



Curtin Water Quality Research Centre

Novel Treatment Technologies for the Minimisation of Bromide and Iodide in Drinking Water

Final report for ARC Linkage Project 100100285

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Technology transfer workshops and/or formal steering group project meetings with all industry and international partners were held on a quarterly basis to discuss project progress, report on work completed and to plan future directions of work packages. The project outcomes were also provided to the industry partners in written format through published papers, interim reports to industry, and this comprehensive final report. In addition to this published report, a range of other outputs has resulted from this project, including five peer reviewed articles published in national and international journals, four refereed conference proceedings, ten unpublished conference presentations and seven reports to industry, as well as several technology transfer sessions to industry partners. Two more journal articles have recently been submitted to high impact journals (one to Water Research and one to Environmental Science and Technology) and another three are in various stages of preparation.

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Executive Summary

This is the final report for ARC Linkage Project 100100285: “*Novel Treatment Technologies for the Minimisation of Bromide and Iodide in Drinking Water*”. The original objectives of this project were:

- To better understand the impact and occurrence of high concentrations of bromide and iodide in source waters.
- To develop innovative new water treatment processes to selectively remove both bromide and iodide from potable water sources that are relatively easy to install and operate and that are economically viable for installation at both metropolitan and regional schemes.
- To determine if reducing the bromide and iodide concentration reduces the concentration of DBPs and improves the organoleptic properties of chlorinated and chloraminated finished waters.

A survey of the concentrations of bromide, iodide and dissolved organic carbon (DOC) in many Western Australian drinking water source waters was conducted. The bromide concentrations ranged from 400 µg/L to 8450 µg/L, while iodide concentrations ranged from less than 5 µg/L to 593 µg/L. This survey demonstrated the significant concentrations of the disinfection by-product (DBP) precursors, bromide and iodide, in many Western Australian source waters, challenging the production of drinking water meeting the Australian Drinking Water Guidelines for DBPs. The concentrations of dissolved organic carbon (DOC) ranged from 0.4 mg/L to 16 mg/L.

Distributed waters from two Western Australian drinking water sources were evaluated in terms of their bromide and iodide concentrations (in the source waters), disinfection by-product (DBP) formation, halogen-specific adsorbable organic halogen (AOX) formation and aesthetic properties after disinfection. The first water was a groundwater (GW) from the south-eastern region of Western Australia containing high bromide (750 µg/L) and iodide (70 µg/L) concentrations and a relatively low DOC (1.2 mg/L) concentration. The second water was a surface water (SW) containing a moderate DOC (3.5 mg/L) concentration and high bromide (400 µg/L) and iodide (90 µg/L) concentrations. Both source waters were disinfected using chlorine prior to distribution. In both the GW and SW distribution system samples, the more toxic brominated DBPs dominated the measured DBPs. Higher concentrations of bromo- and iodo-DBPs were formed in the SW sample than in the GW sample due to the higher DOC concentration in the SW raw water. For the SW system, all measured DBPs increased further into the distribution system except for the I-THMs. In both cases, the measured DBPs accounted for only 30% of total organohalogens, demonstrating that AOX measurements are essential to provide an understanding of the full formation of halogenated DBPs in drinking water. In both systems, the primary fate of iodide in the raw water after chlorination was conversion to the non-toxic iodate, with only minor concentrations of iodo-THMs formed, highlighting a benefit of using chlorine as the disinfectant when the source water contains iodide.

Evaluation of the aesthetic properties of the distributed waters showed that they both had chlorinous odours above and below the odour threshold concentration (OTC) for free chlorine, confirming previous studies that chlorinous odours were more prevalent in waters with elevated bromide concentrations. No medicinal odours were detected by the panellists as all the iodo-organic compounds were below their OTCs.

The following potential treatment processes for removal or mitigation of bromide and iodide from drinking water source waters were investigated:

- Use of silver (Ag)-based materials for removal of bromide and iodide by formation of immobilised silver halides

- Use of polyphenolic materials for removal of bromide and iodide by formation of immobilised halophenols
- Pre-chlorination/ammonia addition in chloramination for mitigation of iodide issues and subsequent control of regulated DBPs
- Selective oxidation of iodide to iodate, while controlling the formation of bromate, using ozone prior to chloramination for mitigation of halogenated DBPs

Silver materials studied by PI von Gunten and Dr Sánchez-Polo were: silver-doped carbon aerogels, silver-doped cloth and Ag-chitosan membranes. In previous studies, Ag-doped carbon aerogels have shown promise for the removal of bromide and iodide from drinking waters, by formation of the corresponding silver halides on the aerogel, with bromide removal of 1.38 mg (halide)/g (aerogel) and iodide removal of 2.55 mg/g. It must be noted, however, that the presence of DOC and chloride in the water can decrease the efficiency of this removal process. Furthermore, the presence of silver, a highly effective bactericide, on the surface can prevent bacterial mass growth, and the high adsorption capacity of the dissolved organic carbon content of the aerogels give these materials added value as an adsorbent in water treatment. To determine if the Ag-aerogels would be suitable for drinking water treatment, the possible leaching of precursors of the organic polymer and the potential reduction in the concentration of Ag on the surface of the aerogels were investigated during different adsorption/regeneration cycles. Results from the adsorption/regeneration experiments showed that there was no leaching of the organic polymer precursors and the concentration of the silver adsorption sites was not significantly reduced after two adsorption/regeneration cycles. However, one of the drawbacks of the carbon aerogels is the low fraction of Ag that can be used for halide removal. Therefore, this aspect needs to be improved and further research is required to synthesise materials with a higher Ag fraction. In order to produce materials with a higher fraction of silver available for halide binding, the use of silver-based cloth was explored. In this material, the silver is immobilized onto the fabric, ensuring that after the selective adsorption of halide ions, the silver halide would be retained on the cloth and not leach into solution. The removal of iodide by the Ag-cloth was slightly higher (1.7 mg/g) than that for bromide (1.2 mg/g). However, based on current data, it was not possible to determine the fraction of silver in the Ag-cloth which is available for halide removal. The Ag-chitosan membranes showed the lowest halide removal, with bromide removal of 0.95 mg/g and 1.56 mg/g for iodide. Water quality parameters, such as pH and chloride concentration, reduced the halide removal efficiency of the membranes. Thus, while the silver-based materials show promise for halide removal, they still need further development. The economics of applying these materials at plant scale must also be evaluated.

The idea that bromide and iodide could be removed during water treatment by oxidation to bromine and iodine, respectively, and subsequent reaction with polyphenols to form immobilised halophenols was investigated. It was identified as being crucial to choose a phenolic structure where halogen incorporation (halophenol formation) will occur rather than oxidation (to form, e.g., quinones). A detailed study of the reaction kinetics and pathways of a variety of phenols with bromine was conducted, allowing identification of phenolic structures favouring halogen incorporation. Future research will focus on the phenolic functionalities leading to 100% bromine incorporation, as potential monomers for polyphenolic materials for bromide removal in drinking water treatment.

