl) in terms of AOB formation presented as % Br-Incorporation (a), the inorganic bromine species measured as bromide after quenching (b), bromoform formation (c), and chlorine equivalent residual (d) measured after 1 h experimental time for different HOBr/Br⁻ concentrations. Experimental conditions: SR-DOM (4 mgC L⁻¹); phosphate buffer (1 mM), pH = 8; for bromination: [HOBr] = 1.0 - 6.26 μM, for chlorination: [Br⁻] = 1.0 - 6.26 μM, [HOCl] = 75 μM; Na₂SO₃ solution (10 % molar excess based on chlorine equivalent residual) was used to quench the reactions.

For bromoform formation, as illustrated in Figure 3-5c, increasing bromine/bromide concentrations increased bromoform formation. At the lowest dose of HOBr or bromide ($1 \mu\text{M}$, $80 \mu\text{g L}^{-1}$), no bromoform was formed because there was not enough bromine available for triple bromination of a single reactive site. Bromoform started to form at $3.13 \mu\text{M}$ of HOBr or bromide, with 5.8 nM and 3.7 nM formed, respectively. For $6.26 \mu\text{M}$ of HOBr or bromide, the bromoform concentration was 16.6 nM and 46.8 nM , respectively. In these cases, increasing Br^-/HOBr concentrations increased the HOBr to reactive sites ratio, which increased the possibility for triple bromination of the same reactive site and therefore the formation of bromoform.

Overall, in bromination experiments around 35 to 40 % of HOBr reacted through electrophilic substitution/addition, while 60 to 65 % reacted through oxidation reactions. In chlorination experiments, the % Br-incorporation reached almost 100 %, since, after oxidation reactions, the formed bromide can be recycled (re-oxidised by HOCl to HOBr) until almost complete bromine incorporation into DOM occurs. Bromoform, which is a regulated THM, was not well-correlated to AOB_r and therefore cannot be reliably used to assess the formation of brominated organic compounds in drinking waters.

3.3.3 Effect of Water Matrix Constituents on AOC_l Formation during Chlorination experiments ($\text{Br}^- + \text{HOCl}$)

In terms of AOC_l formation, as expected, no AOC_l was formed during the bromination experiments since there was no chlorine added to the sample (Figure 3-6). In the chlorination experiments, AOC_l was formed in various concentrations depending on the types and concentrations of organic and inorganic precursors in the synthetic waters. Chlorination of synthetic waters containing different types of DOM resulted in high AOC_l formation ($>10 \mu\text{M}$) for SR- and NR-DOM (DOM with high SUVA₂₅₄ value), while PL-DOM produced only half ($5.3 \mu\text{M}$) of AOC_l formed in SR- and NR-DOM. Interestingly, high formation of AOC_l in SR- and NR-DOM reflected only 13.3 % of Cl-incorporation into DOM reactive sites of the added HOCl ($75 \mu\text{M}$) and with another 40 % of HOCl remained present in the solution (measured as chlorine equivalent residual), majority of HOCl were consumed for oxidation of either bromide to form HOBr or DOM reactive sites to release chloride.

In addition, increase SR-DOM concentrations from 1 to 8 mgC L⁻¹ enhanced AOCl formation accounted for 1 and 30 μM, respectively. However, when chlorine was spiked to synthetic waters containing different bromide concentrations, AOCl decreased from 17 to 10 μM with the increase of bromide concentrations. The low Cl-incorporation indicates that there was strong competition between HOCl and HOBr with DOM reactive sites for halogenation. The detailed explanations for this competition are presented in Chapter 4.

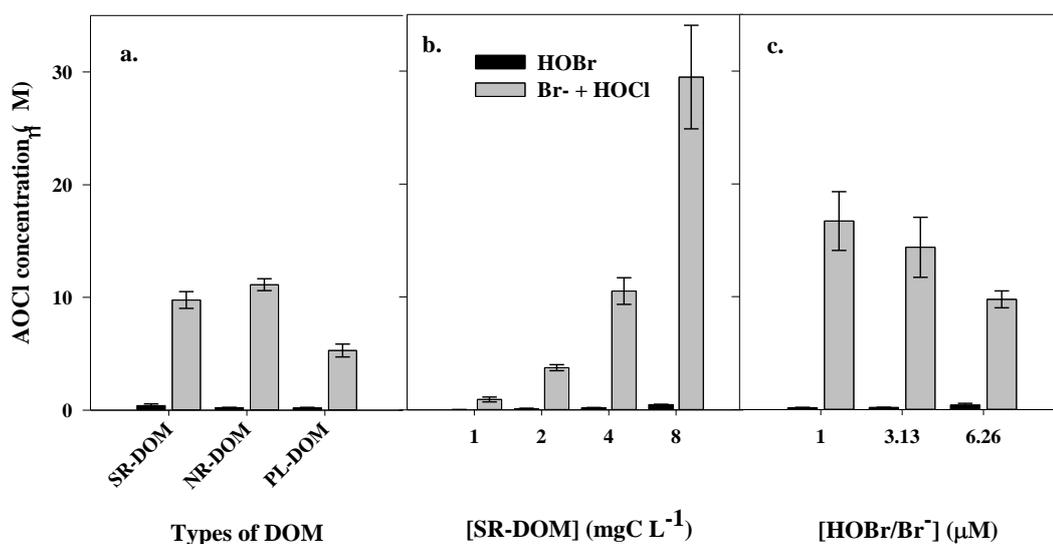


Figure 3-6: AOCl formation of bromination (HOBr) and chlorination (Br⁻+HOCl) measured after 1 h experimental time of different types of DOM, varying SR DOM doses and varying HOBr/Br⁻ concentration (a). DOM types (SR, NR, PL) (4 mgC L⁻¹), phosphate buffer pH = 8 (1 mM), for bromination: [HOBr] = 6.26 μM, for chlorination: [Br⁻] = 6.26 μM, [HOCl] = 75 μM (b). SR-DOM (1, 2, 4 and 8 mgC L⁻¹), phosphate buffer pH = 8 (1 mM), for bromination: [HOBr] = 6.26 μM, for chlorination: [Br⁻] = 6.26 μM, [HOCl] = 30, 50, 75 and 140 μM for 1, 2, 4 and 8 mgC L⁻¹ of SR-DOM respectively (c). SR-DOM (4 mgC L⁻¹), phosphate buffer pH = 8 (1 mM), for bromination: [HOBr] = 1.0, 3.13, 6.26 μM, for chlorination: [Br⁻] = 1.0, 3.13, 6.26 μM, [HOCl] = 75 μM. Na₂SO₃ (10 % molar excess based on chlorine equivalent residual) was used to quench the reactions.

3.3.4 Implications for Drinking Water Distribution Systems

In order to simulate real water treatment conditions, bromide was added to synthetic waters prior to chlorine addition. Samples were chlorinated at doses ranging from 15 μM to 90 μM (1 to 6 $\text{mgCl}_2 \text{L}^{-1}$) and sampled at two different contact times (1 h and 24 h) to mimic residence time of a real distribution system.

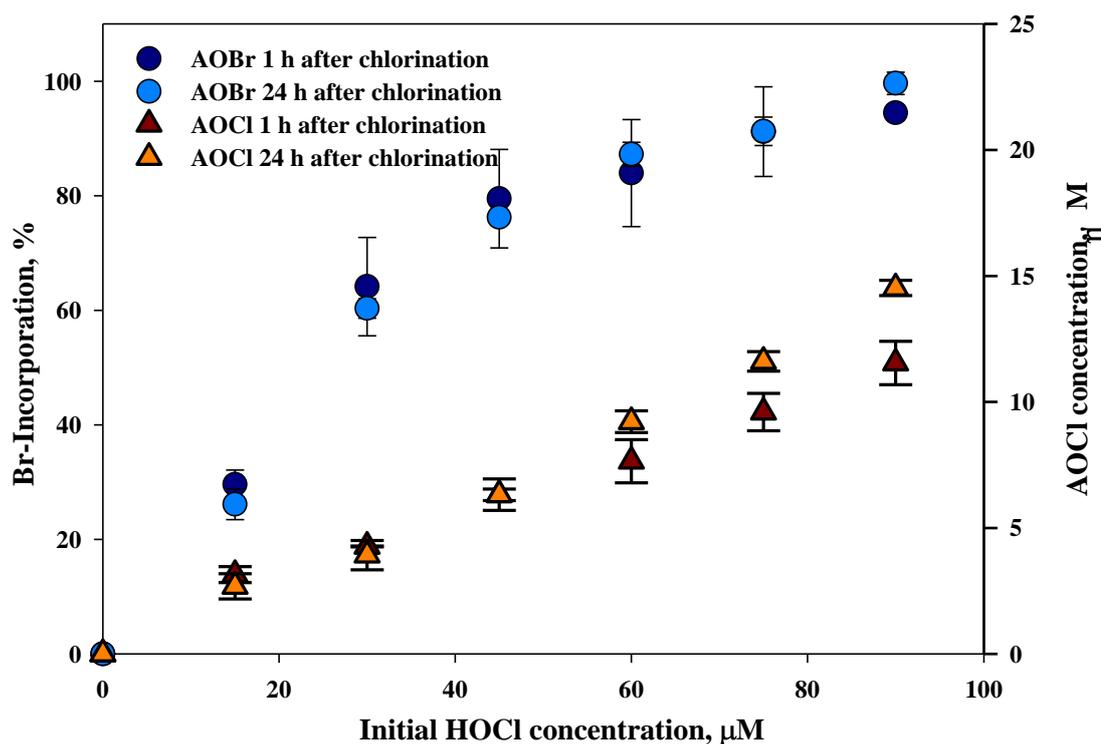


Figure 3-7: Effect of different chlorine dose on AOBromine and Active Oxygen Chlorine formation for synthetic waters containing SR-DOM and bromide. Experimental condition: SR-DOM (4 mgC L^{-1}), $[\text{Br}^-]$ ($6.26 \mu\text{M}$, $500 \mu\text{g L}^{-1}$), phosphate buffer (1 mM), $\text{pH} = 8$, $[\text{HOCl}]$ ($15, 30, 45, 60, 75, 90 \mu\text{M}$) for 1 h and 24 h, Na_2SO_3 (10 % molar excess based on chlorine equivalent residual) for quenching.

As shown in Figure 3-7, AOBromine formation was similar for the two different sampling times, while Active Oxygen Chlorine increased with increasing reaction time (1 h and 24 h) for high initial chlorine concentrations. As expected, for low chlorine concentrations ($15 \mu\text{M}$ to $45 \mu\text{M}$), where there was no/low disinfectant residual after 1 h (Figure 3-8), the Active Oxygen Chlorine concentration remained constant between 1 h and 24 h. For the highest initial

chlorine concentrations, substantial oxidant residual was measured after 1 h, and a corresponding increase in AOC_l was observed from 1 h to 24 h. For example, for an initial chlorine concentration of 90 μM , the AOC_l concentration formed increased from 11.5 μM to 14.5 μM , while the oxidant residual decreased from 33 μM (2.3 mgCl_2 equivalents L^{-1}) to 13 μM (0.9 mgCl_2 equivalents L^{-1}) for 1 h and 24 h, respectively. The increase of AOC_l formation with increasing reaction time indicates that chlorine is a slower halogenation agent than bromine for reaction with DOM reactive sites, as previously reported by (Nokes et al., 1999; Westerhoff et al., 2004). Therefore, while bromine reacted quickly with DOM reactive sites to complete the formation of AOB_r in 1 h reaction time, the reaction between chlorine and DOM reactive sites still continued and formed more AOC_l after 1 h reaction time for the high chlorine concentrations ($\geq 60 \mu\text{M}$). The formation of AOB_r increased from 1.75 μM (30 % Br-incorporation) to 5.61 μM (94 % Br-incorporation) for initial chlorine concentrations of 15 μM and 90 μM , respectively, demonstrating the role of Br-recycling in the presence of a chlorine residual in excess for the optimum formation of AOB_r. AOC_l formation also increased from 3.2 μM to 11.6 μM with increasing initial chlorine concentrations (15 μM and 90 μM , respectively) in 1 h reaction time.

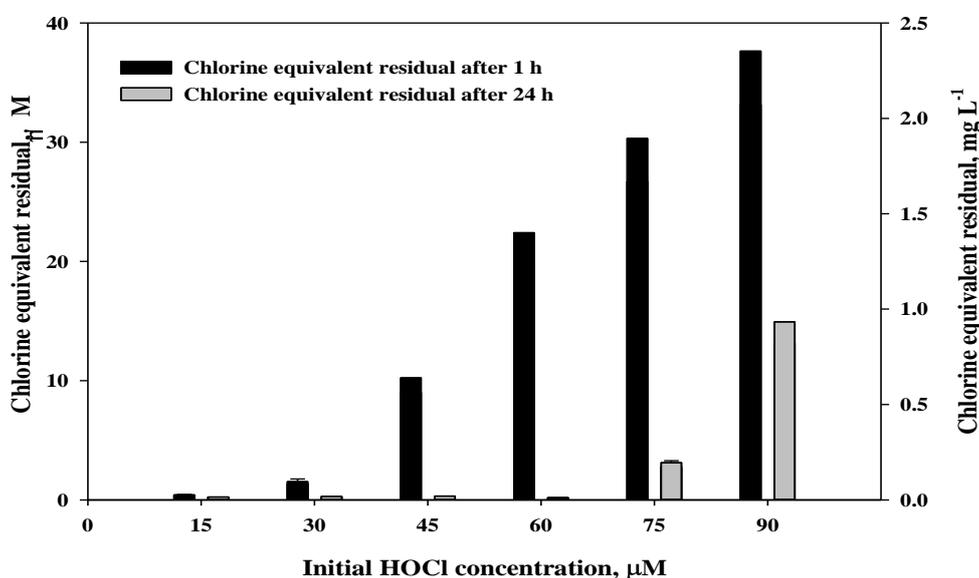


Figure 3-8: Chlorine equivalent residual measured after 1 h and 24 h experimental time. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), pH = 8, $[\text{Br}^-]$ (6.26 μM), $[\text{HOCl}]$ (15, 30, 45, 60, 75, 90 μM) for 1 h and 24 h, Na_2SO_3 solution (10% molar excess based on chlorine equivalent residual) for quenching.

As shown in Figure 3-9, following the same trend as the AOB_r formation, the concentrations of bromoform formed after 1 h and 24 h were similar. This finding again demonstrates that the reaction between HOBr and DOM reaction sites occurs very fast and bromoform, as one of the brominated DBPs, was rapidly formed, with the reaction complete in 1 h. The bromoform concentration increased continuously with increasing initial HOCl concentration, from 5 nM for 15 μM of HOCl to 51 nM for 45 μM of HOCl, and plateaued at 56 nM for the high HOCl concentrations (≥ 60 μM).

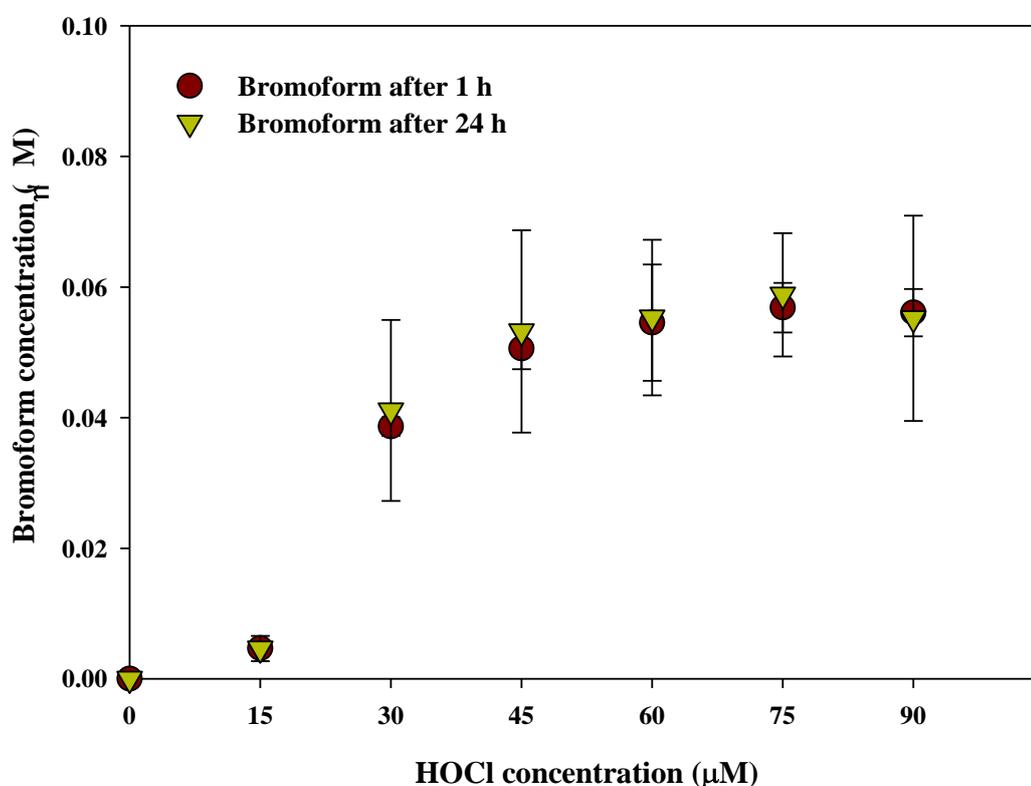


Figure 3-9: Bromoform formation measured after 1 h and 24 h experimental time. Experimental conditions: SR-DOM (4 mgC L⁻¹), phosphate buffer (1 mM), pH = 8, [Br⁻] (6.26 μM), [HOCl] (15, 30, 45, 60, 75, 90 μM) for 1 h and 24 h, Na₂SO₃ solution (10% molar excess based on chlorine equivalent residual) for quenching.

This shows that in distribution systems where a disinfectant residual (~ 1 mgCl₂ equivalents L⁻¹; 15 μM) is present over a long period of time, almost 100% of the bromide is expected to be converted to AOB_r, which is a potential health concern,

while AOCl will continuously increase during the residence time in the distribution system.

3.4. Conclusions

The good mass balance obtained for bromine in the kinetic experiments using SR-DOM and PL-DOM with HOBr and HOCl indicated that the halogen specific AOX method is a valid and robust method for the analysis of AOB_r. These experiments also allowed differentiation of the fraction of bromine reacting with DOM through electrophilic substitution and addition, leading to the formation of AOB_r, and the fraction of bromine reacting with DOM through oxidation (electron transfer), leading to the release of bromide in solution. If free chlorine was available, the reduced bromide was recycled and reoxidised to HOBr, with the opportunity to react with DOM to produce additional AOB_r, resulting in an increased formation of AOB_r.

AOB_r formation resulting from bromination (HOBr) and chlorination ($\text{Br}^- + \text{HOCl}$) experiments showed that there was a significant influence of bromide recycling on AOB_r formation. On one hand, in bromination experiments, where HOBr alone was added to the SR-DOM solution, only 40 % of HOBr was incorporated into DOM reactive sites and formed AOB_r through electrophilic substitution and addition, while the majority of HOBr was reduced to bromide (60 %) via redox (electron transfer) reactions. Since no chlorine was present in the solution, bromide could not be recycled. Therefore the dominant reaction pathway in bromination was oxidation of DOM. On the other hand, Br-incorporation in chlorination accounted for 90 % of the initial bromide concentration 1 h after chlorine contact time, while less than 10 % of the initial bromide concentration was present as bromide. The higher Br-incorporation in chlorination experiments compared to bromination experiments was due to Br-recycling, i.e. in the presence of excess chlorine, bromide formed from HOBr oxidation of DOM is reoxidised to HOBr which reacts further with DOM to produce more AOB_r (and more oxidised DOM and bromide, which can be recycled again).

The character of the DOM also affected the formation of AOB_r. AOB_r concentrations were higher from high SUVA₂₅₄ DOM (SR and NR) than low

SUVA₂₅₄ DOM (PL) during bromination and chlorination, as bromine reacted quickly with DOM containing a high proportion of aromatic structures. In addition, increasing DOM concentrations resulted in a constant increase of AOB_r in both bromination and chlorination experiments.

Bromoform formation didn't necessarily follow the same trend as AOB_r formation. For example, in the bromination experiments of different DOM types, the trend of bromoform formation was similar to AOB_r formation. However, in the chlorination experiments, where chlorine was in excess, the bromoform formation was sometimes inversely correlated with the formation of AOB_r. Therefore, the concentration of bromoform cannot be used as a surrogate for the concentration of all brominated organic compounds (AOB_r) in a disinfected water. For accurate assessment of brominated organic compounds in treated drinking waters, analysis of the regulated THMs and HAAs, as well as AOB_r analysis, should be performed.

The maximum formation of potentially harmful brominated organic compounds (AOB_r) is likely to be obtained for high chlorine concentrations during disinfection of bromide-containing water, since this situation allows constant bromide recycling and therefore almost 100 % bromine incorporation in DOM. In drinking water distribution systems where a disinfectant residual ($\sim 1 \text{ mgCl}_2 \text{ L}^{-1}$) is needed over a long period of time, high disinfectant concentrations are usually applied to ensure optimal disinfection over long distances through the distribution system. However, applying high doses of disinfectant to bromide-containing waters will quickly produce potentially harmful organic bromine (AOB_r) in high concentrations, while organic chlorine (AOCl) will also be continuously formed. Therefore, bromide removal strategies, such as reverse osmosis, are recommended for source waters containing high bromide concentrations which are disinfected with chlorine to minimise or mitigate AOB_r formation.

Chapter 4

MECHANISTIC STUDY OF THE FORMATION OF ADSORBABLE ORGANIC BROMINE IN SYNTHETIC WATERS: COMPETITION BETWEEN CHLORINE AND BROMINE FOR DOM REACTIVE SITES

4.1 INTRODUCTION

Chlorination is one of the most widely used disinfection techniques in drinking water treatment. During chlorination of drinking water containing naturally occurring bromide, the bromide is quickly oxidised to bromine. The presence of chlorine and bromine in the water induces competition for reaction with DOM and subsequent formation of chlorinated DBPs (Cl-DBPs) and brominated DBPs (Br-DBPs).

Bromine has been reported to react faster with DOM than chlorine (Heeb et al., 2014; Westerhoff et al., 2004). For example, Westerhoff et al. (2004) found that rate constants for reaction of bromine with DOM extracts were 10 times higher than the corresponding reaction with chlorine. Furthermore, in a review on bromine reactivity during water treatment, Heeb et al. (2014) specified that the species-specific rate constants of bromine with a series of phenolate compounds, representative of DOM reactive moieties, are on average 3000 times higher than with chlorine (Gallard et al., 2003; Heeb et al., 2014). Bromine affects the yield/magnitude and species distribution of halogenated DBPs (Cowman and Singer, 1995; Hua and Reckhow, 2006; Richardson, 2003; Symons et al., 1993). A more recent study showed that bromine also enhanced Cr(VI) formation during chlorination of bromide-containing waters in the presence of Cr(III) (Chebeir and Liu, 2016).

Overall, during chlorination of bromide-containing waters, brominated organic compounds are expected to be formed more readily than their chlorinated analogues and in higher yield. The formation of these compounds is of interest due to their potential health effects. Besides these negative effects, HOBr formed from the reaction of chlorine with bromide can have positive impacts on the degradation of micropollutants (Lee and von Gunten, 2009), on mitigation of the formation of iodinated DBPs by enhancing iodate formation (Allard et al., 2015; Criquet et al., 2012), and on Mn(II) oxidation rate during primary chlorination, which avoids its carry over to distribution systems (Allard et al., 2013).

The effect of bromide concentrations on the formation of halogenated DBPs in treated drinking waters has been previously reported (e.g. Hua et al., 2006; Pourmoghaddas et al., 1993). Hua et al. (2006) reported that during chlorination of

bromide-containing waters, molar yields of trihalomethanes (THMs) and haloacetic acids (HAAs) increased with increasing initial bromide concentration. Similarly, Pourmoghaddas et al. (1993) found that chlorination of bromide-containing waters resulted in an increase of brominated DBP species as it shifted the distribution of HAAs from chlorinated-AAAs to more brominated-AAAs (both di- and tri-bromoAA). A recent study revealed that when bromide is present at high concentrations in drinking waters treated with chlorine, it increases the formation of DBPs such as dichloro-4-hydroxybenzaldehydes, dichloro-4-hydroxybenzoic acids, dichlorosalicylic acids, and trichlorophenols (Pan and Zhang, 2013a). On one hand, it was found that the di- and tri-chloro species of each group, which were initially the dominant products, decreased with increasing bromide concentration. On the other hand, the di- and tri-bromo species increased rapidly at the beginning of the chlorine contact time and became the dominant products. A shift from fully chlorinated species followed by mixed chloro-bromo species and finally the predominance of brominated species indicated that the increasing bromide concentration greatly affected the speciation of DBPs (Pan and Zhang, 2013a). These findings reveal that bromide plays an important role in the formation of Cl-DBPs and Br-DBPs. Therefore, understanding the reactions between bromine and organic precursors in the presence of chlorine will be essential for controlling AOB formation.

Pre-chlorination has been implemented in conventional water treatment for different purposes. Pre-chlorination is commonly used by many water utilities to control taste and odour caused by natural (aquatic growth, i.e., algae, organic and inorganic compounds) and synthetic (industrial and domestic waste discharge) sources. It is also an effective strategy to remove iron and manganese from water and to improve coagulation or filtration efficiency (Haas, 1999; White, 1999). Unfortunately, a pre-chlorination step during drinking water treatment can also cause some negative effects. Chiu and Wang (2008), for instance, found that pre-chlorination of water samples containing algae species (*Microscystis aerugin*) increased the formation of DBP precursors and therefore increased regulated THM formation. Moreover, adding bromide to an algal suspension during chlorination resulted in a shift in DBP formation from chlorinated to brominated species (Chiu and Wang, 2008).

Recently, there has been growing interest in studying AOB_r formation. It has been reported that AOB_r formation through electrophilic substitution and addition reactions varies depending on the type of disinfectant and the characteristics of organic precursors (e.g. aromaticity content) (Criquet et al., 2015; Echigo and Minear, 2006; Song et al., 1996; Westerhoff et al., 2004; Westerhoff et al., 1998). For instance, Westerhoff et al. (1998) reported that a maximum of 10% of bromine was incorporated into DOM as AOB_r when water samples containing bromide and DOM fractions from four source waters were treated with ozone. Further study by Westerhoff's group (Westerhoff et al., 2004) revealed that pre-ozonation of water containing DOM reduced the rate of reaction of bromine with DOM, however it did not influence the substitution/addition efficiency of bromine with DOM. In another study by Song et al. (1996), Br-incorporation of 20 % was reported when aqueous bromine was added directly to DOM-containing water. A more recent study by Criquet et al. (2015) reported about 20% of Br-incorporation for all selected DOM extracts with the exception of the Pony Lake DOM extract (< 10 %). It was also reported that bromination of phenolic model compounds at pH 7 and 8 generally resulted in higher Br-incorporation (60-100%) than the corresponding experiments using the DOM extracts ((Criquet et al., 2015)). It is noteworthy that in their studies, Criquet et al. (2015) used a large excess ($\geq 50:1$) of DOM/model compound to bromine. Finally, Tan et al. (2016), who studied the behaviour of bromide through different treatment processes in a drinking water treatment plant, reported that about 70 % of the initial bromide was incorporated into DOM, forming AOB_r, after final chlorination.

4.1.1 Scope of Study

The study in this Chapter focused on investigating the extent of chlorine and bromine competition for DOM reactive sites and the impact on the formation of AOB_r. In this context, different pre-chlorination scenarios were investigated. In order to investigate if a pre-chlorination step is able to reduce the formation of AOB_r by consuming DOM reactive sites, synthetic waters containing DOM were pre-chlorinated at different concentrations followed by the addition of bromine (HOBr) or bromide (Br⁻). The effect of the pre-chlorination contact time before bromine addition on AOB_r formation was studied. The effect of bromine addition at different concentrations on pre-chlorinated DOM samples was also investigated. Finally,

another pre-chlorination approach, where DOM samples were left until full consumption of the chlorine (no chlorine residual detected) before the addition of HOBr at different concentrations, was also examined.

4.2 EXPERIMENTAL

4.2.1 Chemicals and Reagents

Inorganic salts and standards used in this study were all of analytical grade purity. Reagents used for the measurement of the residual chlorine concentration were also of analytical grade purity. Analytical grade sodium hypochlorite solution (11 %) was used to prepare chlorine dosing solutions.

High purity water, which is referred to as MilliQ (MQ) water and which is free of interfering organic and inorganic compounds, was prepared by passing distilled water through a Purelab Ultra Analytic purification system (Elga, UK). MQ water was used to prepare all aqueous solutions.

4.2.2 Dissolved Organic Matter (DOM) Sample

For this study, SR-DOM was selected since it contains a relatively high aromatic content (indicated by the $SUVA_{254} = 4.45$) that produces high AOB_r concentrations in both chlorination and bromination experiments (see Chapter 3).

Detailed information on the SR-DOM sample characteristics and the procedure for the preparation of solutions of SR-DOM are presented in Section 3.2.2.

4.2.3 Preparation of Oxidant Solutions

Detailed procedures for the preparation of oxidant (chlorine and bromine) solutions are given in Section 3.2.3.

4.2.4 Analysis of THMs

THMs in the water samples were analysed as detailed in Section 3.2.5.

4.2.5 Pre-Chlorination of Synthetic Water Experimental Procedure

Synthetic waters containing SR-DOM (4 mgC L^{-1}) were prepared in MQ water. The pH of the solution was maintained at 8.0 with 1.0 mM phosphate buffer (1 mM). The

waters were pre-chlorinated at different initial chlorine concentrations (15, 30, 45, 60, 75, and 90 μM) for 1 h followed by bromine addition to achieve a concentration of 6.26 μM . Different pre-chlorination scenarios were studied including pre-chlorination at fixed initial concentration (75 μM and 30 μM) and different contact times (5, 15, 30 and 60 min) followed by HOBr addition, pre-chlorination at fixed initial concentration (75 μM) followed by addition of HOBr at different concentrations (1.0, 3.13, and 6.26 μM), and pre-chlorination at different initial concentrations followed by addition of bromide to achieve a concentration of 6.26 μM . Immediately after the 1 h pre-chlorination time, subsamples were withdrawn for chlorine residual measurement, and analysis of THMs and AOX (subsamples were quenched with Na_2SO_3 solution in 10 % molar excess based on the chlorine equivalent residual).

4.2.6 Effect of Bromine Addition on Chlorinated Water Samples

Synthetic waters similar to those described in 4.2.4 were prepared. The waters were pre-chlorinated with HOCl (initial concentration 45 μM) for 24 h to allow a high formation of AOC1 and full consumption of chlorine. HOBr solution was then added to the chlorinated waters in different concentrations (5, 10, 20, and 50 μM). The solutions were left for 1 h after bromine addition. Subsamples were quenched with Na_2SO_3 solution (10% molar excess based on the chlorine equivalent residual) prior to analysis of THMs and AOX.

4.2.7 Bromination of Model Chlorinated Compound

A model compound, hexachlorobenzene (HCB), was selected for this study and was purchased from Sigma-Aldrich Australia (analytical grade, 98% purity). An HCB stock solution (10 mM) was prepared by dissolving the desired amount of HCB in MTBE. The stock solution was diluted in MeOH to prepare an HCB working solution of 1 mM. The working solution was then added to ultrapure water to achieve HCB concentration of 50 μM . This solution was then treated with HOBr at different concentrations (100, 500, and 1000 μM). The mixtures were left for 5 days when most of HOBr was consumed before analysis for bromoform.

4.3 RESULTS AND DISCUSSION

4.3.1 Competition between Chlorine and Bromine: Halogenation of DOM Reactive Sites

4.3.1.1 Effect of Pre-Chlorination Concentrations before HOBr Addition on AOB_r Formation

The effect of pre-chlorination concentrations on AOB_r and bromoform formation from SR-DOM is presented in Figure 4-1. Solutions of SR-DOM were pre-chlorinated at different concentrations for 1 h before HOBr addition. The reaction mixture was then left for 1 h. The pre-chlorination concentration of zero reflects the reactivity of the unaltered SR-DOM with HOBr (bromination of 4 mgC L⁻¹ SR-DOM, Figure 3-3a, black bars, Section 3.3.2.1, Chapter 3).

Increasing AOB_r concentrations were observed with increasing pre-chlorination concentrations (Figure 4-1, left axis). The % Br-incorporation increased from 40 % (2.2 μM AOB_r) for a pre-chlorination HOCl concentration of 15 μM to 100 % (5.7 μM AOB_r) for a pre-chlorination HOCl concentration of 90 μM. In accordance with the % Br-incorporation, the inorganic bromine species (measured as bromide after quenching) decreased with increasing pre-chlorination concentrations, from 54 % (3.0 μM) to 7 % (0.4 μM) for 15 and 90 μM of HOCl, respectively (Figure 4-1, left axis). Likewise, increasing pre-chlorination concentrations also continually and consistently increased bromoform formation (Figure 4-1, right axis). At the lowest HOCl concentration (15 μM), the bromoform concentration produced was 34 nM, while at the highest HOCl concentration (90 μM), it was 227 nM.

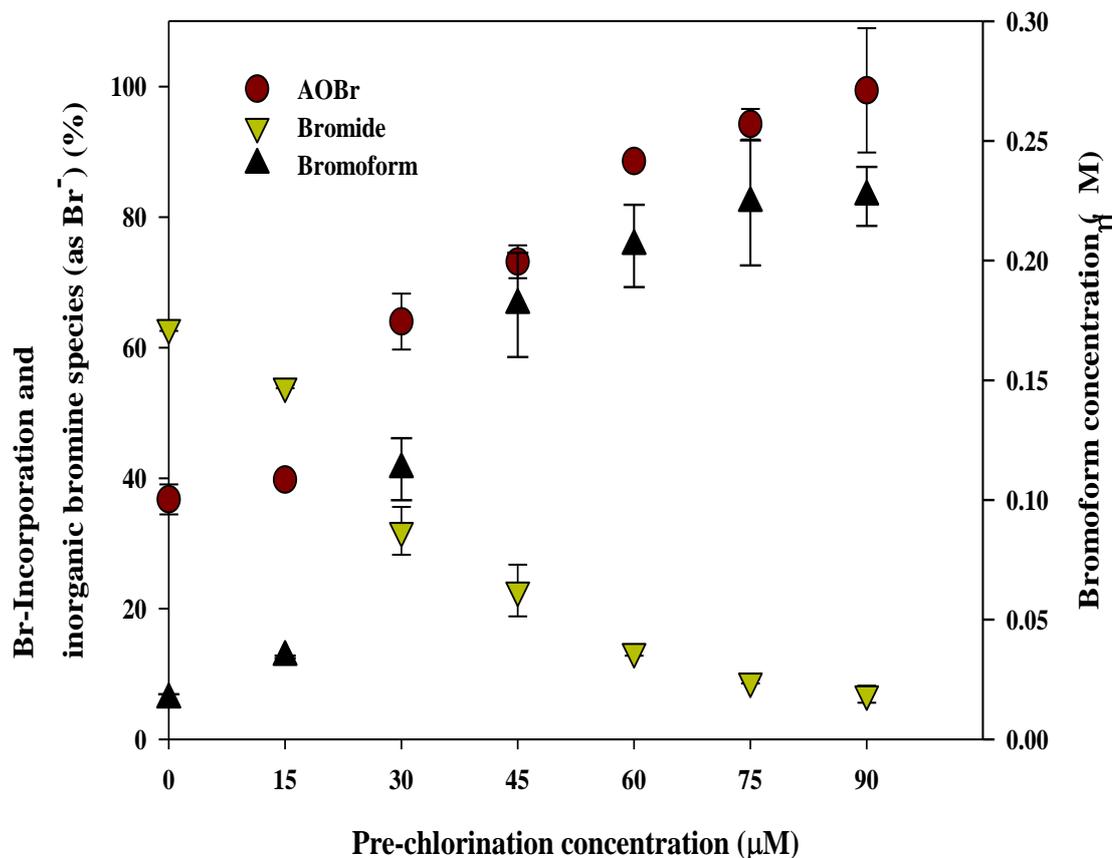


Figure 4-1: Effect of pre-chlorination concentration on AOBBr and bromoform formation. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, pre-chlorination ($15, 30, 45, 60, 75, 90 \text{ } \mu\text{M}$) for 1 h then HOBr ($6.26 \text{ } \mu\text{M}$) for 1 h, Na_2SO_3 solution (10% excess based on chlorine equivalent residual) for quenching.

The AOC1 concentrations and chlorine equivalent residual concentrations for the same set of experiments are presented in Figure 4-2. As expected, AOC1 increased with increasing HOCl concentration (Figure 4-2). For low chlorine concentrations (15 to $45 \text{ } \mu\text{M}$), AOC1 concentrations after 1 h contact time (HOCl only) and after 2 h contact time (1 h HOCl and 1 h HOCl + HOBr) were similar (Figure 4-2, left axis). A large portion of the chlorine was consumed before bromine addition (an oxidant residual concentration only started to be detected after 1 h HOBr addition for a pre-chlorination concentration of $45 \text{ } \mu\text{M}$) (Figure 4-2, right axis). Furthermore, after

HOBr addition, HOCl was utilised not only in reactions with DOM, but also in oxidation of the released bromide (from HOBr oxidation of DOM) to form additional HOBr. Therefore, no or low increases in AOC1 concentration were observed after HOBr addition. For the higher chlorine concentrations (60 to 90 μM), small increases in AOC1 concentrations were observed after bromine addition (Figure 4-2, left axis), since significant concentrations of chlorine were present after 1 h (Figure 4-2, right axis). In these cases, both HOCl and HOBr were in competition for DOM reactive sites, i.e. both AOB1 and AOC1 concentrations increased.

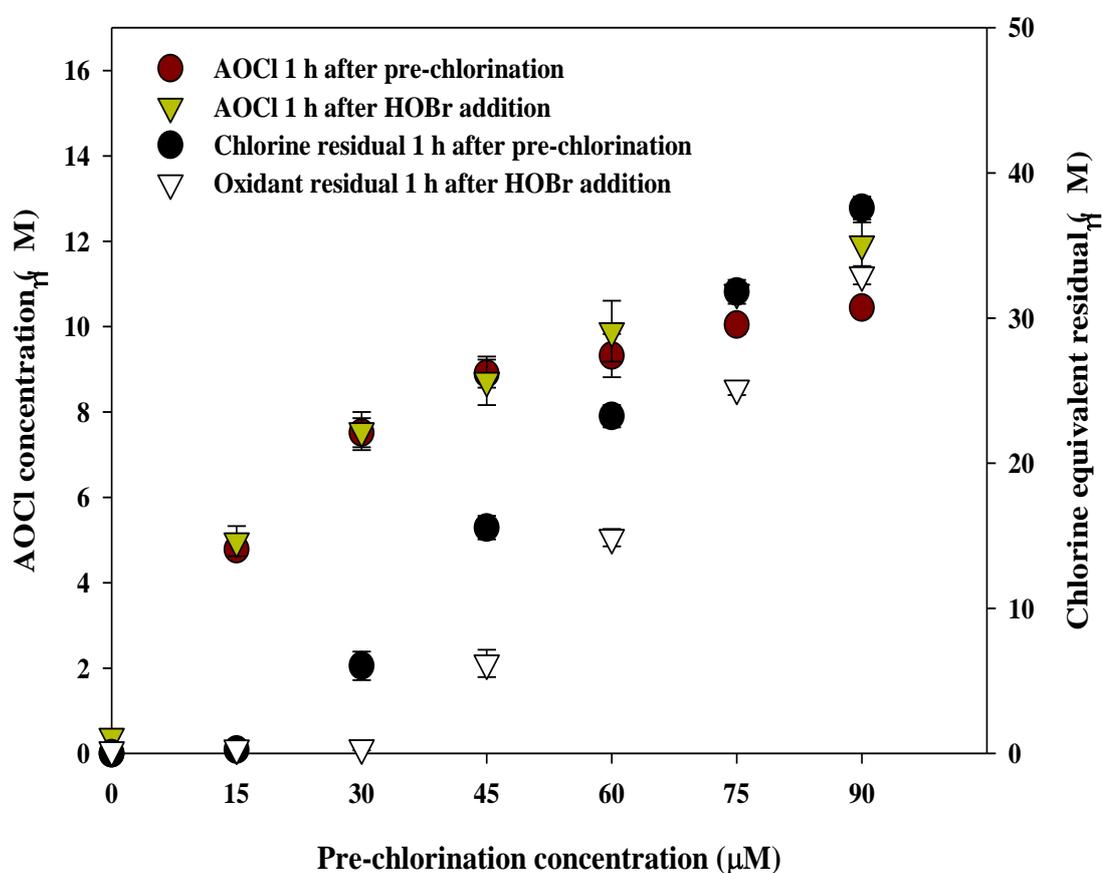


Figure 4-2: Effect of pre-chlorination concentration on AOC1 formation and chlorine equivalent residual. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, pre-chlorination ($15, 30, 45, 60, 75, 90 \mu\text{M}$) for 1 h then HOBr ($6.26 \mu\text{M}$) for 1 h, Na_2SO_3 solution (10 % excess based on chlorine equivalent residual) for quenching.

4.3.1.2 Effect of Pre-Chlorination Concentrations followed by Bromide Addition on AOB_r Formation

An additional set of experiments was carried out for which bromide was added instead of bromine (Figure 4-3). As expected, for a HOCl pre-chlorination concentration of 15 μM , where no oxidant residual was measured after 1 h (Figure 4-4, right axis), i.e. HOBr could not be formed from the addition of bromide, no AOB_r or bromoform were detected. However, as soon as a chlorine residual was measured after 1 h (for 30 μM initial HOCl concentration), allowing the formation of HOBr upon addition of bromide, AOB_r concentrations after the second hour were generally similar (Figure 4-3, left axis) to the corresponding pre-chlorination of DOM experiment with HOBr addition (Figure 4-1, left axis). A pre-chlorination concentration of 30 μM was sufficient for bromoform formation and bromoform concentrations then increased with increasing chlorine concentrations. Interestingly, when the initial HOCl concentration was 30 μM , bromoform (Figure 4-3, right axis) was produced at a lower level compared to the corresponding pre-chlorination followed by HOBr experiment (Figure 4-1). It is hypothesised that there was insufficient chlorine residual to oxidise all of the initial bromide present to HOBr, resulting in a lower concentration of bromoform being produced than when HOBr was added directly to the pre-chlorinated reaction mixture. It is also apparent that as higher initial pre-chlorination concentrations ($\geq 45 \mu\text{M}$) were used with bromide addition, significantly higher bromoform formation was observed, with the bromoform concentration appearing to reach a plateau after 75 μM , again showing the role of Br-recycling of reduced bromide in the presence of a chlorine residual. However, at high HOCl concentrations ($> 60 \mu\text{M}$), bromoform was formed in similar concentrations ($\sim 0.2 \mu\text{M}$) to the previous experiments with HOBr addition (Figure 4-1).

These experiments show that HOCl preferentially reacts with bromide over DOM reactive sites to form HOBr which leads to AOB_r formation. Under these experimental conditions, increasing the pre-chlorination concentration increased the formation of AOB_r. It was expected that a pre-chlorination step would consume part of the DOM sites which can react with HOX, thereby decreasing the number of reactive sites available for electrophilic substitution and addition with bromine,

resulting in mitigation of AOB_r. However, this effect was not observed and instead bromide was continuously recycled to HOBr in the presence of HOCl, allowing more AOB_r formation.