Disinfection with chloramination, where chlorine is added first, followed by ammonia (the chlorine/ammonia process), was shown to reduce the formation of iodo-organic DBPs with sufficient pre-chlorination time (when iodide can be oxidised to non-toxic iodate) compared to the use of preformed monochloramine (where iodide can not be oxidised to iodate). The amount of iodo-DBPs formed depended on water quality parameters, such as the concentration and

nature of the dissolved organic matter (DOM), the bromide concentration, and the chlorine consumption rate. Our study has shown that bromide played an important role in this process, mainly by enhancing the preferred oxidation of iodide to iodate. To evaluate the further applicability of this process, theoretical toxicity calculations were carried out based on the formation of THMs. The results have shown that the chlorine/ammonia process was not always favourable and, in certain circumstances, the use of preformed monochloramine (NH_2Cl) alone was the preferable option. Overall, an increase in the calculated toxicity was observed for low bromide concentrations and/or short pre-chlorination times. However, for highly reactive DOM, the decrease in the theoretical toxicity induced by the conversion of iodide to iodate during the pre-chlorination step was off-set by the toxicity of the regulated THMs. Thus, the mitigation of I-DBPs was not beneficial in this case and preformed monochloramine would be recommended. For DOM with lower reactivity, pre-chlorination reduced the formation of I-THMs and the calculated toxicity of the regulated THMs remained relatively low. In this case, the chlorine/ammonia process would be beneficial.

Ozonation was found to provide several benefits as a pretreatment process before final chloramination of iodide-containing source waters, as ozone selectively oxidises iodide to iodate, thereby minimising the formation of I-DBPs. Ozone can also oxidise I-THMs already present in the treated water. However, bromate formation needs to be carefully controlled. In our experiments, conducted using different raw waters, complete conversion of iodide to iodate, while minimising the bromate formation to below the guideline value of $10 \mu\text{g/L}$, was achieved for a wide range of ozone doses. The water matrix strongly affected the formation of bromate, especially alkalinity and the nature of the natural organic matter (NOM). Bromate formation increased as the alkalinity increased, and the consumption of ozone increased with the aromaticity of the NOM, thus a higher ozone dose was required for waters with high SUVA_{254} values.

Key Outcomes for Industry

Impact of high bromide and iodide concentrations on finished waters

- For waters with high bromide concentrations, the more toxic bromo-organic DBPs will predominate over the chloro-organic DBPs.
- For waters containing iodide, during chlorination iodide can be oxidised to iodate, the non-toxic sink for iodine, with the presence of bromine catalysing this reaction, thus avoiding I-organic DBP issues. It is important to note, however, that the extent of conversion of iodide to iodate is dependent on the type and concentration of DOM, highlighting that I-organic DBP formation may still occur during chlorination.
- For waters containing iodide, during chloramination iodide can not be oxidised to iodate and I-organic DBP formation occurs.
- High bromide concentrations may play a role in causing chlorinous odours present when the free chlorine concentration is below its odour threshold concentration (OTC) of 0.1 mg/L.

Mitigation of iodide-related problems, such as formation of toxic iodo-organic DBPs

- In iodide-containing waters, the formation of I-DBPs is generally lower during chlorination than in chloramination, as the primary fate of iodide during chlorination is conversion to the non-toxic iodate. However, this process is dependent on other water quality parameters, such as the concentration of bromide, which enhances iodate formation, and the type and concentration of NOM.
- Potential solutions for the mitigation of I-organic DBP formation during chloramination have been identified and developed in this project:
 - Chlorine followed by ammonia addition (i.e. the chlorine/ammonia process) for chloramination (rather than using preformed monochloramine) can be valuable to water utilities for the mitigation of iodide-related problems provided an appropriate pre-chlorination time is applied based on careful consideration of other parameters, such as the concentration of DBP precursors, specifically the concentration of bromide as well as the type and concentration of DOM. The pre-chlorination time should be long enough to ensure full oxidation of iodide to iodate for optimum reduction of I-organic DBPs.
 - Pre-ozonation before chloramination can be useful for reduction of problems arising from source waters with high iodide concentrations.
 - Ozone quickly oxidises iodide to iodate, thereby minimising formation of I-organic DBPs, and the bromate concentration can be controlled to below the Australian drinking water guideline of 10 µg/L, provided the correct ozone dose is used.
 - Ozone can also oxidise I-THMs already present in pretreated water.

Bromide removal from source waters

- While we have developed water treatment processes to mitigate iodide-related problems in drinking water, effective bromide removal from source waters remains a challenge.
- Possible future options for bromide removal involve the use of synthetic clays and layered double hydroxides (LDHs) to remove bromide to low levels (<50 µg/L), with a particular focus on synthesising new LDHs specifically designed for removal of bromide.
- Future studies on better management of bromide-related problems should also aim to develop a better understanding of the chemistry of bromine-related reactions that occur

during oxidative water treatment. In a Water Corporation funded project (PA-005) due to commence in 2015, we aim to investigate oxidation pre-treatment strategies (e.g. ozone (O_3), permanganate (MnO_4^-), chlorine dioxide (ClO_2) and ferrate ($Fe(VI)$)) to decrease the reactivity of dissolved organic matter to form DBPs, particularly brominated DBPs, upon final disinfection.

- The influence of bromide on the stability of the disinfectant residual in drinking water disinfected by monochloramine (NH_2Cl) should also be investigated. In a submitted ARC linkage project proposal (ARC LP150101161), we have proposed studies aimed at elucidating the mechanisms and kinetics of halamine formation and its decay during chloramination of bromide-containing waters.

Acronyms and Abbreviations

AOX	Adsorbable organic halogen
AOBr	Adsorbable organic bromine
AOC1	Adsorbable organic chlorine
AOI	Adsorbable organic iodine
Br-Org DBPs	Bromo-organic disinfection by-products
CWQRC	Curtin Water Quality Research Centre
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
GWTP	Groundwater treatment plant
HAAs	Haloacetic acids
HANs	Haloacetonitriles
HOBr	Hypobromous acid
HOI	Hypoiodous acid
HOX	Hypohalous acid
HS SPME-GC-MS	Headspace solid-phase microextraction-gas chromatography-mass spectrometry
IC	Ion chromatography
I-Org DBPs	Iodo-organic disinfection by-products
I-THMs	Iodo-trihalomethanes
NOM	Natural organic matter
OTC	Odour threshold concentration
THMs	Trihalomethanes
WCWA	Water Corporation of Western Australia

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1.0 Introduction

Some Australian drinking water source waters, particularly those in Western Australia, contain high concentrations of natural organic matter (NOM), as well as elevated concentrations of bromide (Br^-) and/or iodide (I^-). These waters have the potential to form bromo- and iodo-organic disinfection by-products (DBPs) upon disinfection, which are thought to be generally more hazardous to human health than the chlorinated analogues (Richardson *et al.*, 2008), highlighting the importance of managing the inorganic precursors in source waters, in addition to NOM removal. In addition to being more toxic than their chlorinated analogues, the bromo- and iodo-organic DBPs can induce taste and odour issues in the finished waters (Hansson *et al.*, 1987; McDonald *et al.*, 2013). For example, iodo-trihalomethanes (I-THMs), especially iodoform (CHI_3), have been associated with a characteristic medicinal taste and odour which may appear in finished drinking water (Hansson *et al.*, 1987). The iodo-trihalomethanes have low organoleptic threshold concentrations ranging from 0.03 to 8.9 $\mu\text{g/L}$, with the lowest concentration being for CHI_3 (Cancho *et al.*, 2001).