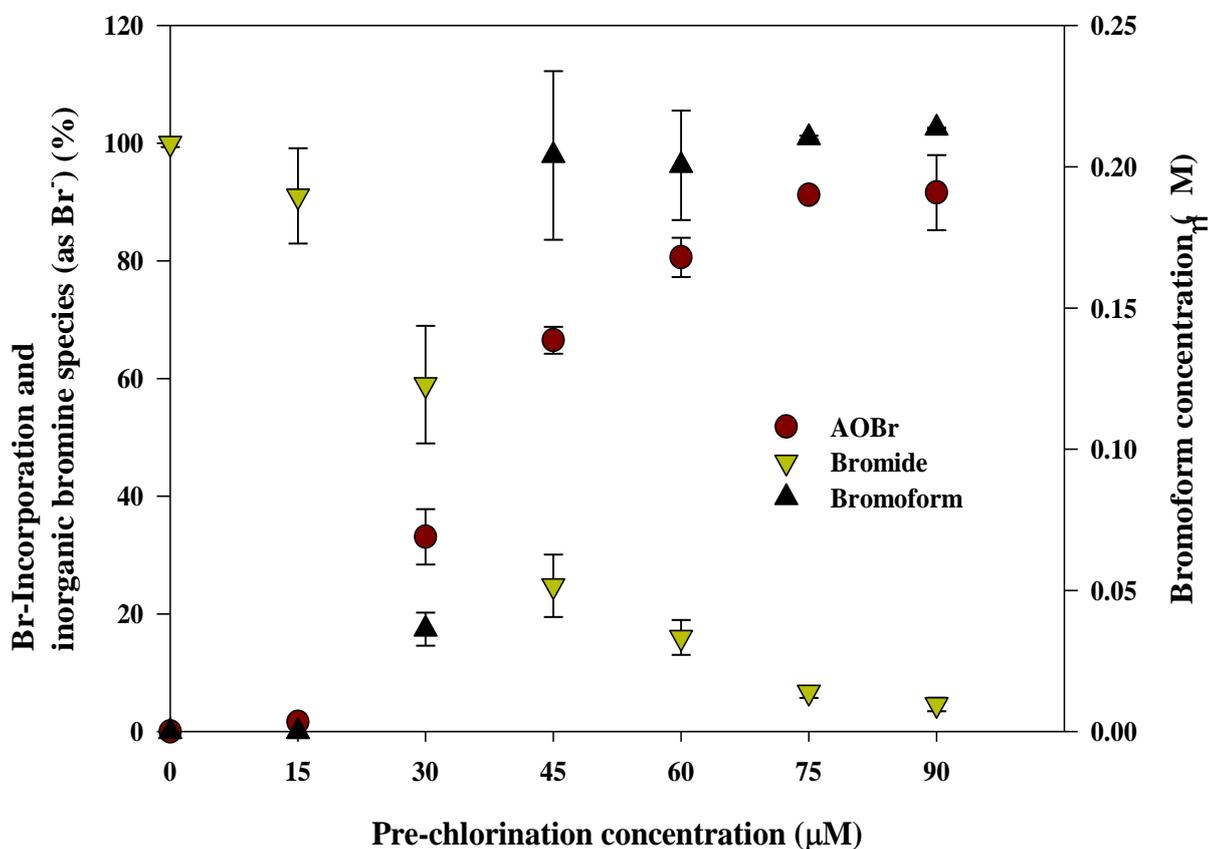


Figure 4-3: Effect of pre-chlorination concentration followed by bromide addition on AOB_r and bromoform formation. Experimental conditions: SR-DOM (4 mgC L⁻¹), phosphate buffer (1 mM), pH = 8, pre-chlorination (15, 30, 45, 60, 75, 90 μM) for 1 h then bromide (6.26 μM) for 1 h, Na₂SO₃ solution (10 % excess based on chlorine equivalent residual) for quenching.

The AOCl formation for these experiments 1 h after pre-chlorination and 1 h after subsequent bromide addition is presented in Figure 4-4 (left axis). Overall, AOCl formation 1 h after bromide addition (Figure 4.4) was similar to AOCl formation 1 h after bromine (HOBr) addition (Figure 4-2). For low chlorine concentrations ($\leq 45 \mu\text{M}$), the AOCl concentrations 1 h after pre-chlorination and 1 h after bromide addition (2 h HOCl contact time) were similar. Increasing the pre-chlorination

concentration resulted in an increase in AOC1 concentration 1 h after bromide addition: up to 14 μM for 90 μM of HOCl. In this experiment, a high chlorine equivalent residual was present (31 μM).

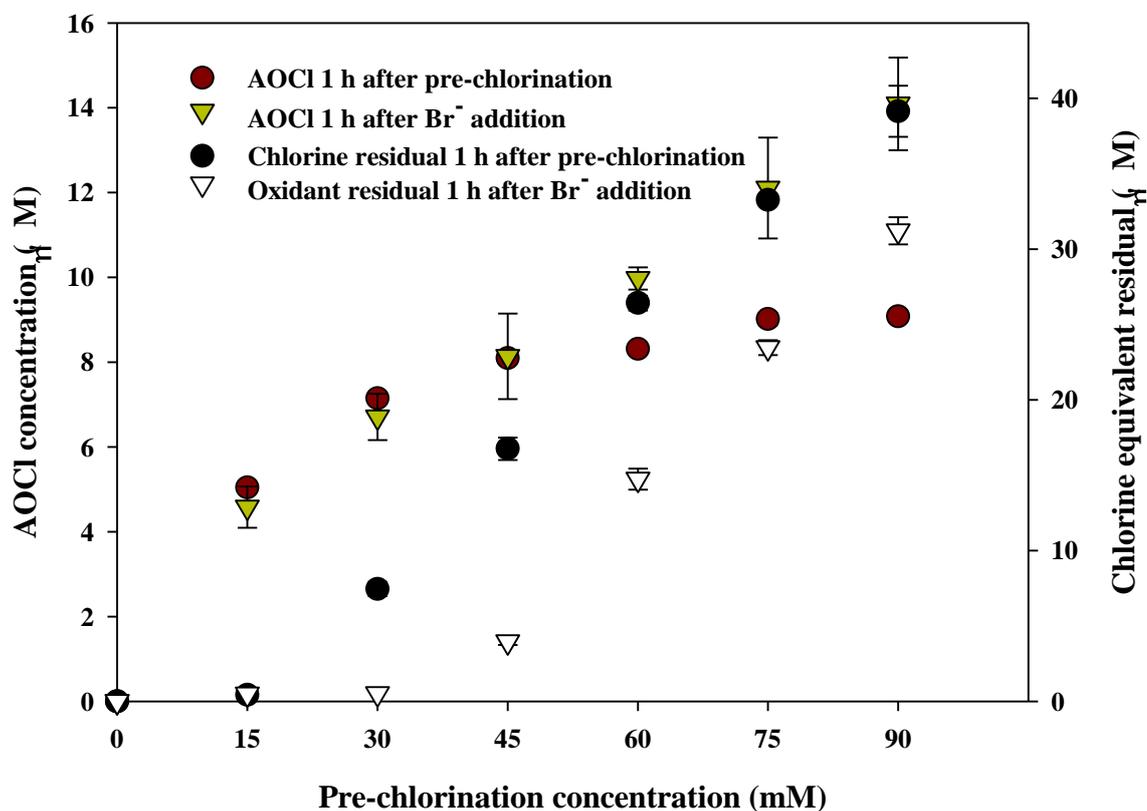


Figure 4-4: Effect of pre-chlorination concentration followed by bromide addition on AOC1 formation and chlorine equivalent residual. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), pH = 8, pre-chlorination (15, 30, 45, 60, 75, 90 μM) for 1 h then bromide (6.26 μM) for 1 h, Na_2SO_3 solution (10 % molar excess based on chlorine equivalent residual) for quenching.

4.3.1.3 Effect of Pre-Chlorination Time followed by HOBr Addition on AOB_r Formation

An experiment was conducted in which SR-DOM was pre-chlorinated with a fixed initial chlorine concentration of 75 μM ($\sim 5 \text{ mgCl}_2 \text{ L}^{-1}$) for various contact times, leading to differing (pre-)chlorine exposures, before HOBr addition (6.26 μM for 1 h). The (pre-)chlorination exposure did not affect the formation of AOB_r, with a constant very high AOB_r concentration formed (approx. 6.0 μM , 96 % Br-incorporation) for pre-chlorination times between 5 min and 60 min (Figure 4-5, left scale). The corresponding concentrations of inorganic bromine species (measured as bromide after quenching) were very low, being between 4.2 – 4.7 % of the initial bromide concentration for all pre-chlorination contact times. With increasing pre-chlorination time, more bromoform was formed (Figure 4.5 right scale). Conversely, the concentration of AOC_l increased continuously with increasing pre-chlorination time: from 6.7 μM to 10.5 μM for pre-chlorination times of 5 min and 60 min, respectively; and 1 h after HOBr addition, from 9.9 to 11.9 μM for pre-chlorination times of 5 min and 60 min, respectively (Figure 4-6, left scale), because of the high chlorine equivalent residual in all experiments (Figure 4-6, right scale).

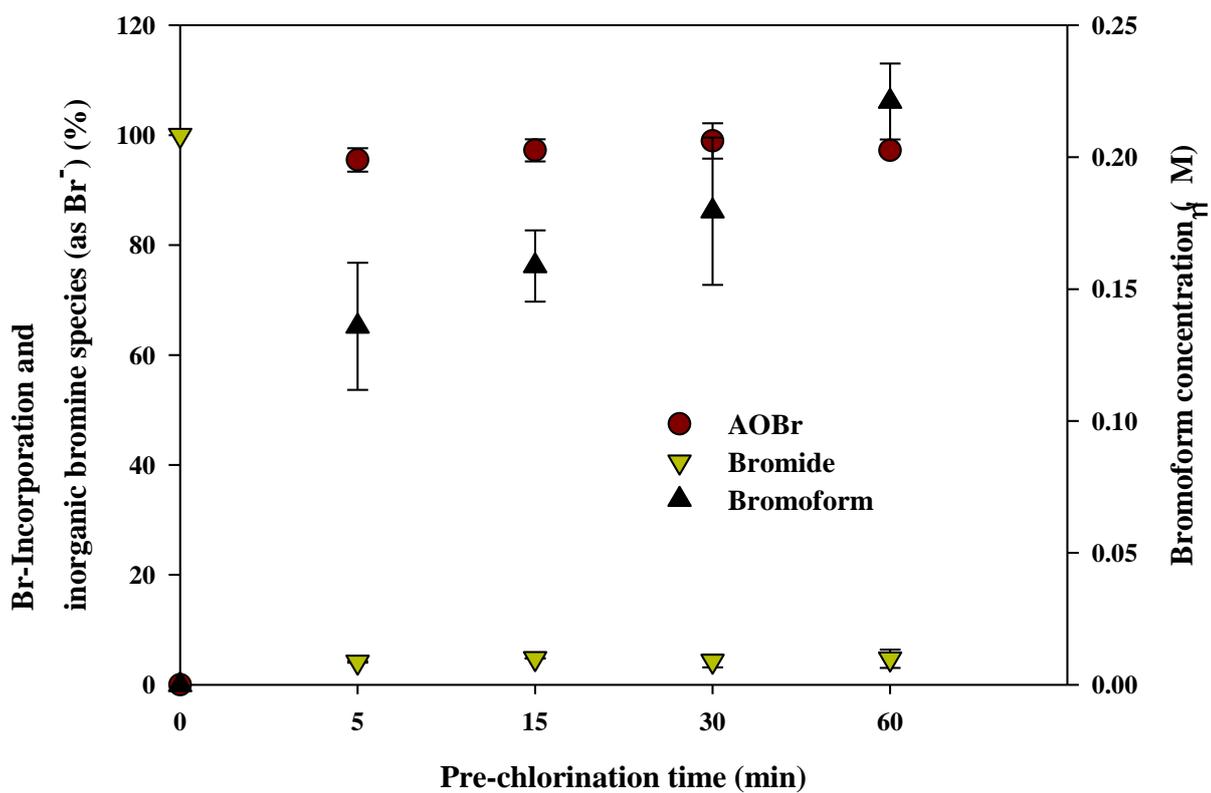


Figure 4-5: Effect of pre-chlorination time on AOBBr formation. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, pre-chlorination ($75 \text{ }\mu\text{M}$) for different times (5, 15, 30 and 60 min) then HOBr ($6.26 \text{ }\mu\text{M}$) for 1 h, Na_2SO_3 solution (10 % excess based on chlorine equivalent residual) for quenching.

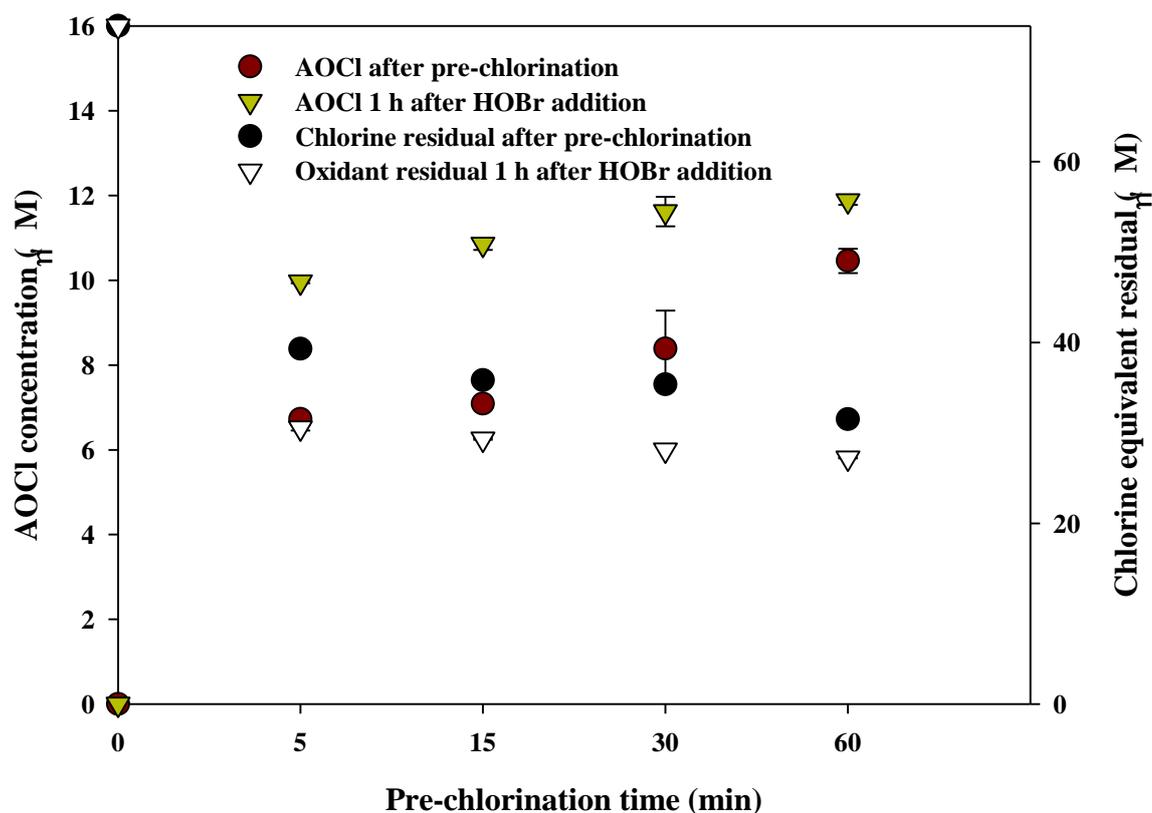


Figure 4-6: Effect of pre-chlorination time on AOCI formation. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, pre-chlorination ($75 \text{ }\mu\text{M}$) for different times (5, 15, 30, 60 min) then HOBr ($6.26 \text{ }\mu\text{M}$) for 1 h, Na_2SO_3 solution (10 % molar excess based on chlorine equivalent residual) for quenching.

The effect of differing pre-chlorination times with a lower initial HOCl concentration of $30 \text{ }\mu\text{M}$ ($\sim 2 \text{ mgCl}_2 \text{ L}^{-1}$) on AOB_r and bromoform formation is presented in Figure 4-7. It is evident that only about 60 % of the bromide was incorporated in DOM as AOB_r after all pre-chlorination times. In fact, a slight decrease of AOB_r formation from 3.70 to $3.35 \text{ }\mu\text{M}$ for pre-chlorination times of 5 min and 60 min was also observed. The inorganic bromine species measured as bromide were relatively constant at 37 % for the short pre-chlorination times ($\leq 30 \text{ min}$) but slightly higher (46 %) at the highest pre-chlorination time. Bromoform formation was found to increase consistently from $0.09 \text{ }\mu\text{M}$ to $0.15 \text{ }\mu\text{M}$ for 5 min and 30 min pre-chlorination times, respectively, but was slightly lower ($0.12 \text{ }\mu\text{M}$) for the highest pre-

chlorination time (60 min). However, even though the concentration of AOCl increased 1 h after HOBr addition under conditions of low pre-chlorination contact times (0 to 30 min) (Figure 4-8), for the highest contact time of 60 min, an opposite trend was observed. After 60 min pre-chlorination contact time, an AOCl concentration of 9.1 μM was measured, but, 60 min after HOBr addition, the AOCl concentration had decreased to 6.4 μM (Figure 4-8). In this experiment, the total oxidant concentration (HOCl + HOBr) was consumed within the 120 min (60 min pre-chlorination + 60 min after HOBr addition) reaction time (Figure 4.8). This suggests that, as expected, HOBr reacts with reactive DOM sites to form AOB_r. AOB_r concentrations may have decrease very slightly with increasing pre-chlorination times from 3.7 μM for 5 min to 3.4 μM for 60 min of pre-chlorination time (Figure 4-7), however this decrease is likely to be within experimental error. The outcome of these experiments of the decrease in AOCl formation, with minimal change to AOB_r formation, when the pre-chlorination time was increased is of interest.

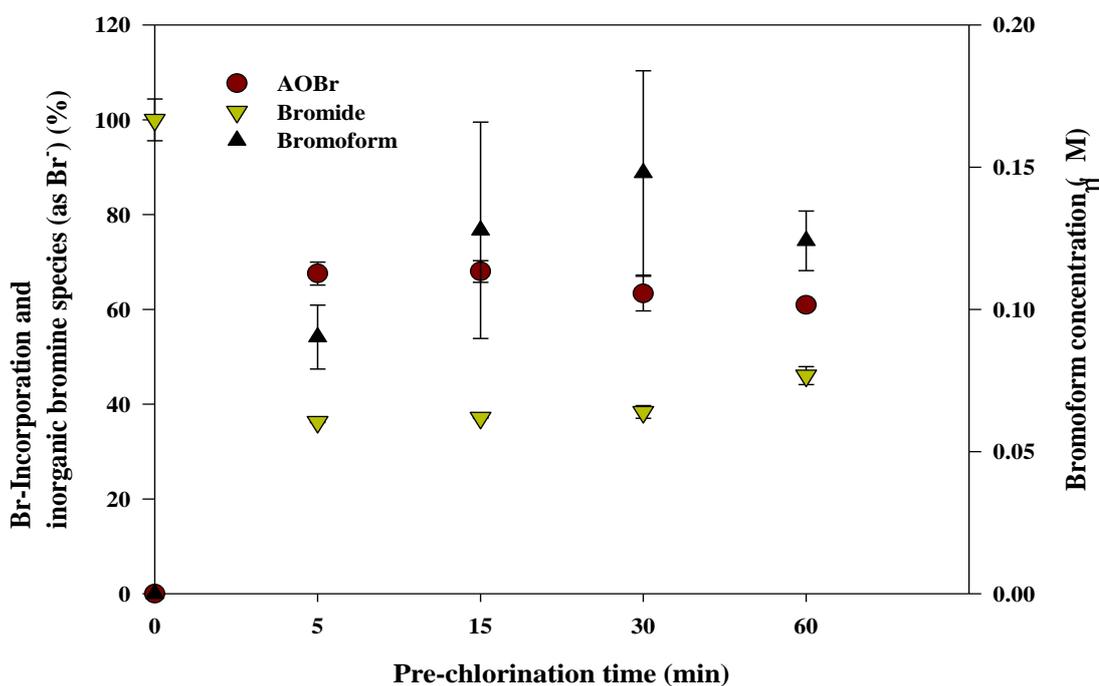


Figure 4-7: Effect of pre-chlorination time (low fixed initial chlorine concentration) on AOB_r formation. Experimental conditions: SR-DOM (4 mgC L⁻¹), phosphate buffer (1 mM), pH = 8, pre-chlorination (30 μM) for different times (15, 15, 30 and 60 min) then HOBr (6.26 μM) for 1 h, Na₂SO₃ solution (10 % molar excess based on chlorine equivalent residual) for quenching.

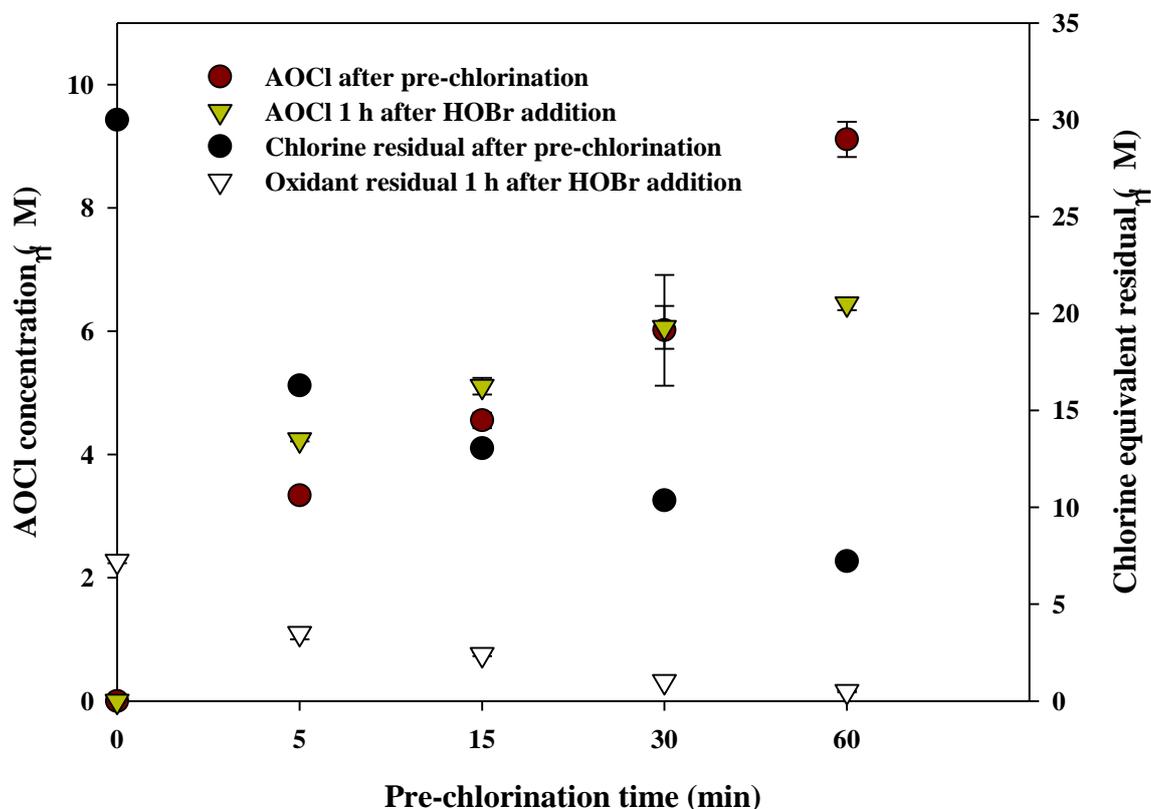


Figure 4-8: Effect of pre-chlorination time (low fixed initial chlorine concentration) on AOCI formation. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, pre-chlorination ($30 \mu\text{M}$) for different times (15, 15, 30 and 60 min) then HOBr ($6.26 \mu\text{M}$) for 1 h, Na_2SO_3 solution (10 % excess based on chlorine equivalent residual) for quenching.

Prechlorination of SR-DOM extracts with high ($75 \mu\text{M}$, Figure 4-5) and low ($30 \mu\text{M}$, Figure 4-7) chlorine concentrations at different chlorine contact times followed by addition of HOBr provides valuable information about the behaviour of HOBr when in contact with chlorinated waters. It was found that SR-DOM samples pre-chlorinated at high chlorine concentration at various reaction times followed by HOBr addition resulted in a constant maximum AOB_r formation (96 % Br-incorporation). At low chlorine concentration, however, AOB_r formation was observed to be lower after 5 min (68 % Br-incorporation) and found to slightly decrease to 61 % Br-incorporation after 60 min of pre-chlorination time. Bromoform,

in addition, was found to consistently and continually increase with increasing pre-chlorination time to achieve a maximum value of 0.22 μM from SR-DOM samples at high chlorine concentration, while in SR-DOM samples pre-chlorinated at low chlorine concentration, bromoform appeared to continually increase at short pre-chlorination times only, before decreasing to a level of 0.12 μM at 1 h pre-chlorination time.

The comparison between AOCl formed after pre-chlorination for different contact times and 1 h after HOBr addition from SR-DOM pre-chlorinated at high chlorine concentration (Figure 4.6) and low chlorine concentration (Figure 4.8) is also of interest as it provides important insights into the interaction between chlorine, bromine and chlorinated waters. It is evident that AOCl concentrations continuously increased with increasing pre-chlorination times for both samples (after pre-chlorination and 1 h after HOBr addition) in pre-chlorination experiments at high chlorine concentration. Similarly, AOCl measured after pre-chlorination at low chlorine concentration showed the same trend as AOCl formed after pre-chlorination at high chlorine concentration. However, it is important to note that the AOCl concentration formed 1 h after HOBr addition was higher than the AOCl formed after pre-chlorination in chlorinated SR-DOM samples at high chlorine concentration, while this increase was not observed in the low chlorine concentration experiments. In fact, AOCl measured 1 h after HOBr addition was found to be slightly higher in concentration than AOCl formed after pre-chlorination at short pre-chlorination times only (5 and 15 min); however, at the highest pre-chlorination time (60 min), the AOCl concentration measured 1 h after HOBr addition was lower than the AOCl concentration measured after pre-chlorination. The presence of a high chlorine equivalent residual (Figure 4.7, right axis) was responsible for the higher AOCl concentration for 1 h after HOBr addition than for AOCl formed after pre-chlorination, as well as for longer oxidant contact times (up to 2 h from 1 h pre-chlorination + 1 h after HOBr addition). In contrast, the chlorine equivalent residual 1 h after HOBr addition in the low chlorine concentration experiments was very low ($< 1.0 \mu\text{M}$ ($\sim 0.7 \text{ mg Cl}_2 \text{ L}^{-1}$)) (Figure 4.8, right scale)) for long pre-chlorination times ($> 30 \text{ min}$), leading to the decrease in AOCl after 2 h oxidant contact time.

4.3.1.4 Effect of HOBr Concentration on AOB_r and AOCl Formation from Pre-Chlorinated DOM.

In order to better understand the mechanism of AOB_r formation along with the AOCl formation, a set of experiments where DOM was pre-chlorinated with a fixed initial chlorine concentration followed by addition of HOBr to achieve different concentrations was conducted. As shown in Figure 4-9 (left scale), for SR-DOM pre-chlorinated at high concentration (75 μM, ~5 mgCl₂ L⁻¹), approximately 100 % Br-incorporation was obtained for the 3 HOBr concentrations studied (1.0, 3.13, and 6.26 μM). The near complete Br-incorporation for the highest HOBr concentration and the minimal amount of inorganic bromine species remaining are consistent with the outcomes of earlier identical experiments presented in Figures 4-1 and 4-5. Near complete Br-incorporation for the two lower HOBr concentrations was then expected based on the higher proportion of DOM reactive sites to HOBr. In terms of bromoform formation, at the lowest HOBr concentration (1.0 μM), no bromoform was observed (Figure 4-9, right scale). This is likely to be because there was insufficient HOBr to achieve triple bromination at the bromoform precursor sites. Some bromoform (0.05 μM) was formed when the HOBr concentration used was 3.13 M and the maximum concentration (0.24 μM) of bromoform was measured when the highest HOBr concentration (6.26 μM) was used, consistent with the higher availability of HOBr to react with DOM and achieve triple bromination of some reactive sites.

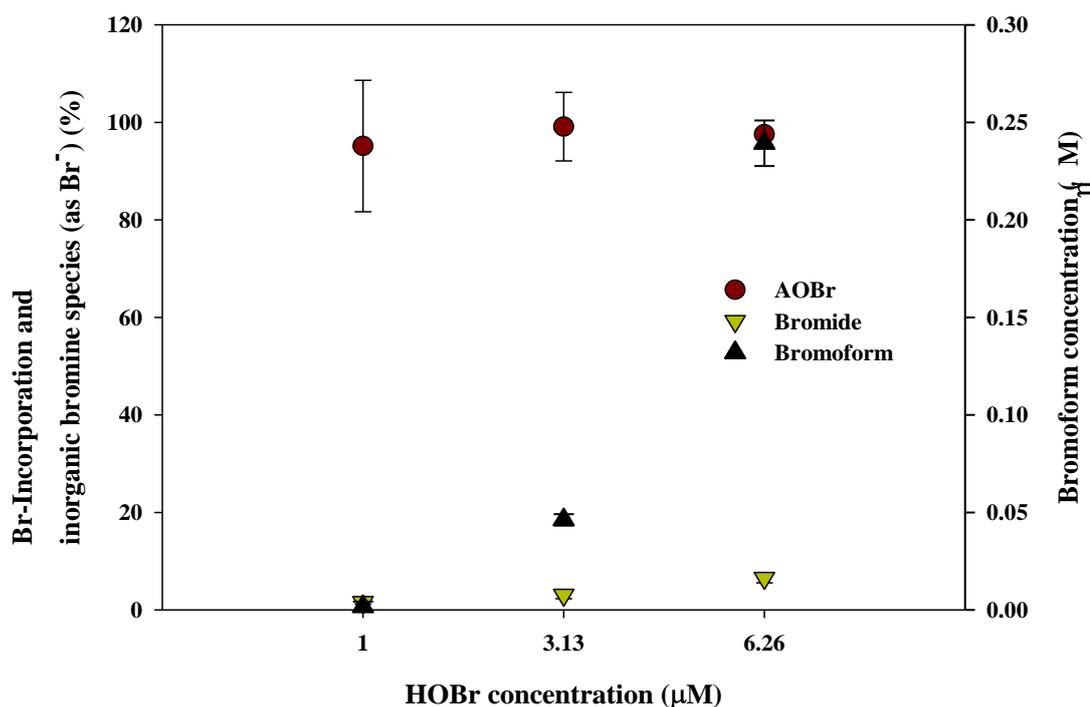


Figure 4-9: Effect of pre-chlorination (fixed initial chlorine concentration, 75 μM) followed by HOBr at different concentrations on AOBBr and bromoform formation. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), pH = 8, pre-chlorination (75 μM) for 1 h then HOBr (1.0 – 6.26 μM) for 1 h, Na_2SO_3 solution (10 % excess based on chlorine equivalent residual) for quenching.

AOCl formation (Figure 4-10, left scale) shows a different trend compared to AOBBr formation. AOCl produced after 1 h pre-chlorination time was 10 μM . For the lowest concentration of HOBr added, after 1 h subsequent exposure to HOBr, the AOCl concentration increased to 13.1 μM . But as higher HOBr concentrations were added, less additional AOCl was formed. For example, when the highest HOBr concentration (6.26 μM) was used, the AOCl concentration increased from 10 μM to only 10.8 μM . Again, these reaction systems exhibited the interesting result of decreasing concentrations of AOCl formed, when higher concentrations of HOBr were used.

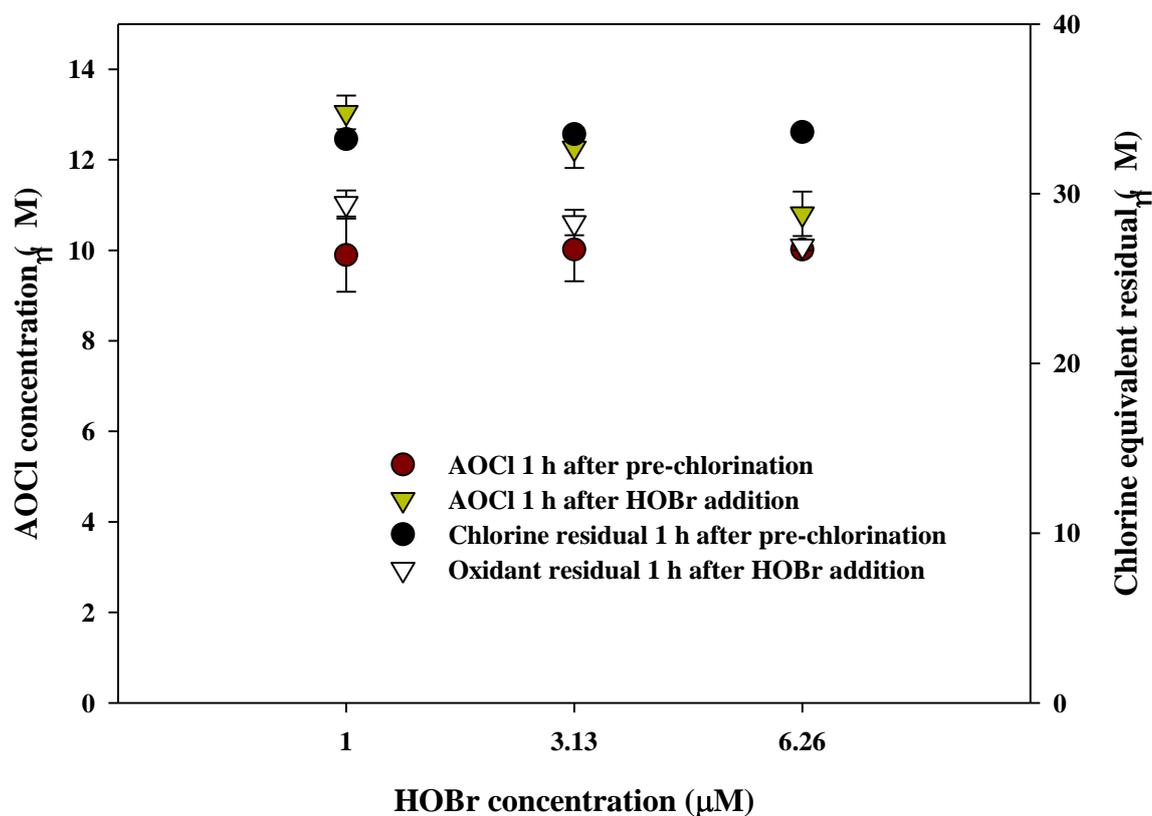


Figure 4-10: Effect of pre-chlorination (fixed initial chlorine concentration, 75 μM) followed by HOBr at different concentrations on AOCI formation. Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), $\text{pH} = 8$, pre-chlorination (75 μM) for 1 h then HOBr (1.0 – 6.26 μM) for 1 h, Na_2SO_3 solution (10 % excess based on chlorine equivalent residual) for quenching.

4.3.2 Absence of Competition between Chlorine and Bromine: Effect of HOBr Concentration after Consumption of HOCl during Pre-Chlorination on AOB_r and AOCI Formation

To further investigate the decreasing concentrations of AOCI formed when higher concentrations of HOBr were added in the experiments in Sections 4.3.1.3 and 4.3.1.4, a related set of experiments were undertaken. SR-DOM samples (4 mgC L^{-1}) were pre-chlorinated (initial HOCl concentration: 45 μM) until full consumption of the oxidant to avoid competition between HOCl and HOBr for DOM reactive sites. Thereafter, different concentrations of HOBr (5 to 50 μM) were added to the samples for 1 h.

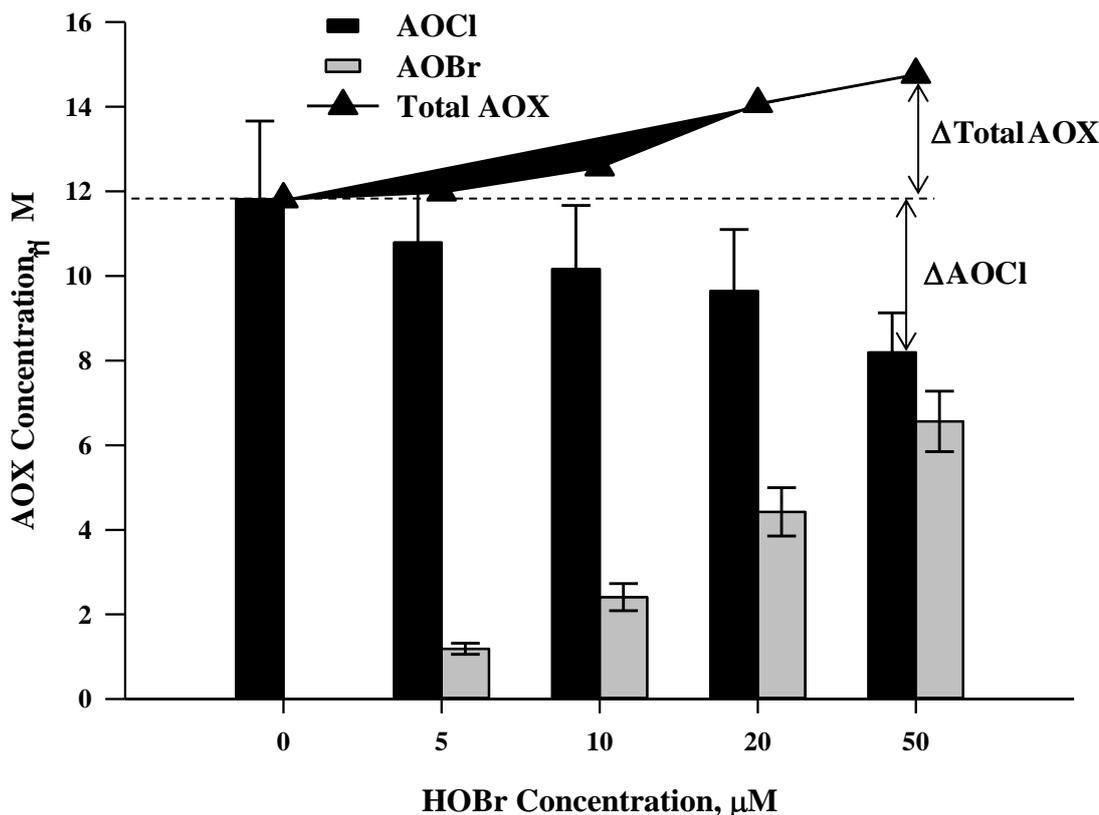


Figure 4-11: Effect of HOBr concentration after consumption of HOCl during Pre-Chlorination on AOX Formation. Experimental conditions: SR-DOM (4 mgC L⁻¹), phosphate buffer (1 mM), pH = 8, pre-chlorination (45 μM) for 24 h then HOBr (5 – 50 μM) for 1 h, Na₂SO₃ solution (10 % excess based on chlorine equivalent residual) for quenching.

As illustrated in Figure 4-11, the AOBr concentration increased from 1 μM to 7 μM, for bromine concentrations ranging from 5 to 50 μM. AOCl gradually decreased from 12 μM (without addition of HOBr) to 8 μM for a HOBr concentration of 50 μM. Furthermore, an increase of total AOX (sum of AOCl and AOBr) with increasing concentrations of bromine was observed (Δ Total AOX), indicating that a portion of bromine reacts with DOM reactive sites via electrophilic substitution and addition. AOCl again decreased (~ 33% AOCl reduction, Δ AOCl in Figure 4-11), while the AOBr increased, when the HOBr concentration increased. Two reaction pathways were proposed to account for these results. The first option was that HOBr not only reacted with DOM in substitution/addition reactions to form AOBr, but also oxidised DOM, including DOM already in the form of AOCl, where the Cl

substituent was removed in the oxidation process. Zhao et al. (2012) reported the formation of 2,6-dichlorobenzoquinone (identified by liquid chromatography-tandem mass spectrometry (LC-MS-MS)) from reaction of HOCl with phenol, proposing a reaction pathway through 2,4,6-trichlorophenol, where HOCl converts the 4-chlorophenol moiety to the benzoquinone moiety, i.e. removal of a chlorine substituent during an oxidation process. The second hypothesis was that HOBr not only oxidised DOM, but also reacted with DOM in substitution/addition reactions to form AOB_r, including DOM already in the form of AOCl, where a bromine substituent replaced a chlorine substituent. It is also possible that both hypothesised pathways operate in the reaction mixture. A model compound experiment was conducted to provide evidence for the second hypothesis.

4.3.3 Evidence of Chlorine Replacement by Bromine in DOM

An experiment was carried out with a model compound in an attempt to further support the second hypothesis. For this purpose, hexachlorobenzene (HCB) was selected as the model compound. HCB was a perfect candidate for this test because its aromatic ring is fully substituted by chlorine without any polar functional groups (i.e. hydroxyl) that may react with HOBr to form oxidation products. As HCB is not soluble in methanol, MTBE was used as the solvent before further dilution in methanol. Aliquots of HOBr solution (1 mM) were added to solutions containing 50 µM of HCB to achieve initial HOBr concentrations of 250 to 1000 µM (each of volume 25 mL). Corresponding control (blank) experiments were also conducted by adding the same volume of MTBE and methanol into purified water without the addition of HCB, followed by addition of HOBr. The concentrations of the THMs were measured after 120 h, but the scale of these experiments was low due to insufficient HCB available and it was not possible to measure AOX during these experiments.

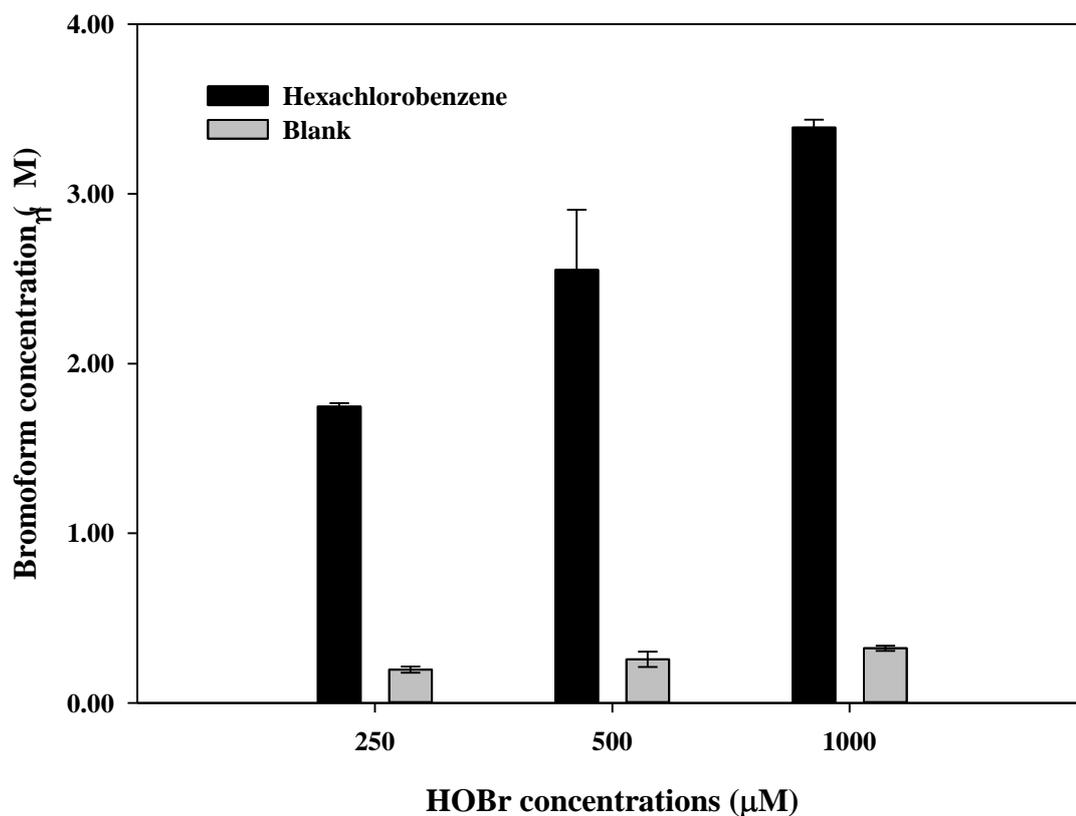


Figure 4-12: Bromoform produced from the reaction between hexachlorobenzene (HCB) and HOBr. Experimental conditions: HCB 50 μM , HOBr (250, 500, 1000 μM) for 120 h (no oxidant residual remaining). Samples extracted with MTBE (1:1), shaken for 5 min, MTBE layer passed through MgSO_4 filter into GC vial, internal standard (1,2-dibromopropane, 50 $\text{ng } \mu\text{L}^{-1}$, 50 μL) added into final MTBE extract (1mL). Blank: methanol + HOBr (250, 500, 1000 μM) for 120h (no oxidant residual remaining).