Natural processes, such as salt water intrusion and water from special geological formations, as well as pollution from increasing industrial activities, may elevate both bromide and iodide levels present in natural waters (von Gunten, 2003b; Agus, *et al.*, 2009). It has been reported that high bromide concentrations tend to originate from freshwaters in arid regions with high rates of evaporation, including South-Western Australia, the Mediterranean and Western United States (Agus *et al.*, 2009). While bromide concentrations in drinking water source waters can vary from just a few micrograms per litre ($\mu\text{g/L}$) to as much as several milligrams per litre (mg/L) (von Gunten and Hoigné, 1994), iodide concentrations are generally fairly low ($< 10 \mu\text{g/L}$) and are usually lower than chloride and bromide concentrations (von Gunten, 2003b; Agus, *et al.*, 2009). However, in some cases, iodide concentrations can reach levels of $\geq 50 \mu\text{g/L}$ due to special geological formations or seawater intrusion (von Gunten, 2003b).

Bromide and iodide present in source waters react differently with different disinfectants. The fate of bromide and iodide during oxidative drinking water treatment processes is shown in Figure 1. During chlorination, bromide reacts with the free chlorine (HOCl) to produce hypobromous acid (HOBr), which may then react with NOM to form bromo-organic DBPs (Br-Org DBPs). When ozone (O_3) is used as the disinfectant, HOBr is further oxidised to bromate (BrO_3^-), a potential human carcinogen, hence ozone application is often limited in bromide-containing waters (von Gunten, 2003b). Iodide also reacts quickly with free chlorine to form hypoiodous acid (HOI), which can then react with NOM to form the more toxic iodo-organic DBPs (I-Org DBPs). In the presence of excess free chlorine or during ozonation, HOI is further oxidised to iodate (IO_3^-), a non-toxic, and thus preferred, sink for iodine (Bichsel and von Gunten, 1999; Allard *et al.*, 2013). Unlike chlorine and ozone, monochloramine (NH_2Cl) is not able to oxidise the formed HOI to iodate and thus formation of iodo-organic DBPs occurs during chloramination of iodide-containing waters (Bichsel and von Gunten, 1999).

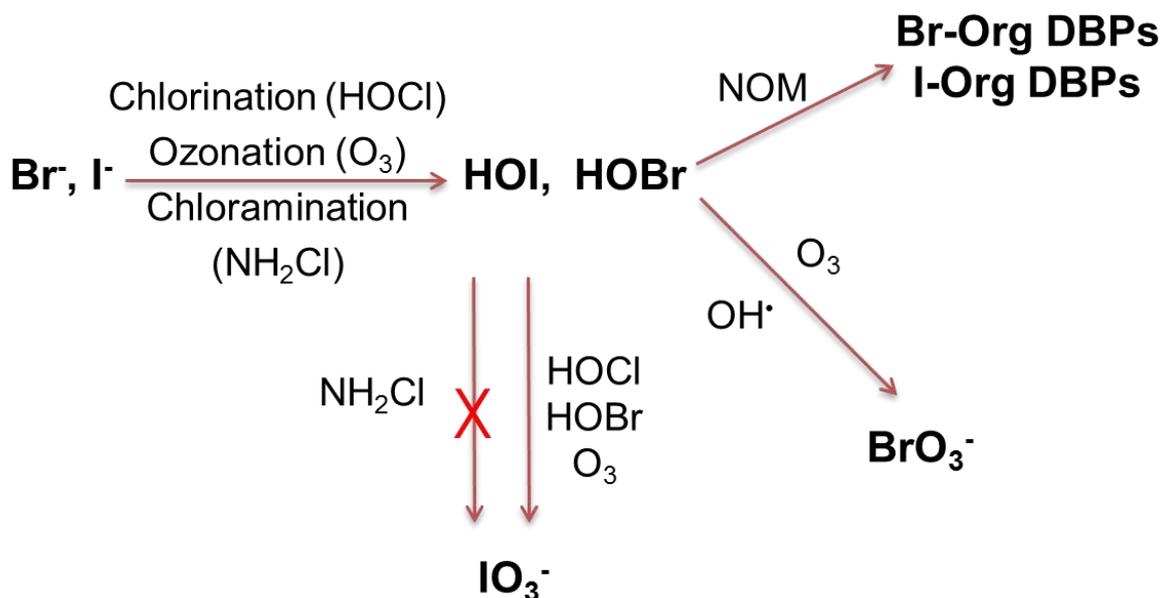
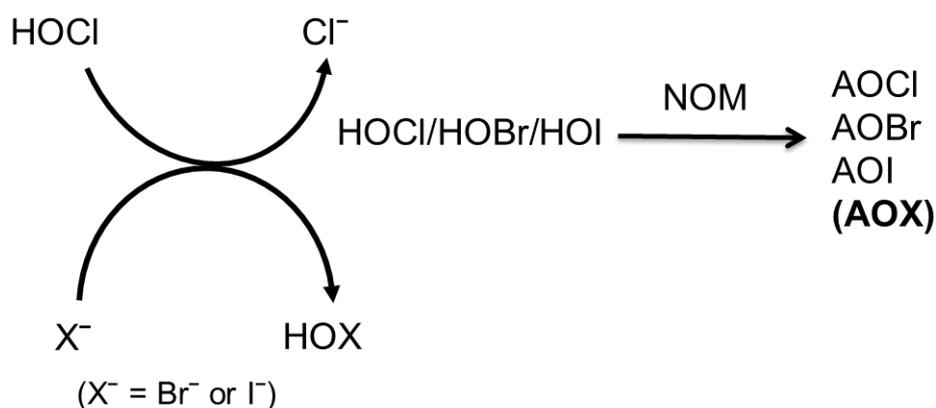


Figure 1. The fate of bromide and iodide during oxidative drinking water treatment processes (modified from Bichsel and von Gunten, 1999).

Halogenated DBPs can be measured as individual species, e.g. THMs, haloacetic acids (HAAs) and haloacetonitriles (HANs), or in a bulk measurement such as halogen-specific adsorbable organic halogen (AOX). Halogen-specific AOX provides a measure of all of the individual halogens (Cl, Br, I) incorporated into organic compounds in a sample. The measurement of halogen-specific AOX in drinking water is an alternative to the analysis of individual DBPs, since analytical methods do not exist for many of the individual compounds that comprise AOX. The formation of AOX in chlorinated waters is illustrated in Figure 2, where AOX consists of the halogen incorporation (AOCl, AOBr and AOI) into known and unknown DBPs.



AOX = Halogen incorporation into known DBPs and unknown DBPs

Figure 2. Formation of AOX in chlorinated waters.

In chlorinated waters, the measured individual DBPs have been reported to account for only 40-70% of the total AOX (Pressman, *et al.*, 2007; Richardson, 2011), while in chloraminated waters, less than 20% of AOX can be assigned to individual species of DBPs, according to Hua and Reckhow (2007). AOX is particularly useful for evaluating the overall formation of halogenated DBPs in waters disinfected using halogen-based disinfectants, such as chlorine and chloramines, or in waters containing high concentrations of halide ions.

The formation of organic DBPs can be minimised by removal of their precursors (NOM and halides), optimisation of the disinfection parameters to minimise their formation or removal of DBPs after their formation. Treatment of water to remove DBP precursors (NOM, bromide and iodide) prior to disinfection and distribution is by far the most effective approach to solving the dual problems of disinfectant loss and DBP formation. Different disinfection methods can produce different known and unknown DBPs, however, minimising the availability of precursors for their formation is applicable regardless of the disinfection process used, thereby minimising the formation of all DBPs (Watson *et al.*, 2012). Although aeration has been used to remove THMs after they have formed (Trolio *et al.*, 2007), the efficiency of this process can be highly variable and depends on the THM concentration and air and water flow rate (Hua and Yeats, 2010), and the process simply transfers the THMs to the atmosphere, impacting the environment. Furthermore, the difficulty of THM removal using aeration increases with increasing molecular weight from chloroform to bromoform, since the Br-THMs are much less volatile than the Cl-THMs (Symons *et al.*, 1981; Hua and Yeats, 2010). Also aeration does not remove THM precursors (Symons *et al.*, 1981), and does not remove the less volatile DBPs, such as haloacetic acids (Brooke and Collins, 2011). This is a particular issue since the concentration of THMs is often used as an indicator of the overall halogenated DBP concentration, but if the THMs are selectively removed by aeration, their resultant low concentration will no longer represent the overall halogenated DBP concentration remaining in the water.

While there are several treatment processes for effective removal of NOM (e.g. Hammes *et al.*, 2006; Warton *et al.*, 2007), currently there are no economical and effective methods for the removal of bromide and iodide from natural waters. Methods for bromide and iodide removal which have been studied previously include: membrane, electrochemical and adsorptive techniques (Watson *et al.*, 2012). Membrane techniques, particularly reverse osmosis, have proven to be effective in the removal of both halides and NOM (Magara *et al.*, 1996; Xu *et al.*, 2008), however, these techniques can be expensive and not energy efficient (Watson *et al.*, 2012) and subject to membrane fouling issues. Electrochemical techniques (e.g. electrolysis, capacitive deionization (CDI) and membrane capacitive deionization (MDCI)) have also been shown to have good halide removal capabilities, however they do not efficiently remove NOM, which is also vital for minimising formation of DBPs (Watson *et al.*, 2012). In addition, application of electrochemical techniques for halide removal during drinking water treatment may be limited due to potential difficulties in scaling up the process. However, this has not yet been investigated (Watson *et al.*, 2012). Studies on bromide and/or iodide removal using adsorption techniques (e.g. silver impregnated activated carbon and carbon aerogels, ion-exchange resins and alum coagulation) have shown that most of these methods can reduce the concentrations of these ions to varying extents, however their efficiency was limited by interference from NOM and/or competition from other ions present at higher concentrations (Watson *et al.*, 2012 and references therein).

1.1 Project Aims

The aims of this project were:

- To better understand the impact and occurrence of high concentrations of bromide and iodide in source waters.

- To develop innovative new water treatment processes to selectively remove both bromide and iodide from potable water sources that are relatively easy to install and operate and that are economically viable for installation at both metropolitan and regional schemes.
- To determine if reducing the bromide and iodide concentration reduces the concentration of DBPs and improves the organoleptic properties of chlorinated and chloraminated finished waters.

1.2 Project Scope

The work in this project was divided into five Work Packages (WPs) as outlined below. Before commencing work on the various work packages, a survey of the concentrations of bromide, iodide and dissolved organic carbon (DOC) in many Western Australian drinking water source waters was conducted. The survey established which sites were still operational and suitable for use in this project and confirmed that the historically recorded bromide and iodide concentrations for these sites were representative of present concentrations, as measured at the Curtin Water Quality Research Centre (CWQRC).

Work Package (WP) 1. Selective removal of bromide and iodide by silver-doped materials.

This process was based on the high affinity of halide ions towards silver. Three types of Ag-based materials were investigated for the removal of bromide and iodide: Ag-doped carbon aerogels; Ag-doped cloth and Ag-chitosane membranes. This work was conducted in Switzerland under the guidance and supervision of PI Urs von Gunten in collaboration with Dr Manuel Sánchez-Polo.

WP 2. Pre-oxidation of bromide and iodide and removal of produced hypobromous and hypoiodous acids on reactive materials.

This process was based on the oxidation of bromide and iodide by chlorine (or chloramine) to hypobromous (HOBr) and hypoiodous (HOI) acids, respectively, and subsequent reaction of these hypohalous (HOX) acids with polyphenolic materials for removal of bromide and iodide from source waters. This work was conducted at Eawag, Switzerland, by Research Fellow Dr Justine Criquet, under the guidance and supervision of PI Prof Urs von Gunten.

WP 3. Selective oxidation of iodide to iodate.

This process was based on the oxidation of iodide to iodate, an inert form of iodine, for the mitigation of iodide-related issues. Most of this work was conducted at the CWQRC, with portions of experimental work for the chlorine/ammonia process conducted at Eawag. Two processes were explored within this WP:

- 1) Chlorine followed by ammonia addition for chloramination (chlorine/ammonia process): process based on chloramination with a sufficient free chlorine contact time followed by ammonia addition, rather than preformed monochloramine, as a mitigation strategy for the minimization of I-DBPs, since exposure to free chlorine should promote the formation of non-toxic iodate.
- 2) Selective oxidation by ozone: this process was based on the oxidation of iodide to non-toxic iodate using ozone. It involved: (a) selection of local waters with elevated iodide concentrations; (b) ozone dose experiments to determine the optimum dose required for complete oxidation of iodide to iodate; and (c) analysis of the ozone treated waters for bromate and iodate, as well as THMs.

WP 4. Comparison of the novel bromide and iodide removal processes with existing methods.

This comparison study was proposed to involve the following: (a) comparative adsorption study of bromide and iodide for silver-impregnated carbon, ion exchange and hydrotalcite-like materials

(capacity and kinetics) in batch systems; (b) influence of water quality parameters (ie. DOC, chloride, alkalinity, pH) on bromide and iodide removal; (c) comparison of the newly developed methods with the methods listed in point (a) above; and (d) comparison of the finished waters from all the bromide and iodide removal methods for taste and odour properties, DBP and AOX formation. Due to the reduction in ARC funding granted and the remaining challenges in developing effective bromide removal methods, subtopics (c) and (d) above were not studied in this project. The influence of water quality parameters (subtopic (b)) was studied for bromide removal with silver-doped materials in WP1 and for iodide removal in WP3. Subtopic (a) forms the basis of Curtin Civil Engineering PhD student Babak Rajaeian's project, commenced in 2014, supervised by CIs Heitz and Joll. His PhD project will also include subtopic (b).

WP 5. Study of source waters in terms of bromide and iodide concentrations, and DBP formation and aesthetic properties after disinfection.