Bromoform was the only THM found in the samples. As shown in Figure 4-12, bromoform was formed in both the HCB samples and blank (methanol) samples. However, the bromoform concentration from the blank (methanol) was relatively constant (0.3 μM) for the different HOBr concentrations and represents about 10 % of the total bromoform measured in the HCB samples (3.4 μM). The bromoform formation from the HCB samples continually and consistently increased (1.8 μM to 3.4 μM) with increasing HOBr concentration. Although these experiments were

carried out with high concentrations of reactants and the yield of CHBr_3 formation was low, these experiments provide evidence that chlorine replacement by bromine is possible, even though the mechanism of bromoform formation from HCB is still unclear.

4.4. Conclusions

A pre-chlorination step did not reduce the formation of AOBr by consuming DOM reactive sites before bromine addition. Pre-chlorination of DOM reactive sites at different HOCl concentrations followed by the addition of bromine/bromide rather resulted in an enhancement of AOBr and bromoform formation. AOCl formation increased with increasing HOCl concentrations during these experiments. In terms of the water industry, the finding that pre-chlorination, with high chlorine concentrations, of water containing bromide could lead to increased formation of brominated DBPs is of significance. The use of a coagulation/filtration process after pre-chlorination is therefore very important to remove both the formed AOBr and DOM, the latter to reduce the formation of AOBr upon disinfection. Similar AOBr concentrations were detected when bromide was added instead of bromine, as long as a chlorine residual remained after the 1 h pre-chlorination step. When a chlorine residual remained 1 h after pre-chlorination (HOCl concentrations $\geq 30 \mu\text{M}$), the chlorine oxidised the bromide to HOBr which reacted with DOM reactive sites to form AOBr. These experiments also revealed that use of HOBr or bromide in the reaction with HOCl does not affect the formation of AOBr.

Variation of the pre-chlorination contact time with a high fixed initial chlorine concentration ($75 \mu\text{M}$) before bromine addition did not influence AOBr formation. The full conversion of bromine to AOBr for pre-chlorination times between 5 min and 60 min (chlorine residual concentration $\geq 32 \mu\text{M}$) indicated that the (pre-)chlorination exposure time did not affect AOBr formation. In contrast, AOCl concentrations continuously increased with increasing pre-chlorination times and 1 h after bromine addition, due to the presence of the high chlorine residual in all experiments. A slightly different trend for AOBr formation was observed for a similar experiment with a lower chlorine concentration ($30 \mu\text{M}$). For short pre-chlorination times (≤ 15 min), a constant AOBr concentration was measured after 1 h

of bromine addition. For the highest pre-chlorination time of 60 min, 1 h after bromine addition, the AOB_r concentration appeared to be slightly lower than for a pre-chlorination time of 30 min, however this variation may be within experimental error, while the AOCl concentration was 30% lower than for a pre-chlorination time of 60 min.

Pre-chlorination of DOM reactive sites at a high-fixed HOCl concentration (75 μM) for 1 h followed by the addition of bromine to achieve different concentrations resulted in almost 100% Br-incorporation as AOB_r for the three bromine concentrations tested. The final AOCl concentration, in contrast, decreased with increasing HOBr concentration. The decrease in AOCl concentration with increasing HOBr concentration was also observed in pre-chlorination experiments for which DOM reactive sites were pre-chlorinated until full consumption of the oxidant before the addition of HOBr to achieve different concentrations. Two reaction pathways were proposed to explain the phenomenon of AOCl decreasing in parallel with increasing HOBr concentrations. The first pathway was that HOBr not only reacted with DOM in substitution/addition reactions to form AOB_r, but also oxidised chlorinated DOM intermediates (AOCl), where the Cl substituent was removed in the oxidation process. The second pathway was that HOBr not only oxidised DOM, but also reacted with DOM in substitution/addition reactions to form AOB_r, including DOM already in the form AOCl, where a bromine substituent replaced a chlorine substituent. It was also proposed that both hypothesised pathways may operate in the reaction mixture. A model compound experiment with HCB, where the formation of bromoform was observed, provided some evidence for the second pathway. The second pathway was utilised for the empirical modelling undertaken in Chapter 5 to study and define the various pathways leading to AOB_r formation in order to model the experimental outcomes.

Overall, pre-chlorination of DOM did not lead to a reduction in AOB_r formation by consumption of DOM reactive sites. Instead, if a chlorine residual remained after pre-chlorination, higher AOB_r formation occurred than if no residual remained, due to the effect of bromide recycling, where HOCl is available to re-oxidise bromide, formed from the HOBr oxidation of DOM, to HOBr for further reaction (oxidation and substitution/addition) with DOM. The apparent replacement of chlorinated

organic compounds by brominated organic compounds constitutes another pathway that has to be taken into account to fully understand the formation of AOB_r.

Chapter 5

ADSORBABLE ORGANIC BROMINE FORMATION IN SYNTHETIC WATERS: VALIDATION BASED ON KINETIC MODEL CALCULATIONS

5.1 INTRODUCTION

There are more than 600 disinfection by-products (DBPs) which have been reported to be identified in drinking waters (Richardson and Postigo, 2015). However, the mechanisms of formation and degradation of these DBPs are largely unknown and only a few have been thoroughly studied. The recent development of new analytical instrumentation and methods have allowed the characterisation and quantification of various DBPs formed in treated waters (Allard et al., 2012; Cho et al., 2003; Domino et al., 2004; Eaton et al., 2005; Kristiana et al., 2012; Pan and Zhang, 2013b; Peters et al., 1990; Salhi and Von Gunten, 1999). Based on the knowledge acquired by using these analytical methods, statistical or kinetic models have been created to predict and simulate the yield of formation and speciation of halogenated DBPs under a variety of conditions (Chowdhury et al., 2009; Clark et al., 2001; Duirk and Valentine, 2006; Fabbicino and Korshin, 2009; Nokes et al., 1999; Roccaro et al., 2015; Sadiq and Rodriguez, 2004).

To date, more than 100 models used to study and predict halogenated DBP formation have been reported (Chowdhury et al., 2009). The use of kinetic modelling to predict/study the formation of halogenated DBPs occurring from multiple reactions in oxidative water treatment has recently become a popular tool (Fabbicino and Korshin, 2009; Lee et al., 2014; Liu et al., 2012; Yan et al., 2016; Zhai et al., 2014; Zhu and Zhang, 2016). In terms of halogenated DBP formation, most of the reported models focus on predicting the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) (Chowdhury et al., 2009; Yan et al., 2016), while only a few models predict the formation of halogen-specific AOX (Zhai et al., 2014; Zhu and Zhang, 2016).

Modelling software programs have been proven to be reliable in simulation of heterogeneous processes involved in chemical reactions. Simulation software has been used in many studies to validate experimental data. In the area of water research, several software programs have been used to determine rate constants of multiple step aqueous reactions. For example, Allard et al. (2013) used the R program (a language and environment for statistical computing) to determine the species specific rate constants for the oxidation of manganese (II) in bromide-

containing waters. The species specific rate constants for chlorine and bromine were determined based on the different adsorbed Mn(II) species calculated from model simulations. Another quantitative empirical software program for modelling, called Dynafit, was used by Zhai et al. (2014) who identified new polar brominated DBP species during chloramination of bromide-containing waters. With the model, the formation mechanisms of the new brominated DBPs were able to be elucidated, including their overall kinetics. Moreover, in their study, they calculated the contribution of the different active oxidants obtained from oxidation of bromide with chloramines (i.e. bromine, bromochloramine, monobromamine) to the formation of AOB_r. Bromochloramine and monobromamine were the two major oxidants that contributed 54 – 58 % and 42 – 46 % of total AOB_r, respectively, while bromine (HOBr) was responsible for only 0.2 % of the AOB_r formation (Zhai et al., 2014). A more recent study by Zhu and Zhang (2016) reported the application of a kinetic model (similar to the model used by Zhai et al. (2014)) to predict the formation of halogen-specific AOX compounds (AOCl, AOB_r, and AOI) during chlorination and chloramination of raw waters. This model involved a total of 47 reactions with 25 rate constants determined based on best fitting with TOX measurements. The total concentration of DOM reactive sites were based on the number of carbon atoms in aromatic moieties estimated in the Suwannee River fulvic acid extracts from the International Humic Substances Society (IHSS), with 31 % as the total reactive site fraction of DOM (Zhai et al., 2014). This approach is different to the one reported by Duirk et al. (2005), who used the ScientistTM program to determine the number of reactive sites based on the oxidant decay and found values around 65% for the slow reactive site fraction for DOM extracts with similar SUVA₂₅₄ values. The outcomes of their model calculations for AOCl, AOB_r, and AOI formation, as well as predictions of total oxidant residual concentrations, fitted well with their experimental data, indicating the usefulness of kinetic modelling for simulation of halogenated DBP formation during oxidative treatment processes.

Kintecus, another conceptual kinetic modelling software program, has also attracted interest for validation of experimental data. Liu et al. (2012) used Kintecus to model the formation of bromate (BrO₃⁻) from multiple reactions involving HOCl, HOBr, and copper(II) oxide. With the model, the enhancement of bromate formation was better understood, since CuO was found to act as a catalyst which initiated a complex

reaction pathway between CuO and HOBr to form bromite which was further oxidised to form bromate by a second CuO-catalysed process (Liu et al., 2012). In another study, Liu et al. (2014) used Kintecus to simulate the complex reactions during chlorination of iodide-containing waters with the presence of bromide and CuO for the oxidation of iodate to periodate. Kintecus was also applied to study the kinetics of the reaction between ferrate (VI) and 2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate) (ABTS) (Lee et al., 2014).

5.1.1 Scope of Study

The aim of the study presented in this Chapter was to build an empirical model to assess potential pathways leading to AOB_r formation and define some trends based on different experimental conditions. Model calculations will then allow a better understanding of the contribution of each pathway to total AOB_r formation. The purpose of this model was not to determine accurate kinetic rate constants but to illustrate the different pathways leading to AOB_r production.

Therefore, to obtain better outcomes from model calculations, some principal assumptions regarding the reactivity of chlorine and bromine towards different fractions of DOM reactive sites were proposed based on published data. Kinetic rate constants for reactions involved in AOB_r formation were determined or proposed based on known published data or by iterative adjustment. Likewise, different fractions of DOM reactive sites were introduced to accommodate all reactions: electrophilic substitution/addition leading to formation of AOB_r and AOCl; oxidation of DOM (electron transfer) to release bromide in the solution; and replacement of chlorine constituents/groups by bromine. Finally, a semi-empirical sensitivity analysis for the proposed rate constants and the DOM fractions determined by iteration was performed.

5.2 EXPERIMENTAL

Refer to Sections 3.2 and 4.2 for experimental details for experimental data used in this Chapter.

5.2.1 Modelling Software

A conceptual kinetic model for reactions involved in the formation of AOB_r, as identified in Chapter 3 and Chapter 4, was developed using the software program Kintecus (Ianni, 2015).

5.2.2. Model Formulation

The proposed model is based on the different reaction pathways for chlorine and bromine with DOM reactive sites leading to the formation of AOCl and AOB_r. The pathways include electrophilic substitution and addition for halogenation of DOM, electron transfer for oxidation of DOM and chlorine replacement by bromine in DOM (Figure 5-1). It should also be noted that this study does not attempt to model the formation of AOCl. The following assumptions and definitions were made for the development of the model:

- a. HOBr reacts faster with DOM reactive sites than HOCl (Criquet et al., 2015; Heeb et al., 2014).
- b. The concentration of DOM reactive sites in M (mol L⁻¹) was calculated based on a published formula (Duirk et al., 2002; Duirk et al., 2005):

$$[DOM] = \frac{DOC}{12000} \times S$$

DOC: concentration of dissolved organic carbon in mg L⁻¹

12000: molar mass of carbon in mg mol⁻¹

S: represents a percentage of reactive sites in the DOM (see below for estimations).

[DOM]: represents the concentration of reactive sites in mol L⁻¹.

- c. DOM1 is assumed to react with HOCl and HOBr to form Cl-DOM1 (AOCl) and Br-DOM1 (AOBr) through electrophilic substitution and addition (reactions (2) and (3), Figure 5-1). Cl-DOM1 is an intermediate product (chlorine-substituted functional groups) which may react with HOBr where the chlorine will be replaced by bromine to form additional AOB_r (Br-DOM1-replace) (reaction (4), Figure 5-1). DOM2 and DOM4 are specific reactive sites of DOM that reduced HOBr and HOCl and released bromide and chloride without producing AOB_r and AOCl.

- d. DOM3 represents specific reactive sites of SR-DOM that react only with HOBr. The initial DOM3 concentration was assumed to be lower than concentrations of the other DOM reactive sites.

Table 5-1: Kinetic modelling of AOBBr formation: reactions of HOCl and HOBr with DOM with optimised rate constants.

No.	Reactions	Proposed rate constants	pKa	Note	References
1.	$\text{HOCl} + \text{Br}^- \rightleftharpoons \text{HOBr} + \text{Cl}^-$	$1.55 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		HOBr formation	(Kumar and Margerum, 1987)
2.	$\text{HOCl} + \text{DOM1} \rightleftharpoons \text{Cl-DOM1}$	$200 \text{ M}^{-1} \text{ s}^{-1}$		AOCl formation through electrophilic substitution and addition	this study
3.	$\text{HOBr} + \text{DOM1} \rightleftharpoons \text{Br-DOM1}$	$2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		AOBr formation through electrophilic substitution and addition	this study
4.	$\text{HOBr} + \text{Cl-DOM1} \rightleftharpoons \text{Br-DOM1-replace}$	$400 \text{ M}^{-1} \text{ s}^{-1}$		AOBr formation from Cl-DOM1	this study
5.	$\text{HOBr} + \text{DOM2} \rightleftharpoons \text{DOM2ox} + \text{Br}^-$	$2 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		DOM oxidised by HOBr and bromide is released	this study
6.	$\text{HOBr} + \text{DOM3} \rightleftharpoons \text{Br-DOM3}$	$5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$		AOBr formation through electrophilic substitution and addition of sites that don't react with HOCl	this study
7.	$\text{HOCl} + \text{DOM4} \rightleftharpoons \text{DOM4ox} + \text{Cl}^-$	$500 \text{ M}^{-1} \text{ s}^{-1}$		DOM4 is oxidised by HOCl and chloride is released	this study
8.	$\text{HOBr} \rightleftharpoons \text{H}^+ + \text{BrO}^-$	$1.585 \times 10^3 \text{ s}^{-1}$		HOBr dissociation	
9.	$\text{H}^+ + \text{BrO}^- \rightleftharpoons \text{HOBr}$	$1 \times 10^{12} \text{ s}^{-1}$	8.8	HOBr association	(Haag and Hoigné, 1983)
10.	$\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$	$3.2 \times 10^4 \text{ s}^{-1}$		HOCl dissociation	
11.	$\text{H}^+ + \text{ClO}^- \rightleftharpoons \text{HOCl}$	$1 \times 10^{12} \text{ s}^{-1}$	7.53	HOCl association	(Weast, 1984)

5.3 RESULTS AND DISCUSSION

5.3.1 Proposed Model Calculations for AOBr Formation: A Step-By-Step Process

According to the results obtained in Chapter 3 and Chapter 4, there are 4 main reactions involved in the formation of AOBr (Figure 5-1):

(i) Reaction of HOBr with DOM through electrophilic substitution and addition. Two different sites were determined. DOM1 was assigned to the fraction of sites reacting with both HOBr and HOCl (reactions (2, 3), Figure 5-1 and Table 5-1). DOM3 was assigned to specific reactive sites reacting only with HOBr (reaction (6), Figure 5-1 and Table 5-1).

(ii) Reaction of HOBr with DOM through oxidation. DOM2 was allocated for oxidation of DOM by HOBr (reaction (5), Figure 5-1 and Table 5-1).

(iii) Chlorine replacement in DOM by bromine. Cl-DOM1 was the intermediate product (chlorine-substituted functional groups) that may react further with HOBr (reaction (4), Figure 5-1 and Table 5-1).

(iv) HOBr recycling by oxidation of bromide with chlorine (reaction (1) Figure 5-1 and Table 5-1).

The total AOBr in the model calculations is the sum of Br-DOM1, Br-DOM1-replace and Br-DOM3. Calculated AOBr concentrations resulting from the model were found to be in good agreement with the trend of experimental data in all experiments (Figure 5-4, Figure 5-5, Figure 5-13 and Figure 5-14).

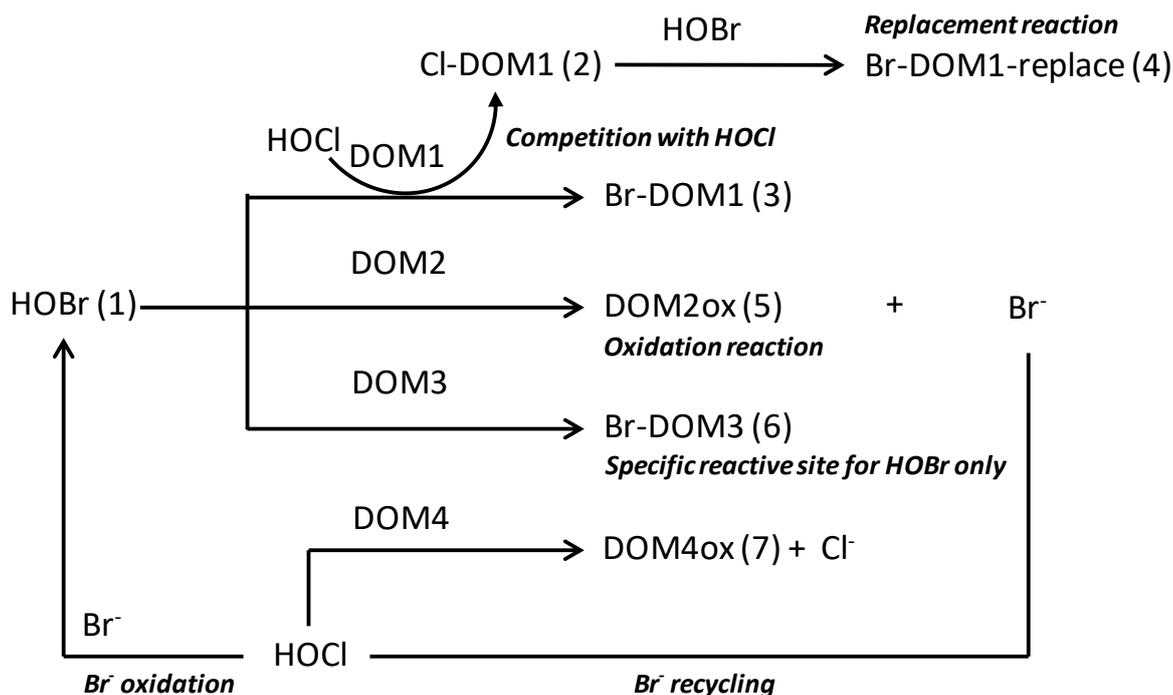


Figure 5-1: Main reactions involved during chlorination in the presence of bromide ($\text{Br}^- + \text{HOCl}$) and in bromination (HOBr) of DOM. Number in brackets refers to model reactions in Table 5.1.

The procedure for the conceptual modelling is described as follows:

1. In the first stage, the simplest scenario, i.e. HOBr and DOM1 reaction through electrophilic substitution/addition (Figure 5-2, black bars, from Figure 3-3a, Chapter 3), was modelled. The reactive site fraction of DOM1 (S in Section 5.2.2b) was set to 0.025 in accordance with data from Duirk et al. (2005) which showed a maximum for fast reacting DOM sites of 0.023 for DOM with a SUVA_{254} of $4.3 \text{ mgC L}^{-1} \text{ m}^{-1}$. Since the SUVA_{254} of SR-DOM is slightly higher ($4.45 \text{ mgC L}^{-1} \text{ m}^{-1}$), a value of 0.025 was used. The proposed rate constant for halogenation via electrophilic substitution/addition with HOBr to form Br-DOM1 was set to $2000 \text{ M}^{-1} \text{ s}^{-1}$ (reaction (3), Figure 5-1, Table 5-1). This corresponds to a middle range value based on second order rate constants for the reaction of DOM isolates with bromine estimated by Westerhoff et al. (2004) which were in the range of $500 - 5000 \text{ M}^{-1} \text{ s}^{-1}$. It should be noted that Westerhoff et al. (2004) did not distinguish between substitution/addition and electron transfer reactions.