A study of some WA source waters in terms of bromide and iodide concentrations, and their disinfection by-product formation (including specific AOX formation) and aesthetic properties after disinfection, was conducted. To assist with some of the analyses required for this study, a fully automated specific adsorbable organic halogen (AOX) analysis system, comprising a sample preparation module, a combustion module and a dual channel ion chromatographic system, was purchased and commissioned. Analytical methods for the analyses of specific AOX, bromide, iodide, bromate and iodate were developed and optimised. This sophisticated analytical system enabled analysis of specific AOX, as well as analysis of low levels of bromide, iodide, bromate and iodate in water samples.

2.0 Methods and Materials

2.1 Water Samples

Samples of raw and distributed waters were collected from various drinking water source waters in Western Australia. The waters were analysed for iodide, bromide, bromate, iodate and dissolved organic carbon (DOC). Selected samples of distributed waters were analysed for the formation of a suite of DBPs: the regulated trihalomethanes (THMs) (THM4: chloroform, bromodichloromethane, dibromochloromethane and bromoform); I-THMs (dichloroiodomethane, bromochloroiodomethane, dibromoiodomethane, chlorodiiodomethane, bromodiiodomethane and iodoform); haloacetic acids (HAAs: chloroacetic acid, bromoacetic acid, dichloroacetic acid, dibromoacetic acid, bromochloroacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid, trichloroacetic acid and tribromoacetic acid) and haloacetonitriles (HANs: chloroacetonitrile, bromoacetonitrile, dichloroacetonitrile, dibromoacetonitrile, bromochloroacetonitrile, trichloroacetonitrile, tribromoacetonitrile, dibromochloroacetonitrile and bromodichloroacetonitrile). Analysis of halogen-specific adsorbable organic halogen (AOX) and evaluation of the aesthetic properties after disinfection were also conducted. The chlorine equivalent residuals in all distributed waters, except those for aesthetic analysis, were quenched with appropriate quenching agents for the various analyses.

2.2 Reagents and Experimental Methods

Deionized water from an ELGA purification system (resistivity of 18.2 m Ω , [TOC] \leq 1 μ g/L) was used for all experiments. All solvents and reagents used in this study were of analytical grade purity (\geq 99% pure). Iodide, bromide, bromate, and iodate were measured simultaneously via ion chromatography using a Dionex ICS3000 (AG9HC/AS9HC) system, followed by a post-column reaction, according to a published method (Salhi and von Gunten, 1999). The limits of detection (LOD) were calculated using the EPA Method Detection Limit (US-EPA, 2004) and were 5 μ g/L for iodide, 2 μ g/L for bromide, 0.5 μ g/L for bromate, and 1 μ g/L for iodate. DOC concentrations were measured using a Shimadzu TOC-Vws Total Organic Carbon analyser. Trihalomethanes (I-THMs

and THM4) were analysed by headspace solid-phase microextraction coupled with gas chromatography-mass spectrometry (HS SPME-GC-MS) according to our method (Allard, *et al.* (2012a)). The nine species of HAAs were analysed according to US EPA Standard Method 552.2 (US EPA, 1995). HANs were analysed by HS SPME-GC-MS according to our published method (Kristiana, *et al.*, 2012). Analysis of halogen-specific AOX was conducted according to a published procedure (Kristiana *et al.*, 2015; Neale *et al.*, 2012). Odour panel assessments of the disinfected waters were performed as described by McDonald *et al.* (2013). Ozonation experiments were conducted according to Allard *et al.* (2013). Kinetic experiments for iodate formation and chlorine-ammonia addition experiments for THM mitigation in iodide-containing waters were conducted as described by Criquet *et al.* (2012). Experiments of reactions of phenolic compounds and NOM with bromine and chlorine were conducted according to Criquet *et al.* (submitted). Experimental methods for the preparation, characterisation and use of silver-doped organic carbon aerogels were as described in Sánchez-Polo *et al.* (2006; 2007a) and Sánchez-Polo and von Gunten (2014). Preparation and use of silver-doped cloth was as described in Sánchez-Polo and von Gunten (2013; 2014).

3.0 Results and Discussion

3.1 Survey of Bromide, Iodide and DOC concentrations in some Western Australian Drinking Water Sources

A survey of the concentrations of bromide, iodide and DOC in many Western Australian drinking water source waters was conducted. The survey provided information on which sites were still operational and suitable for use in this project and confirmed that the historically recorded bromide and iodide concentrations for these sites were representative of present concentrations, as measured at the CWQRC (Gruchlik *et al.*, 2011a; 2011b). The bromide concentrations were found to range from 400 µg/L to 8450 µg/L, while iodide concentrations ranged from less than 5 µg/L to 593 µg/L (Table 1). DOC concentrations ranged from 0.4 mg/L to 16 mg/L (Table 1).

Bromide concentrations of < 50 µg/L in natural drinking water supplies have been reported as low by Gillogly *et al.* (2001). Moderate bromide concentrations have been reported at approximately 110 µg/L (Ates *et al.*, 2007). Bromide concentrations ranging from 76 – 540 µg/L have been referred to as moderate to high (Boyer and Singer, 2005), and concentrations around 700 µg/L have been described as very high (Hansson *et al.*, 1987). Iodide concentrations in natural waters are generally fairly low (< 10 µg/L) and are usually lower than chloride and bromide concentrations (von Gunten, 2003b). However, in some cases, iodide concentrations can reach levels of ≥ 50 µg/L due to special geological formations or seawater intrusion (von Gunten, 2003b). Based on these previously reported classifications, it is apparent from the results in Table 1 that all of the surveyed sites contain high to very high bromide concentrations, with many of the sites also containing high iodide concentrations. Two of the surveyed source waters contained high DOC concentrations, while the majority of sites had low to moderate DOC concentrations compared to other drinking water sources in Australia. For example, DOC concentrations of 10 to 13 mg/L have previously been reported as high, while DOC concentrations of 5 mg/L have been described as moderate (Fabris *et al.*, 2008).

Table 1. Concentrations of bromide, iodide and DOC in some Western Australian raw source waters (*E* = eastern; *GW* = groundwater; *GWTP* = groundwater treatment plant; *SW*= surface water; *W* = western).

Sample	Bromide Concentration ($\mu\text{g/L}$)	Iodide Concentration ($\mu\text{g/L}$)	DOC Concentration (mg/L)
North-West Coastal GW	8455	594	0.8
Great Southern SW1	847	17	10.2
South-East GW	754	72	1.2
North-West SW	448	31	4.3
South-West SW	400	90	3.5
Perth Metro GWTP raw water	743	31	7.6
Mid-West E GW bore	1460	< LOD*	0.6
Goldfields GW bore 1	977	< LOD	0.8
Goldfields GW bore 2	1385	26	1.2
Goldfields GW bore 3	817	< LOD	0.7
Goldfields GW bore 4	868	< LOD	0.9
Goldfields GW bore 5	717	< LOD	0.9
Perth South Coastal GW bore 1	1483	23	1.0
Perth South Coastal GW bore 2	479	< LOD	2.6
Perth South Coastal GW bore 3	1307	25	1.2
Great Southern SW2	561	6	16.2
Mid-West W GW bore 1	2249	215	0.5
Mid-West W GW bore 2	1908	128	0.4
Mid-West W GW bore 3	2807	493	0.6
Perth Northern GW bore	567	36	2.2
Perth Metro artesian GW	2261	37	1.0