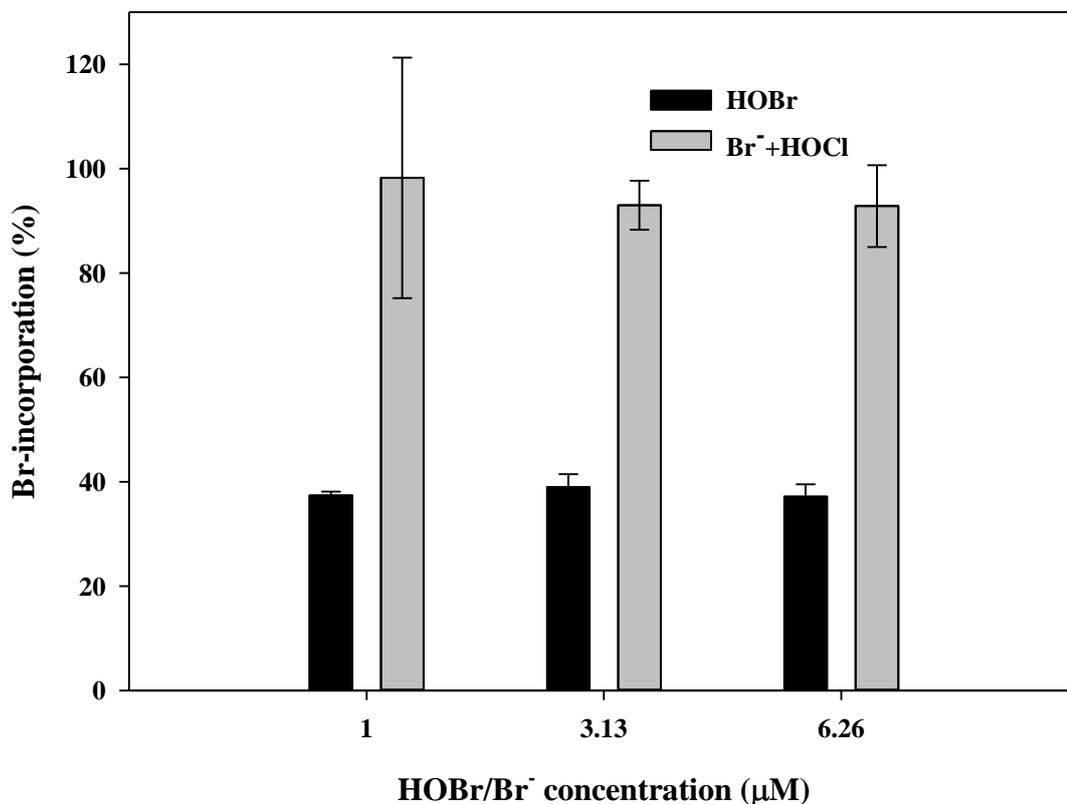


Figure 5-2: AOB_r formation expressed as Br-incorporation (%) of bromination and chlorination experiments used to determine the rate constants for reactions (2) and (3).

The reactive site fraction of DOM3 specifically reacting with HOBr was set at a much lower value of 0.0075 (this parameter was fitted using experimental data from Figure 5-3, Figure 4.11, Chapter 3, see explanation below). The reaction between HOBr and DOM3 was assumed to be very fast. Therefore, the second order rate constant for DOM3 reactive sites reacting specifically with HOBr (formation of Br-DOM3) (reaction (6), Figure 5-1, Table 5-1) was set to $5000 \text{ M}^{-1} \text{ s}^{-1}$, which corresponds to the upper limit of second order rate constants estimated by Westerhoff et al. (2004).

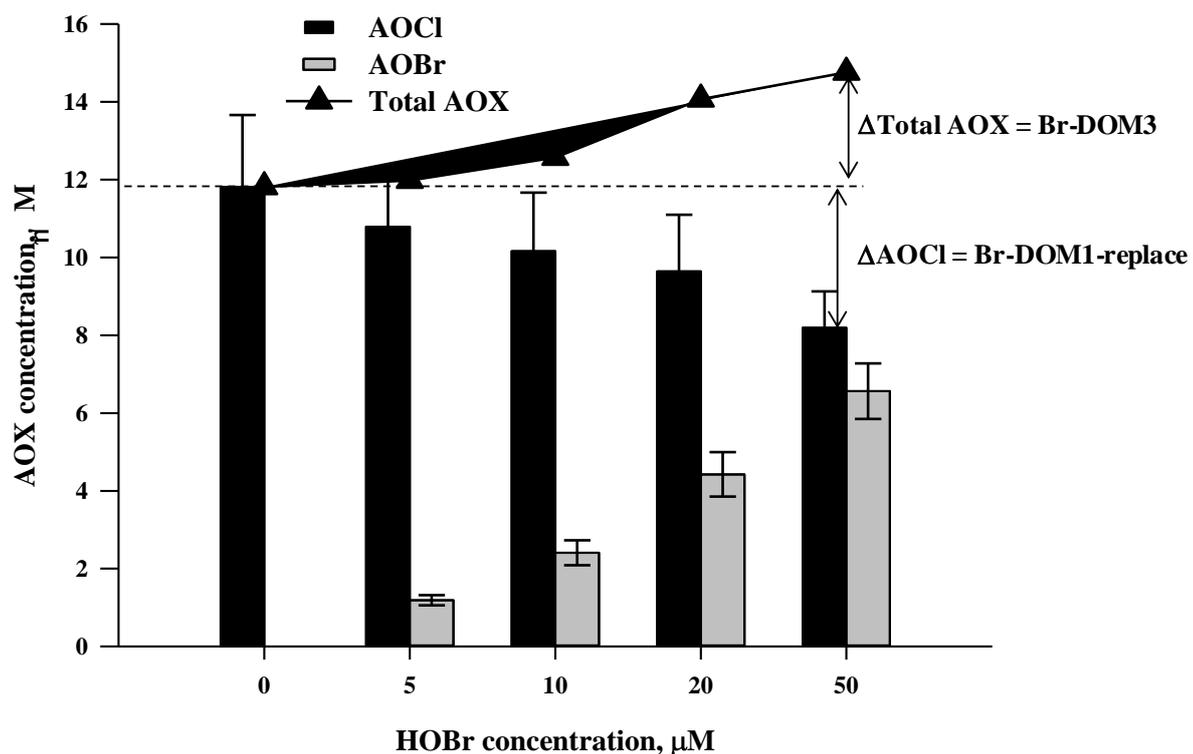


Figure 5-3: Effect of HOBr concentration after consumption of HOCl during Pre-Chlorination on AOX Formation showing specific DOM reactive sites (DOM3) reacting with HOBr only to form AOBBr (Br-DOM3 = Δ total AOX) and the fraction of DOM where HOBr results in a replacement of Cl-DOM1 (Δ AOCI) with additional AOBBr (Br-DOM1-replace). Experimental conditions: SR-DOM (4 mgC L^{-1}), phosphate buffer (1 mM), pH = 8, pre-chlorination ($45 \mu\text{M}$) for 24 h then HOBr (5 – 50 μM) for 1 h, Na_2SO_3 solution (10 % excess based on chlorine equivalent residual) for quenching.

Another reactive site for HOBr reaction by oxidation (electron transfer) of DOM and release of bromide (DOM2) was added. Similar rate constants of $2000 \text{ M}^{-1} \text{ s}^{-1}$ for HOBr oxidation and electrophilic substitution/addition (DOM1) reactions were chosen for simplicity. Therefore, based on Figure 5-2 (black bars) where ~35% of the initial bromine is converted to AOBBr, i.e. ~65% is reduced to bromide (Figure 3-5, black bars, Chapter 3), the fraction of reactive site DOM2 was determined to be 0.06. This represents ~65% of the reactive sites at this stage of the fitting ($0.06/(0.025+0.0075+0.060) = 0.65$).

Figure 5-4 shows a comparison of the experimental data for AOBr formation from SR-DOM treated directly with HOBr at different concentrations with the output data from the model. A good fit (determined based on best visual assessment) was obtained for the three bromine concentrations tested.

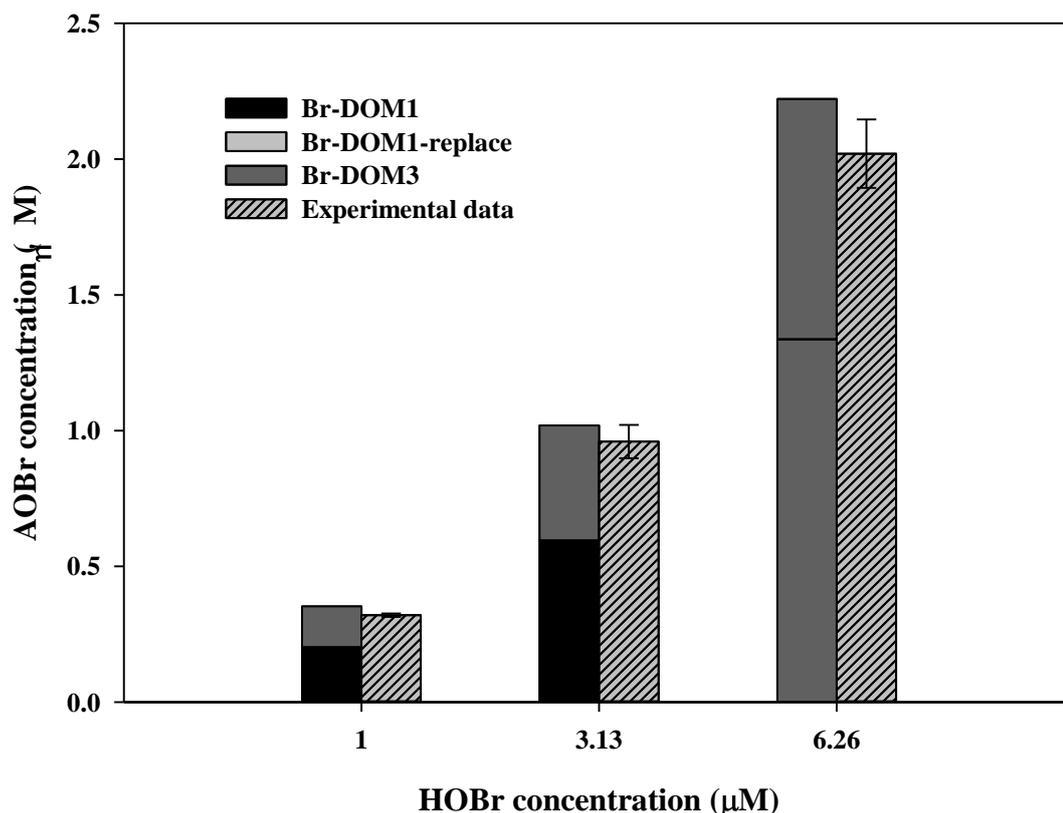


Figure 5-4: Model calculations for AOBr formation from SR-DOM with different HOBr concentrations showing contribution of Br-DOM1, Br-DOM1-replace and Br-DOM3 to total AOBr.

2. In the second stage, the bromide recycling process was introduced (Figure 5.2, grey bars). The well-known second order rate constant for the oxidation of bromide by chlorine was added (reaction (1), Figure 5.1, Table 5.1) (Kumar and Margerum, 1987). In this case, chlorine was in excess, therefore, both the electrophilic substitution and addition and oxidation reactions for HOCl should be added. It is generally accepted that second order rate constants for reactions of HOBr with organic moieties are significantly higher than for HOCl (Criquet

et al., 2015; Heeb et al., 2014). Therefore, for the electrophilic substitution/addition reaction, DOM1 was used (in competition with HOBr) with a second order rate constant of $200 \text{ M}^{-1}\text{s}^{-1}$ for the reaction of HOCl with a DOM of similar SUVA_{254} (reaction (2), Figure 5.1, Table 5.1). This corresponds to the value determined by Duirk et al. (2005). Again, in this work, the electrophilic substitution/addition and the oxidation reactions were not separated for HOCl.

The fraction of reactive site DOM4 and the second order rate constant corresponding to oxidation reactions for HOCl with DOM were set to 0.1 and $500 \text{ M}^{-1} \text{ s}^{-1}$ (reaction (7), Figure 5-1, Table 5-1) by iteration to fit with the experimental data. This is particularly important for experiments with low HOCl concentrations (i.e. Figure 5-9, Figure 3-7, Chapter 3). It should be noted that there was no attempt to accurately model the formation of AOCl, therefore these second order rate constants and fractions of reactive sites were used to control the concentration of chlorine in solution which induces bromide recycling and formation of HOBr. Introduction of the bromide recycling process due to the presence of excess HOCl into the model was successful due to the similarity of modelled and experimental data (Figure 5-5). Figure 5-4 and Figure 5-5 both show a comparison of the experimental data for AOB_r formation from SR-DOM, treated with either HOBr or HOCl/Br⁻, with the output data from the model. For both sets of experimental conditions, a good fit was obtained, indicating the strength of the model.

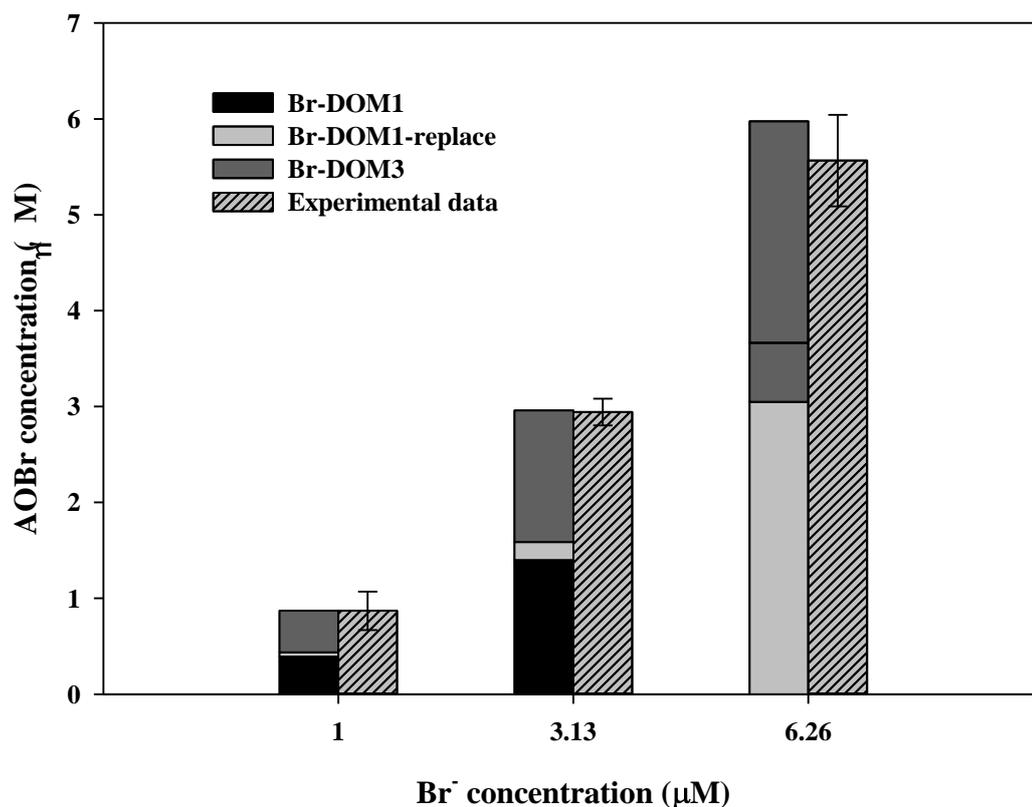


Figure 5-5: Model calculations for AOBBr formation from SR-DOM with different bromide concentrations treated with HOCl showing contribution of Br-DOM1, Br-DOM1-replace and Br-DOM3 to total AOBBr.

3. In the third stage, the DOM reactive site fraction representing the replacement of chlorine constituents/groups by bromine was introduced to the model. It was assumed that the intermediate Cl-DOM1 (reaction (2), Figure 5.1, Table 5.1) subsequently reacted with HOBr leading to Br-DOM1-replace (reaction (4), Figure 5.1, Table 5.1). The fraction of sites (DOM3) reacting specifically with HOBr was also tuned using AOBBr formation data presented in Figure 5.3. It is noteworthy that a substantial part of AOBBr was formed from chlorine replacement by bromine (~33% Δ AOCl reduction). The assumption was made that chlorine replacement by bromine was more significant when most of the other reactions had occurred and the respective DOM reactive sites consumed. Therefore, the kinetic rate constant of HOBr with Cl-DOM1 was set by iteration at a low value (compared to the other second order rate constant related to

HOBr) of $400 \text{ M}^{-1}\text{s}^{-1}$ (reaction (4), Figure 5.1, Table 5.1). It was assumed that most of the DOM reactive sites had been used by chlorine in the experiment where SR-DOM was pre-chlorinated ($45 \text{ }\mu\text{M}$) for 24 h before HOBr addition (Figure 5.3, also in Figure 4.11, Chapter 4) and since the total AOX was increasing, the $\Delta\text{Total AOX}$ represents the DOM reactive sites which were only reacting with HOBr (DOM3). Based on $\Delta\text{Total AOX}$, the fraction of DOM reactive sites (DOM3) was set at a low percentage of 0.0075 by iteration (reaction (6), Figure 5.1, Table 5.1). Figure 5-6 shows a comparison of the experimental data obtained from pre-chlorination experiment for which SR-DOM was pre-chlorinated ($45 \text{ }\mu\text{M}$) until full consumption of HOCl (24 h) before HOBr addition (Figure 5-3) with the further developed model. A good fit was obtained for bromine concentrations ranging from 5 to $20 \text{ }\mu\text{M}$. For the highest bromine concentration of $50 \text{ }\mu\text{M}$, the model over-predicts the formation of AOB_r. This may be explained by the presence of differing AOCl sites: part of the AOCl may react with HOBr, while another fraction of AOCl may be inert and not react with HOBr. For $50 \text{ }\mu\text{M}$ of HOBr, Br-DOM1-replace already exceeds the experimental data for total AOB_r. It can be assumed that most of the AOCl reactive sites were consumed in the experiments, however, in our simplistic model, only one type of AOCl site is taken into account. Therefore, a higher formation of Br-DOM1-replace is possible and a higher AOB_r formation is predicted by the model compared to the experimental data. To improve the model at high bromine concentrations in future work, refined modelling of the AOCl is needed. However, the highest bromide concentrations do not reflect typical bromide concentrations found in drinking water systems. Therefore, for bromide concentrations typical of drinking water systems, the refined model was successful in incorporating the effect of the DOM reactive site fraction representing the replacement of chlorine constituents/groups by bromine.

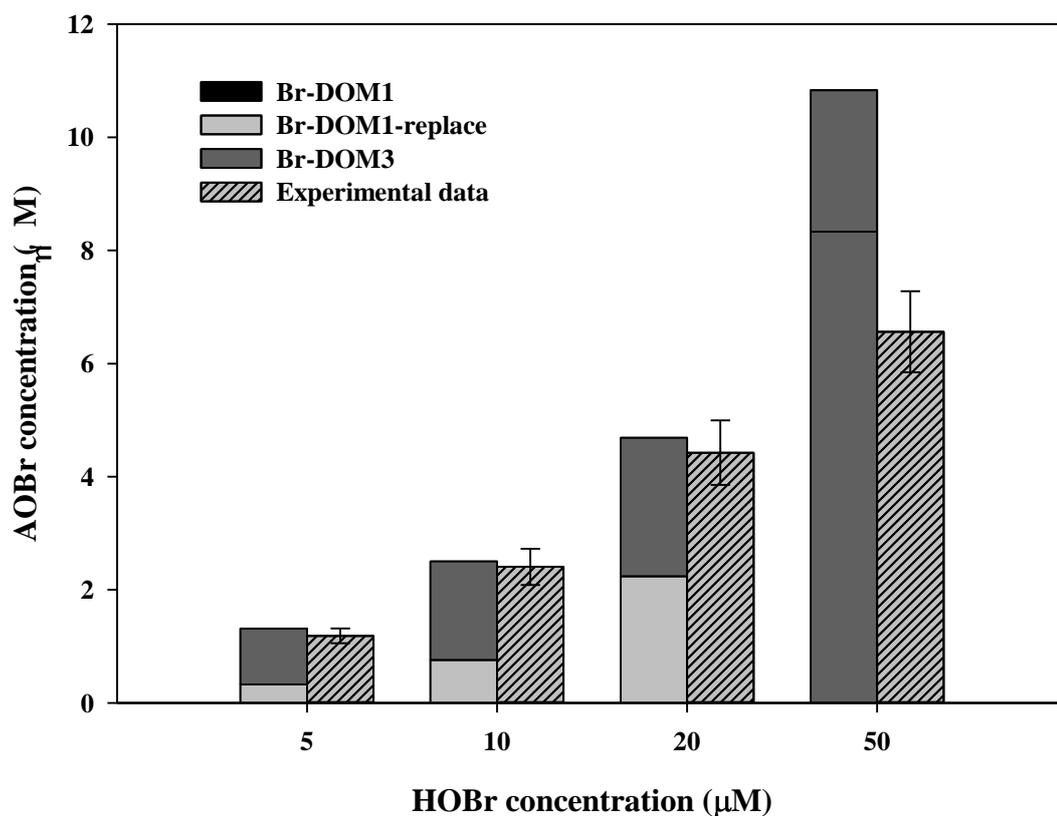


Figure 5-6: Model calculations for AOBBr formation obtained from pre-chlorination of SR-DOM at 45 μM for 24 h followed by HOBr addition at various concentrations showing contribution of Br-DOM1, Br-DOM1-replace and Br-DOM3 to total AOBBr.

5.3.2 Rate Constant Sensitivity Analysis

This semi-empirical model sensitivity analysis was performed to assess the impact of varying second order rate constants and concentrations of DOM reactive sites involved in AOBBr formation on the parameters determined by iteration. For the second order rate constants based on published data (see the first stage of the model's step-by-step process, Section 5.3.1), no sensitivity analysis was performed.

Reaction 4 is the reaction between HOBr and intermediate Cl-DOM1 where chlorine is replaced by bromine to form Br-DOM1. The influence of rate constant variations for reaction (4) on AOBBr formation is presented in Figure 5-7. Simulations showed that increasing the rate constant of reaction 4 from 10 to 1000 $\text{M}^{-1} \text{s}^{-1}$ leads to

increasing AOB_r formation. The best agreement with experimental data was found for the rate constant value of $400 \text{ M}^{-1} \text{ s}^{-1}$.

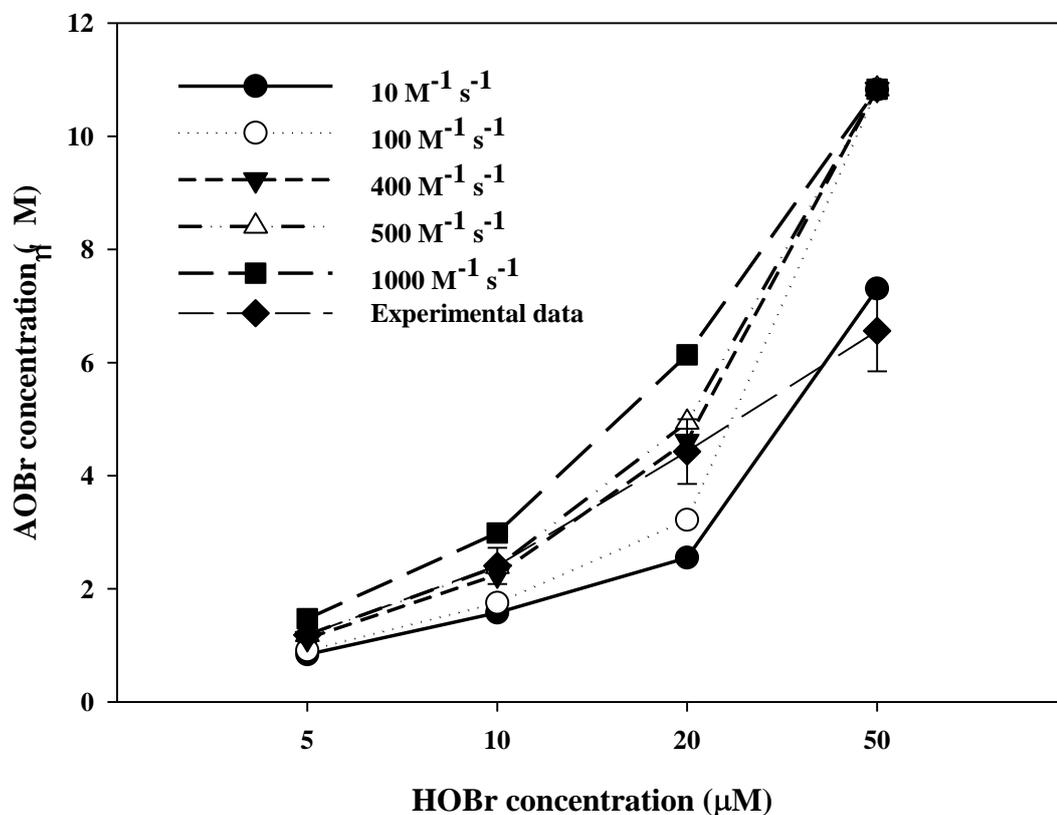


Figure 5-7: The influence of rate constant variations for reaction 4 on AOB_r formation. Model conditions: $[\text{HOCl}] = 45 \text{ } \mu\text{M}$, $[\text{HOBr}] = 5.0 - 50 \text{ } \mu\text{M}$, $[\text{Cl-DOM1}] = 8.33 \times 10^{-6} \text{ M}$, $\text{pH} = 8.0$.

The influence of varying the DOM3 reactive site fraction (reaction 6), corresponding to the DOM reactive sites which are only reacting with HOBr, on AOB_r formation is presented in Figure 5.8. Figure 5-8 shows that decreasing the DOM3 fraction from 0.0075 to 0.005 results in a decrease in AOB_r formation, while increasing the DOM3 fraction to 0.01 leads to an overprediction of AOB_r for 20 μM of HOBr. Therefore, a fraction of DOM3 reactive sites of 0.0075 was used in reaction 6.

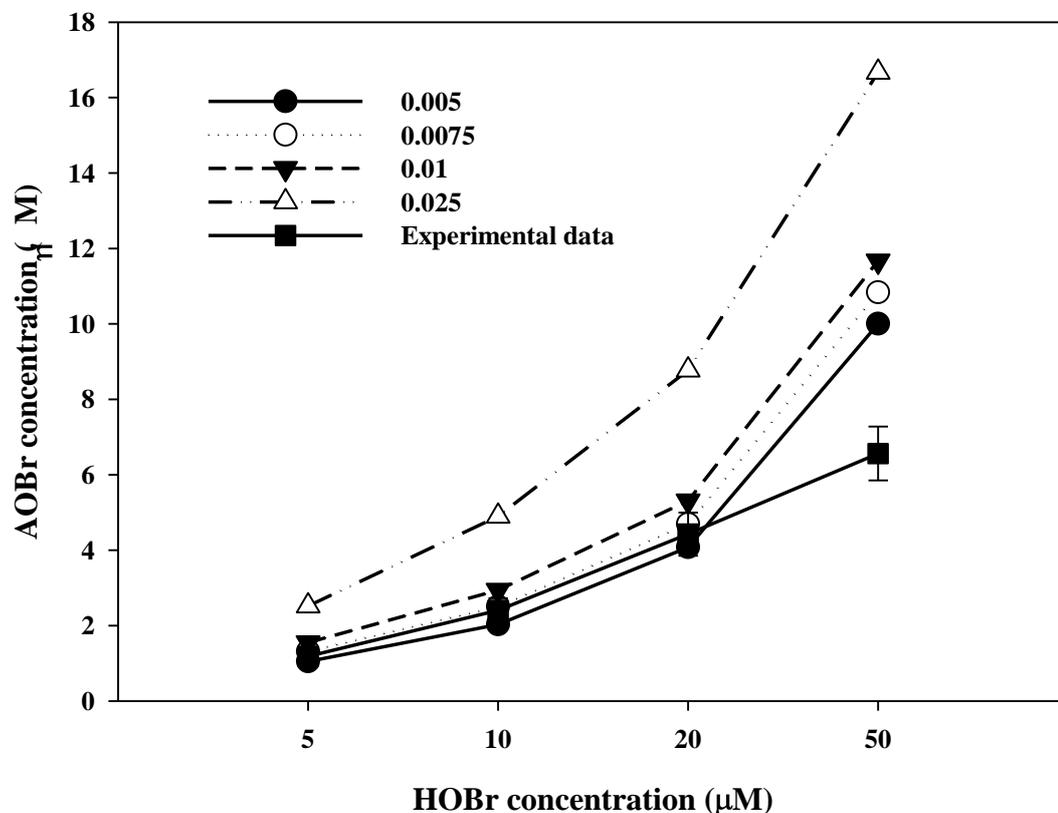


Figure 5-8: The influence of DOM3 fraction variations for reaction 6 on AOBBr formation. Model conditions: $[\text{HOCl}] = 45 \mu\text{M}$, $[\text{HOBr}] = 5.0 - 50 \mu\text{M}$, $[\text{DOM3}] = 1.67 \times 10^{-6} - 8.33 \times 10^{-6} \text{ M}$, $\text{pH} = 8.0$.

Reaction 7 (Table 5-1, Figure 5-1) is the oxidation of DOM reactive sites by HOCl. DOM4 was introduced to accommodate this reaction. The second order rate constant and the fraction of DOM4 reactive sites were determined by iteration using experimental data presented in both Figure 5-2 (grey bars) and Figure 5-9 (from Figure 3-7, Chapter 3).

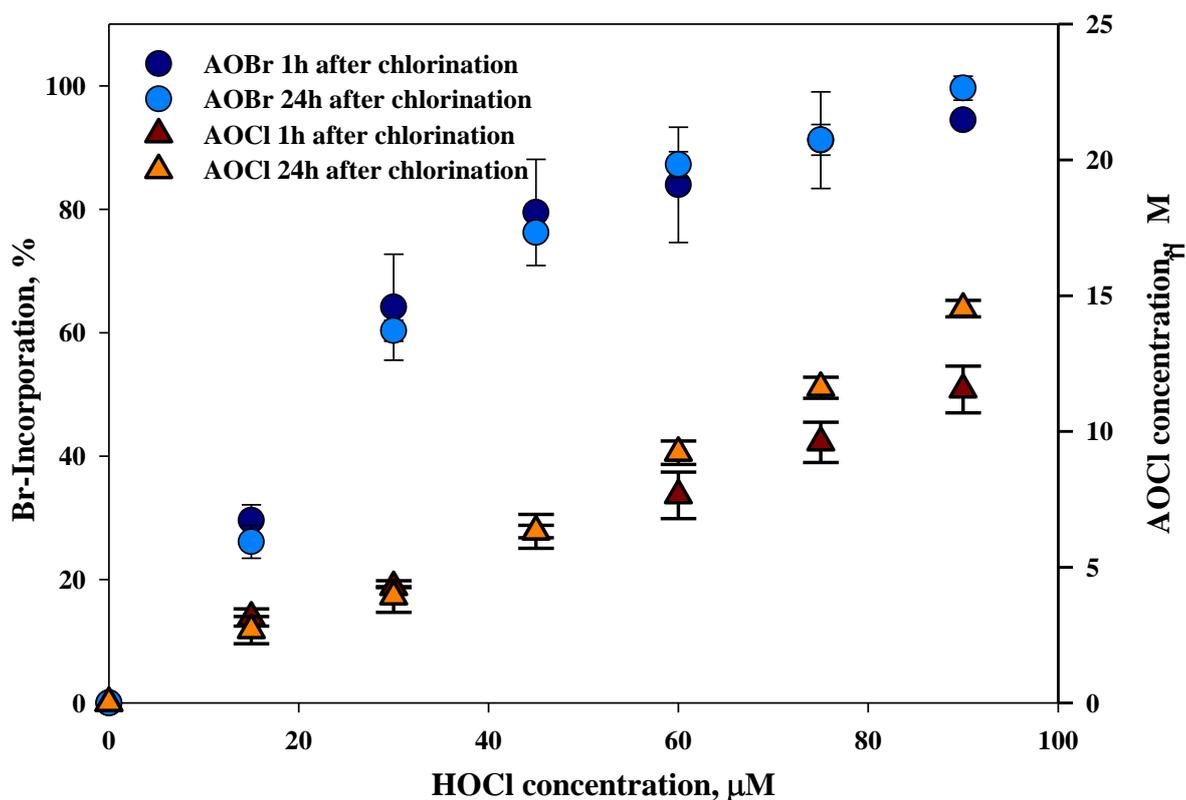


Figure 5-9: Effect of different chlorine dose on AOBBr and AOCI formation for synthetic waters containing SR-DOM and bromide. Experimental condition: SR-DOM (4 mgC L^{-1}), $[\text{Br}^-]$ ($6.26 \text{ } \mu\text{M}$, $500 \text{ } \mu\text{g L}^{-1}$), phosphate buffer (1 mM), $\text{pH} = 8$, $[\text{HOCl}]$ ($15, 30, 45, 60, 75, 90 \text{ } \mu\text{M}$) for 1 h and 24 h, Na_2SO_3 (10 % molar excess based on chlorine equivalent residual) for quenching.

The influence of rate constant variations for reaction 7 on AOBBr formation is shown in Figure 5.10. It is evident that a second order rate constant of $5000 \text{ M}^{-1} \text{ s}^{-1}$ leads to significantly less AOBBr than observed in the experiments. Simulation with rate constants decreasing from 1000 to $50 \text{ M}^{-1} \text{ s}^{-1}$ results in an increase of AOBBr formation with $500 \text{ M}^{-1} \text{ s}^{-1}$ leading to the best fit with experimental data. Therefore, a rate constant of $500 \text{ M}^{-1} \text{ s}^{-1}$ was chosen for reaction 7.

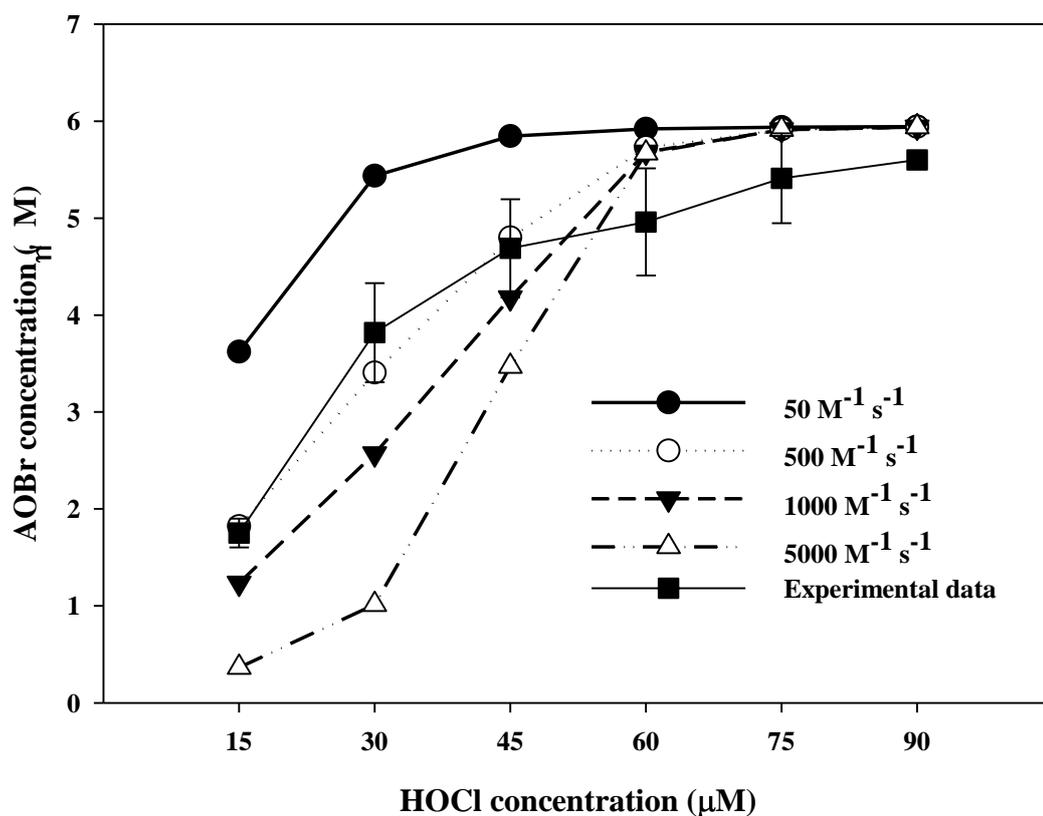


Figure 5-10: The influence of rate constant variations for reaction 7 on AOBBr formation. Model conditions: $[\text{HOCl}] = 75 \mu\text{M}$, $[\text{Br}^-] = 1.0 - 6.26 \mu\text{M}$, $[\text{DOM4}] = 1.67 \times 10^{-4} \text{M}$, $\text{pH} = 8.0$.

A similar sensitivity analysis was applied to examine the impact of varying the reactive site fraction for DOM4 on AOBBr formation (Figure 5-11). It is apparent that increasing the fraction of reactive sites from 0.1 to 0.25 leads to a significant decrease of AOBBr concentration. Similarly, decreasing the DOM4 fraction from 0.1 to 0.05 leads to a slight increase of AOBBr concentration. A reactive site fraction for DOM4 of 0.1 gave the best agreement with the experimental results.

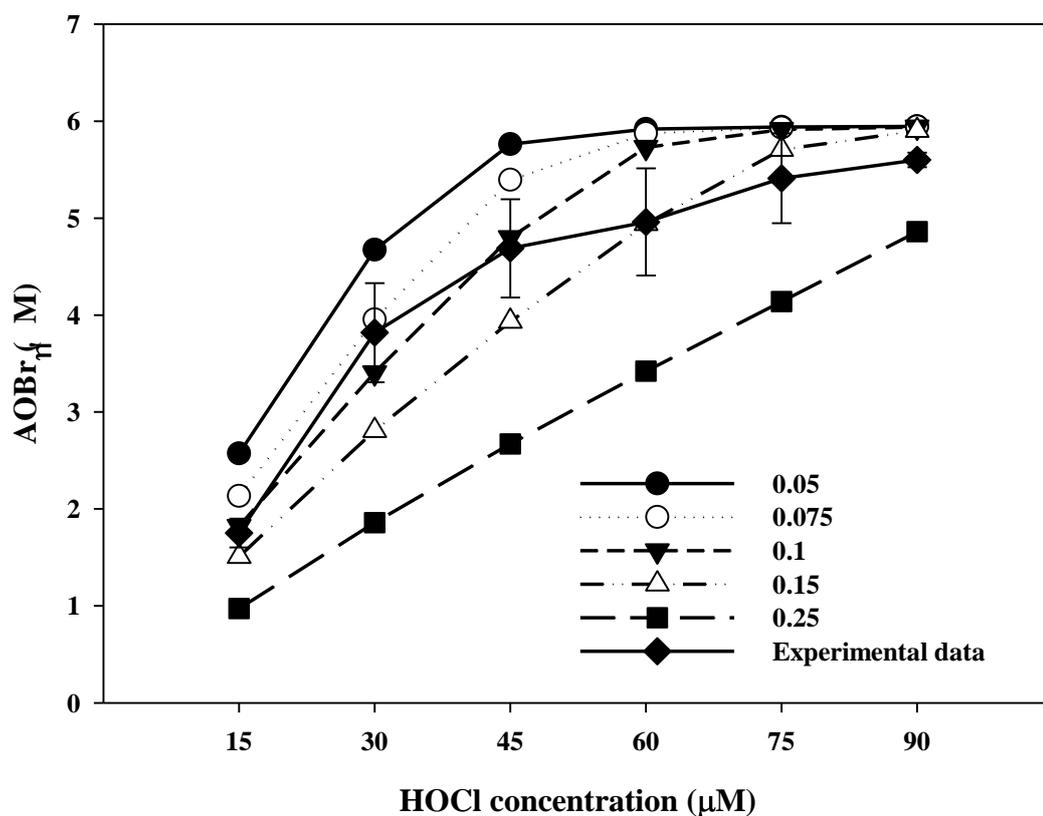


Figure 5-11: The influence of DOM4 fraction variations for reaction 7 on AOBBr formation. Model conditions: $[\text{HOCl}] = 15 - 90 \mu\text{M}$, $[\text{Br}^-] = 6.26 \mu\text{M}$, $[\text{DOM4}] = 1.67 \times 10^{-5} - 8.33 \times 10^{-5} \text{ M}$, $\text{pH} = 8.0$.

5.3.3 AOBBr Formation: Comparison between Model Calculations and Experimental Data

Overall, the total AOBBr based model calculation is the sum of Br-DOM1, Br-DOM1-replace and Br-DOM3 (see example of Kintecus output in Figure 5-12). AOBBr concentrations resulting from the model fit well with the experimental data for a variety of different experimental conditions, i.e., bromination experiments (Figure 5.2), chlorination experiments (Figure 5.3), pre-chlorination experiments of SR-DOM: (i) at fixed HOCl concentration ($75 \mu\text{M}$) for different times followed by HOBr addition at fixed concentration ($6.26 \mu\text{M}$) (Figure 5-13), (ii) at fixed HOCl concentrations ($45 \mu\text{M}$) for 24 h followed by HOBr addition at various concentrations ($5 - 50 \mu\text{M}$) (Figure 5-6), and chlorination experiments to simulate real water treatment conditions (Figure 5-14). The good fitting model with the

experimental data demonstrates the usefulness of Kintecus for simulation of halogenated DBP formation during oxidative treatment processes.

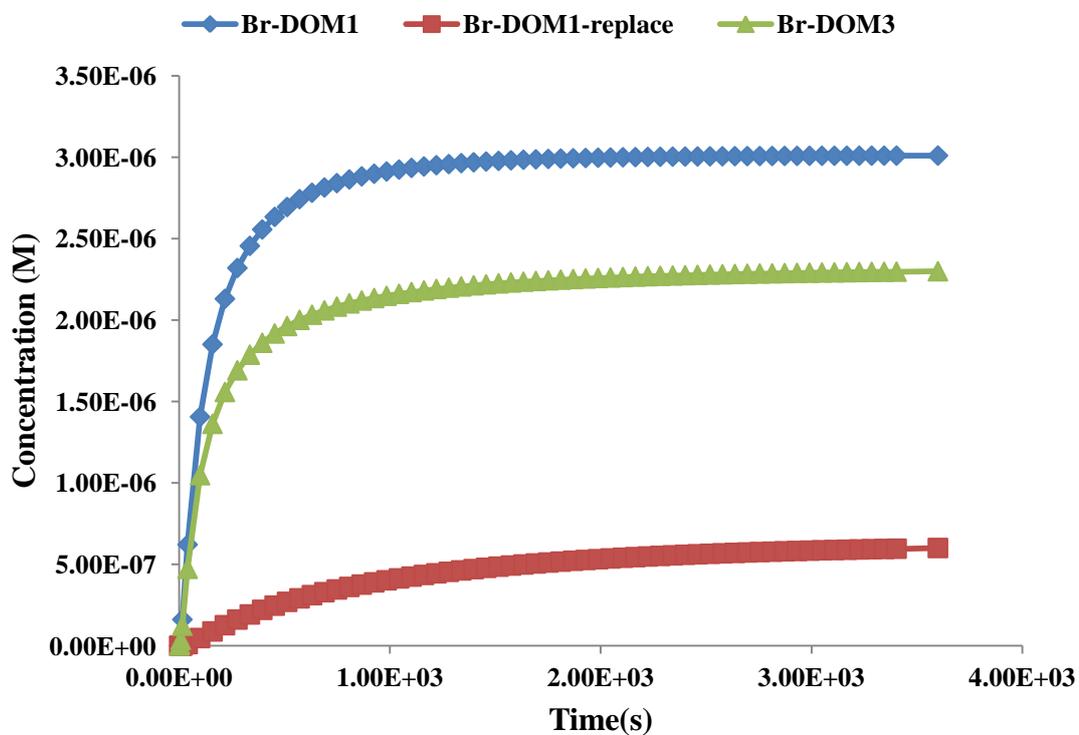


Figure 5-12: Example of Kintecus output for AOB_r formation as a sum of Br-DOM1, Br-DOM1-replace, and Br-DOM3. Model conditions: [HOCl] = 75 μM, [Br⁻] = 6.26 μM, [DOM1] = 8.33x10⁻⁶ M, [DOM2] = 2.0x10⁻⁵ M, [DOM3] = 2.5x10⁻⁶ M, [DOM4] = 5.0x10⁻⁵ M, pH = 8, modelling time = 1h.