*Limit of detection (LOD) = 5 $\mu\text{g/L}$

3.2 WP 1. Selective Removal of Bromide and Iodide by Silver-Doped Materials.

A process based on the high affinity of halide ions towards silver (Ag) ions was investigated. The solubility products for AgX ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) decrease in the order $\text{AgCl}: K_{\text{so}} = 2.8 \times 10^{-10} > \text{AgBr}: K_{\text{so}} = 5.2 \times 10^{-13} > \text{AgI}: K_{\text{so}} = 8.5 \times 10^{-17}$ (Sánchez-Polo, *et al.*, 2007a; 2007b). This means that even in excess of chloride, which is typical for natural waters, bromide and iodide can be selectively removed from solution as silver halide precipitates. However, the direct application of silver ions in water treatment is not practical, because very fine precipitates are formed which would be difficult to remove downstream of a halide removal process. A particle-bound form of silver is a more practical solution because it would allow halide removal with a packed column or a fluidized bed process. In this study, we have investigated three types of silver (Ag)-containing materials: Ag-doped carbon aerogels; Ag-doped cloth and Ag-chitosan membranes.

3.2.1 Previously reported studies on Ag-doped carbon aerogels

The Ag-doped carbon aerogels were previously studied by PI von Gunten and colleagues (Sánchez-Polo *et al.*, 2006; 2007a; 2007b; Sánchez-Polo and von Gunten, 2013; 2014) for the removal of

bromide and iodide from different waters. Table 2 shows the bromide and iodide adsorption capacities (X_m) reported for different aerogel samples.

Table 2. Adsorption capacities of different aerogels for bromide and iodide (adapted from Sánchez-Polo et al., 2006; Sánchez-Polo and von Gunten, 2014).

Sample	Halide	X_m ($\mu\text{mol/g}$)	X_m ($\mu\text{g/g}$)	Ag sites used (%)
A (Ag-doped carbon aerogel)	Br^-	3.01	238	0.017
A-C (after carbonisation treatment)	Br^-	4.68	370	0.028
A-A (after carbonisation and activation)	Br^-	5.78	457	0.034
A	I^-	1.98	249	0.012
A-C	I^-	3.71	467	0.022
A-A	I^-	5.03	634	0.030

Based on the results in Table 2, it is clear that the carbonisation process, followed by the activation process (sample A-A), significantly increased the adsorption capacity of the aerogels for bromide and iodide. This was reported to be mainly attributable to: (1) an increase in microporosity, which increases the Ag-adsorption sites available for halide binding, and (2) an increase in the basicity of the sample (Sánchez-Polo *et al.*, 2006; Sánchez-Polo and von Gunten, 2014). The results in Table 2 indicate that carbonisation and, in particular, the activation process of the aerogel sample produced an increase in the percentage of Ag(I) sites available for halide adsorption. However, this percentage is still very low (Table 2), suggesting that only a small fraction of Ag is available for the precipitation process.

The influence of NOM and chloride on the adsorption capacity (X_m) of bromide and iodide was also investigated and the results for sample A are shown in Table 3. The presence of chloride and NOM reduced the adsorption capacity of the aerogel samples studied (Sánchez-Polo, *et al.*, 2007a).

Table 3. Influence of NOM and chloride on the halide adsorption capacity (adapted from Sánchez-Polo, et al., 2007a).

Sample	Halide	[DOC] (mg/L)	[Cl ⁻] (mg/L)	X_m ($\mu\text{mol/g}$)	X_m ($\mu\text{g/g}$)
A	Br^-	0	0	3.01	238
A	Cl^-	0	0	7.32	256
A	I^-	0	0	1.98	249
A	Br^-	0	40	1.91	151
A	I^-	0	40	1.33	168
A	Br^-	1.4	4.0	2.44	193
A	Br^-	3.6	3.8	2.04	161

Regeneration of bromide-saturated columns was investigated using ammonia (0.02 M, pH 8), and no major changes in the characteristics of the columns after three adsorption/regeneration cycles were observed (Sánchez-Polo and von Gunten, 2014).

3.2.2 Silver-based materials investigated in this project

Ag-doped organic carbon aerogels

The results of the present study showed that Ag aerogels are materials characterized by an elevated meso- and macro-porosity. Surface area values ranged from 400 to 500 m²/g. Chemical characterization showed that these materials have a high surface acidity (pH_{PZC} = 4.5) and that the oxidation state of Ag is +1. Analysis of the adsorption isotherms of chloride, bromide, and iodide on Ag-doped carbon aerogels indicated that a chemisorption process takes place and that the adsorption capacity (X_m) and affinity of the anion for the adsorbent (BX_m) increases with a reduction in the radius of the anion and an increase in its polarizing power. An increase in the adsorption capacity was also observed, regardless of the anion considered, with an increase in the concentration of Ag(I) on the aerogel surface. The presence of chloride ions and dissolved organic matter in the water reduced the adsorption capacity for bromide and iodide on the samples studied, due to (i) a blocking of the porosity from adsorption of organic matter on the aerogel surface, hampering access of Br⁻ and I⁻ to the surface adsorption sites, and (ii) the competitive effect of Cl⁻ for the same Ag(I) adsorption sites.

The adsorption capacity of the aerogels is considerably reduced when the adsorption is performed under dynamic conditions, although the height of the mass transfer zone of the columns is small and therefore their utility degree is very high. The efficiency of these columns to adsorb Br⁻ or I⁻ was reduced when Lake Zurich or mineral waters were used, because of competitive adsorption of matrix components of these waters.

Regeneration of bromide- and iodide-saturated columns was performed using NH₃ (0.02 M, pH 8), and there was no major change in the characteristics of the columns after three adsorption/regeneration cycles regardless of the type of water considered. According to these results, Ag-doped carbon aerogels are highly promising materials for the removal of bromide and iodide from drinking waters, with a much higher adsorption capacity than that of commercially available activated carbons. More data about this process can be found elsewhere (Sanchez-Polo and von Gunten 2014).

Ag-doped cloth

To produce materials with a higher fraction of silver available for halide precipitation, the use of Ag-carbon cloth was investigated (Sánchez-Polo and von Gunten, 2014). In this material, the silver was immobilized onto the fabric, ensuring that the formed silver halide was retained on the cloth and did not leach into solution. For the Ag-carbon cloth, an oxidant needs to be added to oxidise Ag(0) to Ag(I) which can then bind the halide ions via selective precipitation of the silver halides on the surface of the material. In these experiments, hydrogen peroxide (H₂O₂) was chosen as the mild oxidant for the oxidation of Ag(0) to Ag(I). The silver carbon cloths were prepared by an electrospinning technique where Ag-nanoparticles (Ag-NP or Ag(0)) were added during the base polymer preparation (Sánchez-Polo and von Gunten, 2014).

Figure 3 shows the results for halide removal by Ag-carbon cloth as a function of the hydrogen peroxide concentration. The iodide removal was higher than the bromide removal regardless of the H₂O₂ concentration (Sánchez-Polo and von Gunten, 2014). Increasing the hydrogen peroxide concentration enhanced the halide removal capacity of the Ag-cloth up to a maximum H₂O₂ concentration of 55 µM (1.87 mg/L). Adding higher concentrations of hydrogen peroxide did not improve the halide removal, presumably because Ag(I) was reduced back to Ag(0) with superoxide. If hydrogen peroxide is in excess, competing reactions may occur leading to a steady-state concentration of Ag(I), which then defines the maximum adsorption capacity of the synthesised Ag-cloth (Sánchez-Polo and von Gunten, 2014).

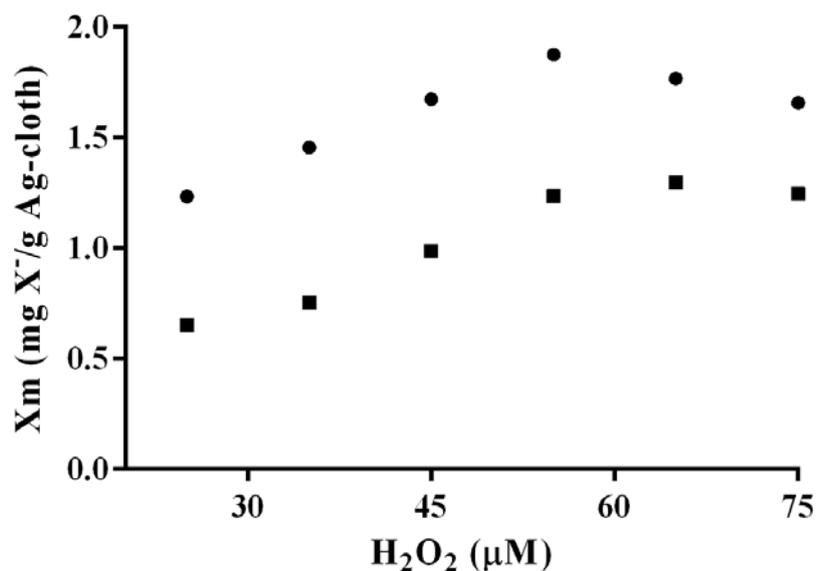


Figure 3. Halide adsorption capacity versus H_2O_2 concentration added for a Ag-cloth. (■), Br^- ; (●), I^- . $[I^-]_0=[Br^-]_0=2.5 \times 10^{-5} M$ (i.e. $[I^-]_0= 3.15 \text{ mg/L}$ and $[Br^-]_0=1.97 \text{ mg/L}$); $[H_2O_2]=25\text{-}75 \mu M$ (0.85-2.55 mg/L); $pH=6.5 \pm 0.5$; Ag-cloth=0.022g \pm 0.002g (adapted from Sánchez-Polo and von Gunten, 2014).

The Ag-cloth showed similar removal efficiency for bromide and iodide. Table 4 shows the effect of the water matrix on bromide removal. Water quality parameters, such as DOC and the presence of chloride, were found to decrease the efficiency of the process (Sánchez-Polo and von Gunten, 2013; 2014). For application of the Ag-cloth materials to real water samples, higher concentrations (≥ 2.55 mg/L) of hydrogen peroxide needed to be added to aqueous solutions because it is required for both silver and organic matter oxidation (Sánchez-Polo and von Gunten 2014).

Table 4. Effect of water matrix on bromide removal by Ag-cloth (adapted from Sánchez-Polo and von Gunten, 2013).

Water	$[Br^-]_0$ (mg/L)	$[H_2O_2]_0$ (mg/L)	mg Br^- removed/g material
Milli-Q water	1.97	2.55	1.25
Wastewater	1.97	2.55	0.83
Milli-Q water with 30 mg/L Cl^- and 5 mg/L TAN*	1.97	2.55	0.88

*TAN = total ammonia nitrogen

The pH range for optimum halide adsorption capacity was found to be pH 3-7 (Figure 4). For higher or lower pH values, a reduction of the removal efficiency was observed (Sánchez-Polo and von Gunten 2014).

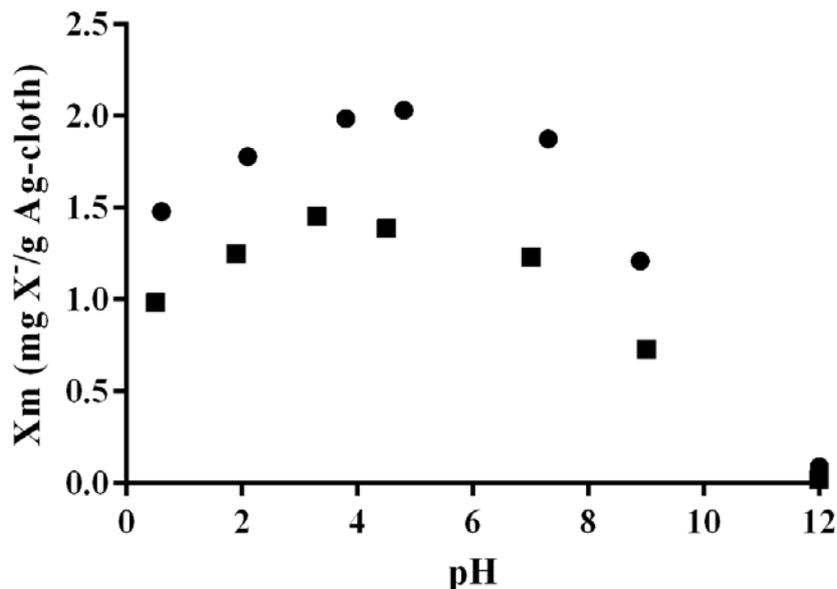


Figure 4. Influence of the solution pH on the bromide and iodide removal by a Ag-cloth. (■), Br⁻; (●), I⁻. $[I^-]_0 = [Br^-]_0 = 2.5 \times 10^{-5} M$ (i.e. $[I^-]_0 = 3.15 \text{ mg/L}$ and $[Br^-]_0 = 1.97 \text{ mg/L}$); $[H_2O_2]_0 = 5.5 \times 10^{-5} \text{ mol/L}$ (1.87 mg/L); pH = 0.5 – 8.9; Ag-cloth = 0.0215 g ± 0.0015 g (adapted from Sánchez-Polo and von Gunten 2014).

Based on current data, it was not possible to determine the fraction of silver in the Ag-cloth which is available for halide removal (Sánchez-Polo and von Gunten 2014).

Ag-chitosan membranes

Different Ag-chitosan membranes were evaluated for halide adsorption. Table 5 shows bromide adsorption of different types of chitosan membranes. The membranes consist of cellulose acetate and Ag-chitosan, where the number indicates the amount of Ag-chitosan added. For example, sample CS20 consists of 20 mg of chitosan and 280 mg of cellulose acetate, while sample CS240 contains 240 mg of chitosan and 60 mg of cellulose acetate (Sánchez-Polo and von Gunten 2013).

Table 5. Bromide adsorption by Ag-chitosan membranes ($[Br^-]_0 = 2.5 \times 10^{-5} M$; 1.97 mg/L) (adapted from Sánchez-Polo and von Gunten, 2013).