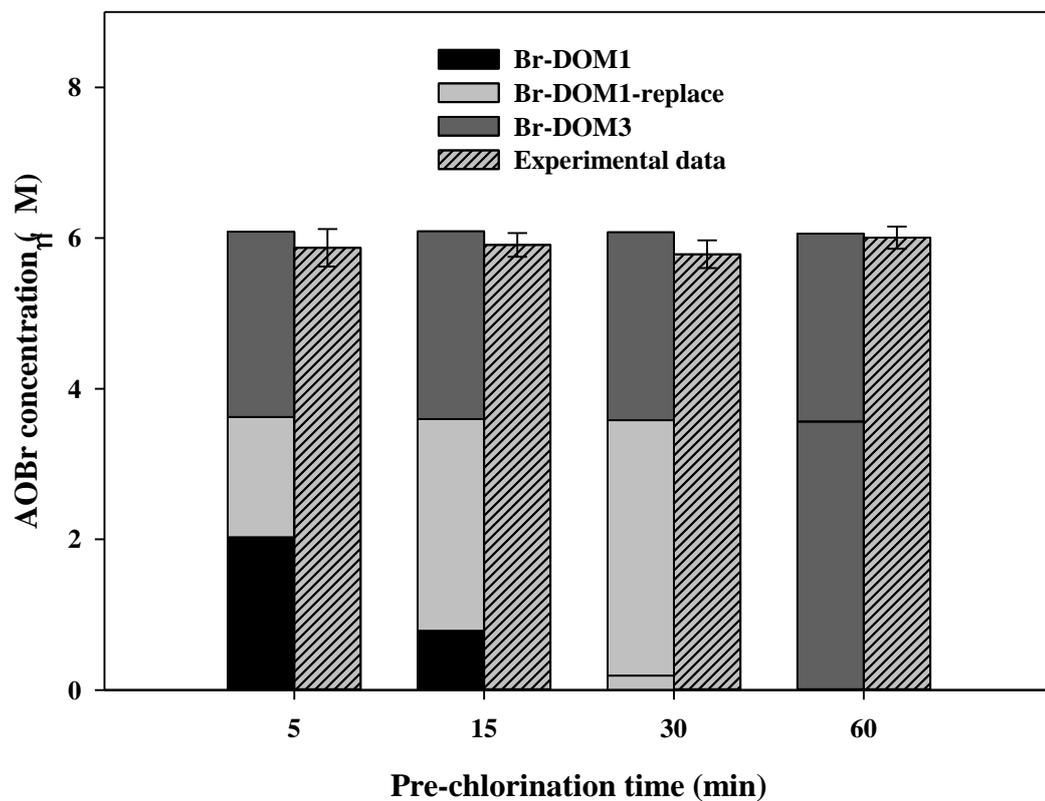


Figure 5-13: Model calculations for AOBBr formation from water containing SR-DOM pre-chlorinated at 75 μM for different times before bromine addition, showing contribution of Br-DOM1, Br-DOM1-replace and Br-DOM3 to total AOBBr.

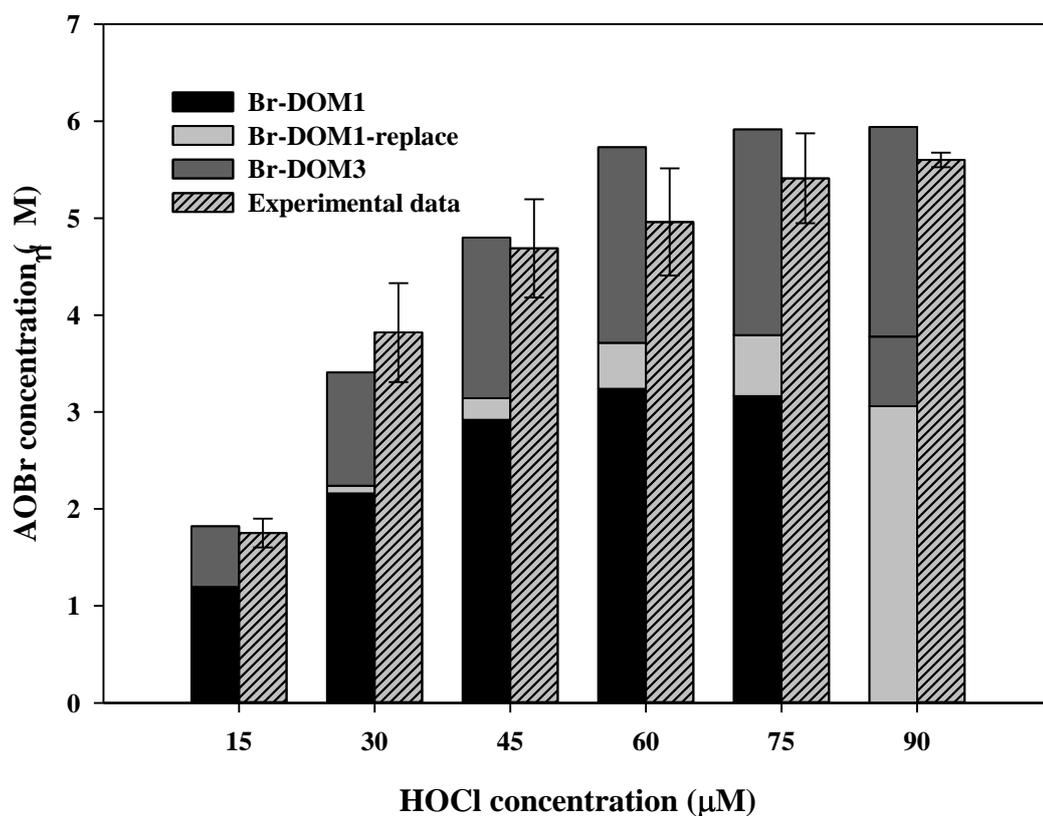


Figure 5-14: Model calculations for AOBr formation of water containing SR-DOM and bromide treated with HOCl for 1h, showing contribution of Br-DOM1, Br-DOM1-replace and Br-DOM3 to total AOBr.

Moreover, model calculations allow us to better understand the contribution of each type of DOM reactive site and reaction pathway to AOBr formation. For example, model calculations showed that the unexpected similar AOBr concentration obtained for different pre-chlorination times in Figure 5.13 was due to the increasing formation of Br-DOM1-replace (bromine replaces Cl in Cl-DOM1, equation (4), Figure 5-1) that compensated for the decrease in Br-DOM1 (formed through electrophilic substitution/addition, equation (3), Figure 5-1), in competition with HOCl to form Cl-DOM1, (equation (2), Figure 5-1) with increasing pre-chlorination exposure.

5.4. Conclusions

This Chapter presents the development and validation of an empirical kinetic model for simulation of AOB_r formation. The simplistic multiple step reactions for AOB_r formation and their second order rate constants were proposed based on the reactivity of bromine and chlorine with organic moieties found in relevant published studies and by fitting of experimental data presented in Chapters 3 and 4. Similarly, different DOM reactive sites were introduced to accommodate different reaction pathways between bromine/chlorine and DOM for AOB_r formation.

DOM1 was introduced to simulate the competition between HOCl and HOBr whereby AOB_r and AOCl is formed through electrophilic substitution and addition reactions. In addition, a DOM fraction (Cl-DOM1) was introduced to represent a fraction of AOCl which could react with HOBr such that the chlorinated sites were replaced by bromine to form additional AOB_r. The proposed second order rate constant for reaction between HOBr and DOM1 via electrophilic substitution and addition to form AOB_r and the fraction of DOM1 were assigned based on relevant published data and set to $2.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and 0.025, respectively. For reaction between HOBr and AOCl (Cl-DOM1), the proposed second order rate constant was determined by iteration and set to $400 \text{ M}^{-1} \text{ s}^{-1}$. DOM2 was proposed for oxidation reactions (electron transfer) with HOBr, leading to a release of bromide. The second order rate constant for this reaction was set at $2.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, similar to the value used for the formation of AOB_r through electrophilic substitution and addition reactions, while the fraction of reactive sites DOM2 was determined by iteration based on bromination experiments. In bromination experiments, it was shown that 60% of HOBr reacted through an oxidation/reduction process. Therefore, DOM2 was set at 0.06 which corresponded to 60% of the total reactive sites for reaction with HOBr. DOM3 was allocated for specific reactive sites reacting only with HOBr (not with HOCl) to form AOB_r through electrophilic substitution and addition reactions. This specific fraction of reactive sites was determined by iteration and set to 0.0075. Thereafter, the second order rate constant was further determined by iteration and was set to $5.0 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Finally, DOM4 was assigned for reaction of DOM with HOCl through electron transfer (oxidation) to control the chlorine equivalent residual that induced bromide recycling. The well-known rate constant for the oxidation of

bromide by HOCl ($k_{\text{HOCl,Br}^-} = 1550 \text{ M}^{-1} \text{ s}^{-1}$) was added to the model. The second order rate constant for the oxidation of DOM4 by HOCl and the fraction of DOM4 were determined by iteration and the values used were $500 \text{ M}^{-1} \text{ s}^{-1}$ and 0.1, respectively. The proposed second order rate constants and DOM reactive sites determined by iteration were validated by a semi-empirical sensitivity analysis.

Simulation of AOB_r formation using the model developed in this study fitted well with the experimental data obtained from different disinfection scenarios (direct bromine addition to synthetic waters, chlorination of synthetic waters containing DOM and bromide, and pre-chlorination followed by bromine addition experiments). The model successfully highlighted the role of bromide recycling in the formation of AOB_r. In bromide recycling, produced bromide is (re-)oxidised in the presence of a chlorine residual, reforming HOBr, which reacts further with DOM reactive sites to form additional AOB_r. Moreover, specific reactive sites reacting only with HOBr for AOB_r formation through electrophilic substitution and addition reactions proposed in the model improved the consistency of the modelled data with the experimental data. Finally, a pathway for AOB_r formation was proposed in this study where chlorinated sites in Cl-intermediates (AOCl) could be replaced by bromine for additional formation of AOB_r. Overall, these model calculations have allowed a better understanding of the contribution of each reaction pathway and DOM reactive site to AOB_r formation.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS FOR THE WATER INDUSTRY

Halogen-specific adsorbable organic halogen (AOX) analysis was demonstrated to be a highly suitable method for study of halogenated organic compounds in disinfected drinking waters. An analytical method for determination of halogen-specific AOX was improved and modified prior to being successfully validated and applied to a drinking water treatment system. Validation of the modified halogen-specific AOX method involved recoveries of a wide range of disinfection by-products (DBPs) and other halogenated organic compounds as model compounds and of total bromine. Very good recoveries of organic halogen from all model compounds were obtained, indicating high or complete conversion of all organic halogen in the model compound solution through to halide in the absorber solution for IC analysis. Most of the selected organobromine compounds showed complete recoveries of around 100 %. In a chlorination experiment of an aqueous solution containing standard DOM and bromide, the recovery of the initial bromide as the measured total bromine (sum of AOB_r and bromide after quenching) was excellent at all times over the 1 h experimental period, demonstrating very low errors in AOB_r measurements and giving an excellent mass balance of bromine in the system. The halogen-specific AOB_r method therefore provides an accurate measure of the AOB_r formed in the system. This is the first report of the use of a mass balance approach for halogen-specific AOX method validation.

The modified halogen-specific AOX method was successfully used to monitor the conversion of bromide in the raw source water to bromine species (AOB_r or inorganic bromine species (HOBr/bromide), measured as bromide after quenching) at various treatment stages in a groundwater treatment plant. Good recoveries (mass balance) of total measured bromine (compared to initial bromide concentration) supported the validity of the halogen-specific AOX method, especially for AOB_r measurement in drinking water systems. These field results also showed that the extent of bromine incorporated in DOM as AOB_r was influenced by the chlorine added and the remaining bromine and DOM concentrations after treatment processes. These results provided useful insights into the treatment conditions that promote the formation of AOB_r and AOX in general.

The rigorous validation of the halogen-specific AOX method and, in particular, the good mass balances of total bromine that were consistently obtained in both real and

synthetic samples provide considerably increased confidence in AOX measurements. Validation of the halogen-specific AOX method using bromine mass balances in real samples has not been previously published to the extent shown in this Thesis. The rigorous method validation is of significant benefit to studies of the toxicology of AOB_r which will eventually feed in to health guidelines on the safe limits of brominated compounds in drinking water. In this context, the Thesis should have significant indirect benefits to the water and health sector and the community in general.

The formation of AOB_r from dissolved organic matter (DOM) extracts in chlorination and bromination experiments was investigated to elucidate the mechanisms of its formation under relevant water treatment conditions. As has been well established, AOB_r formed as a result of reaction between bromine and DOM, primarily through electrophilic substitution and addition reactions. In addition, it was shown in this study that bromine could also oxidise DOM reactive sites and release bromide through electron transfer. Depending on the availability of the oxidant (i.e. chlorine) in the solution, bromide could be re-oxidised and recycled to again form bromine, which could react further with DOM to form additional AOB_r. In bromination experiments, where synthetic waters containing DOM were treated directly with bromine, only 40% Br-incorporation (AOB_r formation) was observed, and the majority of bromine was reduced to bromide in redox reactions with DOM. This showed that the main pathway in bromination experiments was oxidation. However, in chlorination experiments, where synthetic waters containing bromide and DOM were treated with chlorine, much greater proportions of the bromide formed AOB_r (i.e. 85 % Br-incorporation occurred), due to the influence of bromide recycling. Unlike bromination, in chlorination experiments, it was possible to recycle the reduced bromide, due to the presence of excess chlorine residual, to HOBr for further reaction with DOM.

The maximum formation of potentially harmful brominated organic compounds (AOB_r) is therefore likely to be obtained for high chlorine concentrations during disinfection of bromide-containing water, since this situation allows constant bromide recycling and therefore almost 100 % bromine incorporation in DOM. In drinking water distribution systems where a disinfectant residual ($\sim 1 \text{ mgCl}_2 \text{ L}^{-1}$) is

needed over a long period of time, high disinfectant concentrations are usually applied to ensure optimal disinfection over long distances through the distribution system. However, applying high doses of disinfectant to bromide-containing waters will quickly produce potentially harmful organic bromine (AOBr) in high concentrations, while organic chlorine (AOCl) will also be continuously formed.

These studies provided valuable insights into the mechanisms and chemical processes occurring in chlorinated water and the key role of free chlorine as an oxidant in the formation of AOBr. They also highlight the need for further study of the role of bromide in the reactions of chlorine: the consumption of chlorine to produce bromine which eventually is consumed as AOBr may well contribute to chlorine decay and may influence the rates of chlorine decay reactions.

The formation of AOBr in both bromination and chlorination experiments was shown to be affected by the characteristics of the DOM. Higher AOBr concentrations were produced from high SUVA₂₅₄ DOM than from low SUVA₂₅₄ DOM during bromination and chlorination, as bromine reacted quickly with DOM containing a high proportion of aromatic structures. Another key finding in this study was that the regulated THM, bromoform, did not always represent the behaviour of AOBr, demonstrating that bromoform is a poor surrogate for brominated organic DBPs. It was found that the general trends for bromoform formation followed AOBr formation in the bromination of different types of DOM. However, in chlorination experiments where chlorine was applied in excess, this was not the case. Therefore, for the accurate measurement of brominated DBPs formed in treated drinking waters, both the regulated THMs and AOBr need to be analysed. Again, these observations also have strong implications for health regulators engaged in the development of guidelines for drinking water quality: this study has not only provided clear evidence that bromoform concentrations cannot be used to estimate concentrations of total organobromine DBPs, it has also provided key insights into the chemical mechanistic basis for this conclusion.

Subsequent studies in this Thesis further demonstrated the important role of chlorine in the formation of AOBr, specifically the role of competition between chlorine and bromine for reactive DOM sites. In the presence of excess chlorine, bromide in water

samples was oxidised to bromine and reacted with DOM to form AOB_r until a maximum concentration was reached. However, even though AOB_r concentrations plateaued, AOCl continued to increase. Pre-chlorination followed by the addition of bromine was found to enhance the formation of AOB_r to almost 100% Br-incorporation, which was contrary to the expectation that the pre-chlorination step would limit the number of DOM reactive sites available for reaction with bromine and thus reduce the formation of AOB_r.

The enhancement of AOB_r formation was observed under different pre-chlorination scenarios followed by the addition of bromine. High concentration pre-chlorination of synthetic waters containing DOM for different times resulted in only 9 to 14 % of chlorine being incorporated into DOM reactive sites and forming AOCl during the pre-chlorination time. The Cl-incorporation only slightly increased to 13 – 16 % after bromine addition (i.e. total of 2 h HOCl contact time). The addition of bromine to the chlorinated samples resulted in more than 96 % Br-incorporation. At lower concentration pre-chlorination, lower Br-incorporation was observed (65 %). The addition of bromine at different concentrations following pre-chlorination also exhibited maximum Br-incorporation (95 %). The addition of bromide instead of bromine showed similar Br-incorporation to samples where bromine was added following pre-chlorination. Extended pre-chlorination of synthetic waters until all chlorine was consumed for maximum AOCl formation, followed by the addition of bromine, showed a different trend in AOB_r and AOCl formation, with increasing AOB_r concentrations, and simultaneously decreasing AOCl concentrations, with increasing initial bromine concentrations.

This trend in AOB_r and AOCl formation could be explained by two possible reaction pathways. The first pathway involved the reaction of HOBr and DOM in substitution/addition reactions to form AOB_r, as well as the oxidation of chlorinated DOM intermediates (measured as AOCl) by HOBr, where the Cl substituent was removed in the oxidation process. The second pathway involved the oxidation of DOM by HOBr, as well as the reaction of HOBr with DOM in substitution/addition reactions to form AOB_r, including DOM already in the form of AOCl, where chlorine substituents were replaced with bromine substituents, essentially converting some AOCl to AOB_r. Both hypothesised pathways may operate in the reaction

mixture. A model compound experiment with HCB, where the formation of bromoform was observed, provided some evidence for the second pathway. The second pathway was utilised for empirical modelling to study and define the various pathways leading to AOB_r formation in order to model the experimental outcomes.

An empirical kinetic model was successfully developed and validated for simulation of AOB_r formation. This is the first report of a comprehensive study using modelling software to simulate AOB_r formation from various reaction pathways. Simple multiple step reactions for AOB_r formation and their second order rate constants were proposed based on the reported reactivity of bromine and chlorine with organic moieties and by fitting of experimental data. Different DOM reactive sites were introduced to accommodate different reaction pathways between bromine/chlorine and DOM for AOB_r formation. Simulation of AOB_r formation using the model fitted well with the experimental data obtained from different disinfection scenarios. The model supported the role of bromide recycling in the formation of HOBr, the possible existence of reactive sites reacting only with HOBr for AOB_r formation and the proposed pathway for AOB_r formation through replacement of chlorine in DOM (AOCl) by bromine.

While the requirement for effective control of pathogen risk means that it is critical to maintain disinfectant residuals in drinking water distribution systems, this study has shown that high concentration pre-chlorination or final-chlorination of bromide-containing waters could lead to increased formation of brominated DBPs, a potential health concern. Since bromine is more reactive and a better halogenation agent than chlorine toward DOM reactive sites, it is difficult to prevent formation of AOB_r during chlorination of waters containing DOM and bromide. Trials to minimise AOB_r using a prechlorination step found that this in fact exacerbated the problem by leading to increased brominated organic compounds. Further research is needed to study the reactions between bromine and DOM in the presence of chlorine, particularly the mechanism(s) that account for the observation of AOB_r increasing and AOCl increasing with increasing HOBr concentration, which have not yet been unequivocally identified. While a preliminary investigation was carried out by studying the potential for replacement of chlorine by bromine using hexachlorobenzene as a model compound, alternative hypotheses should also be

investigated. In addition, the behaviour of bromine in the presence of organic chloramines should be studied since organic chloramines may play a role in this apparent replacement of chlorine with bromine in DOM. Since covalent bonding between nitrogen and halogen (i.e. chlorine) is weaker than between carbon and chlorine, a direct substitution of chlorine by bromine may be possible in organic chloramines. Moreover, the influence of other oxidants (i.e. ozone, chlorine dioxide, and monochloramine) as a pre-oxidation agent before the addition of bromine should be studied as potential strategies for mitigation of AOB_r.

Growing evidence, both in this study and in previous studies, that the regulated brominated THMs do not represent the behaviour of brominated organic compounds (AOB_r) in drinking water should drive regulators to consider AOX as a key water quality indicator. The studies in this Thesis have significantly contributed to the body of work validating AOX measurements as robust and accurate indicators of bromine speciation in drinking water. Due to the potential health impacts of brominated organic compounds (AOB_r) in drinking waters, minimisation of AOB_r in drinking water treatment plants and distribution systems is essential. The halogen-specific AOX method provides an important tool to monitor and better understand the formation and fate of halogenated organic compounds, in particular the potentially more problematic AOB_r, in drinking water systems. The halogen-specific AOX method provides comprehensive information about the overall incorporation of halogen into organic compounds, rather than the incorporation of halogen into a few small individual DBP molecules (e.g. THMs and HAAs), as are currently monitored and regulated. These specific DBPs have been reported to contribute only 50 % of total AOX formed in drinking waters. It is therefore recommended that drinking water utilities consider inclusion of halogen-specific AOX analysis in their monitoring regimes. Further studies of halogen-specific AOX formation in drinking water systems as related to health impacts (e.g. epidemiological studies) would allow governments and health regulators to consider developing new guideline values for AOX concentrations in drinking waters.

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