Membrane	Br ⁻ adsorbed (μmoles/g)	Br ⁻ adsorbed (μg/g)
CS0	1.86	147
CS20	1.47	116
CS30	2.38	188
CS40	1.79	141
CS60	2.31	182
CS90	2.36	186
CS150	2.38	188
CS240	2.39	189

The CS240 membrane showed the highest bromide adsorption with no silver leaching observed. The maximum uptake of Cl^- , Br^- and I^- by the CS240 membrane was determined (Figure 5), with the highest uptake observed for I^- (Sánchez-Polo and von Gunten, 2013).

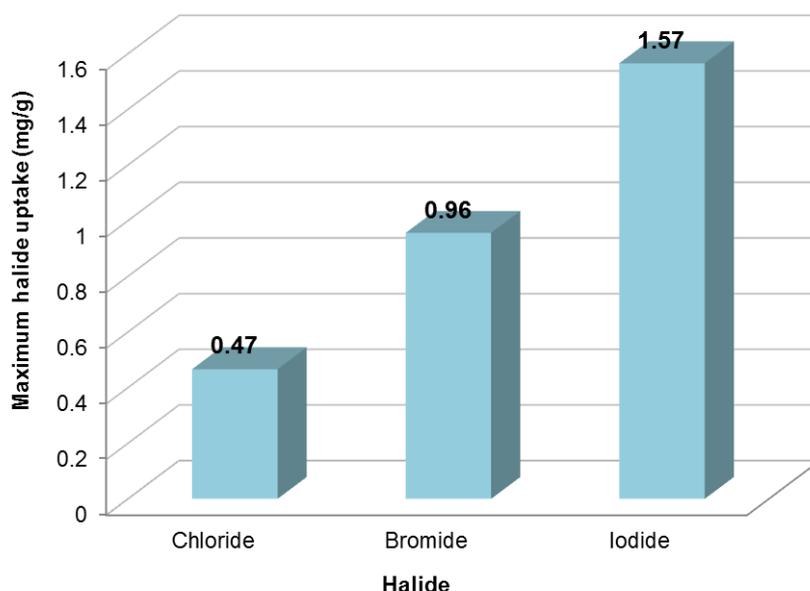


Figure 5. Uptake of chloride, bromide and iodide by a Ag-chitosan membrane ($[\text{I}^-]_0 = [\text{Br}^-]_0 = 2.5 \times 10^{-5} \text{ M}$; $[\text{I}^-]_0 = 3.15 \text{ mg/L}$ and $[\text{Br}^-]_0 = 1.97 \text{ mg/L}$) (adapted from Sánchez-Polo and von Gunten, 2013).

Water quality parameters, such as pH and chloride concentration, again reduced the halide removal efficiency of the membranes (Table 6).

Table 6. Influence of water quality parameters on bromide adsorption by CS240 membrane (adapted from Sánchez-Polo and von Gunten, 2013).

Water matrix	pH	[NaCl] (mol/L)	Br^- adsorption (mg Br^- /g material)
Purified water	2	0	1.23
Purified water	6.7	0	0.96
Purified water	9	0	0.54
Purified water	6.8	0.001	0.68
Purified water	6.8	0.01	0.47
Purified water	6.8	0.1	0.34
Wastewater	7.8		0.65
Milli-Q water with 30 mg/L Cl^- and 5 mg/L TAN*	7.4		0.35

Thus, while the silver-based materials investigated in this study show some promise for halide removal, their halide removal capacity can be reduced by species (e.g. pH, $[\text{Cl}^-]$ and $[\text{DOC}]$) present in real waters. In addition, the very low fraction of silver that is available for halide precipitation may make these materials not viable for large scale application.

3.2.3 Materials currently under investigation for bromide removal

In research ongoing from ARC LP100100285, materials currently under investigation for removal of bromide to low levels (i.e. $<50 \mu\text{g/L}$) include synthetic clays and layered double hydroxides (LDHs), with a particular focus on synthesising new LDHs specifically designed for removal of bromide. This study will involve mechanistic studies on bromide uptake by LDHs, to determine how the chemical properties and physicochemical structure of the different materials affect the selective removal of bromide ions from water. It will involve studies of LDHs both with and without silver incorporation (using silver nanoparticles) and will aim to develop new materials that have the potential for commercial development as water treatment products.

3.3 WP 2. Preoxidation of Bromide and Iodide and Removal of Produced Hypobromous and Hypoiodous Acids on Reactive Materials.

Oxidation of bromide and iodide by chlorine (or chloramine) to hypobromous acid (HOBr) and hypoiodous acid (HOI), respectively, during drinking water treatment and the subsequent removal of the hypohalous acids (HOX) by reaction with reactive materials (e.g. polyphenols) to form immobilised halogen-substituted structures was investigated. The rate constants for the reactions of HOBr and HOI with activated aromatic systems are orders of magnitude higher than those of HOCl (Lee *et al.*, 2005). Therefore, even though HOCl is always in large excess under water treatment conditions, the combination of its lower reactivity and a pH shift to ≥ 8.5 , for which mainly the non-reactive OCl^- is present, enables HOBr and HOI to be the main reactive species. Thus, preoxidation of bromide and iodide to the corresponding hypohalous acids, followed by pH adjustment and reaction with an immobilized or phase-separated form of an activated aromatic compound, could be a powerful process for selective removal of bromide and iodide. The bromide/iodide removal step would ideally be implemented after NOM removal to minimise reactions of HOX with NOM. This proposed process can be modelled on the reactivity of the hypohalous acids with phenols, where the reaction rates are pH dependent (Acero *et al.*, 2005; Bichsel and von Gunten 2000). One of the main types of products of the reaction of HOX with phenols are the halogenated phenols, which are even more reactive than phenol, due to their lower pK_a values due to the electron withdrawing effect of the halogen group (Acero *et al.*, 2005). Under drinking water treatment conditions, the use of dissolved phenols is not possible due to the formation of by-products such as iodo- and bromo-phenols and THMs (Acero *et al.*, 2005). Therefore, the phenols would need to be immobilised by polymerisation into polyphenols. Depending on the experimental conditions, the size and structure of the polymer can be varied from a polymer with a few phenolic rings up to polyphenol particles.

Initially, to examine the feasibility of using polyphenolic materials for removal of bromide and/or iodide during drinking water treatment, kinetic studies of the reactions of various phenolic compounds (model compounds for polyphenolic materials and moieties within NOM) with bromine and chlorine at various pH were conducted. In general, for phenols at pH 7, the rate constants of reaction with bromine were much higher than those for reaction with chlorine (Criquet *et al.*, submitted).

The propensities for different phenolic compounds and NOM extracts to react with bromine via electrophilic aromatic substitution (EAS) (leading to bromine incorporation, i.e. AOX production, and potentially removal of bromide from water samples) or oxidation (leading to quinone formation and bromide recycling, without removal of bromide from water samples) were examined at pH 7 and 8. The phenolic compounds were present in excess to avoid the further reaction of bromine with the initial products formed (Criquet *et al.*, submitted). A wide range in reactivity was observed (Figure 6), ranging from 100 % bromine incorporation for compounds based on the phenol structure (i.e. one hydroxyl substituent) to almost complete oxidation to the quinone with minimal bromine

incorporation for compounds based on the catechol (1,2-dihydroxybenzene) structure (Criquet *et al.*, submitted).

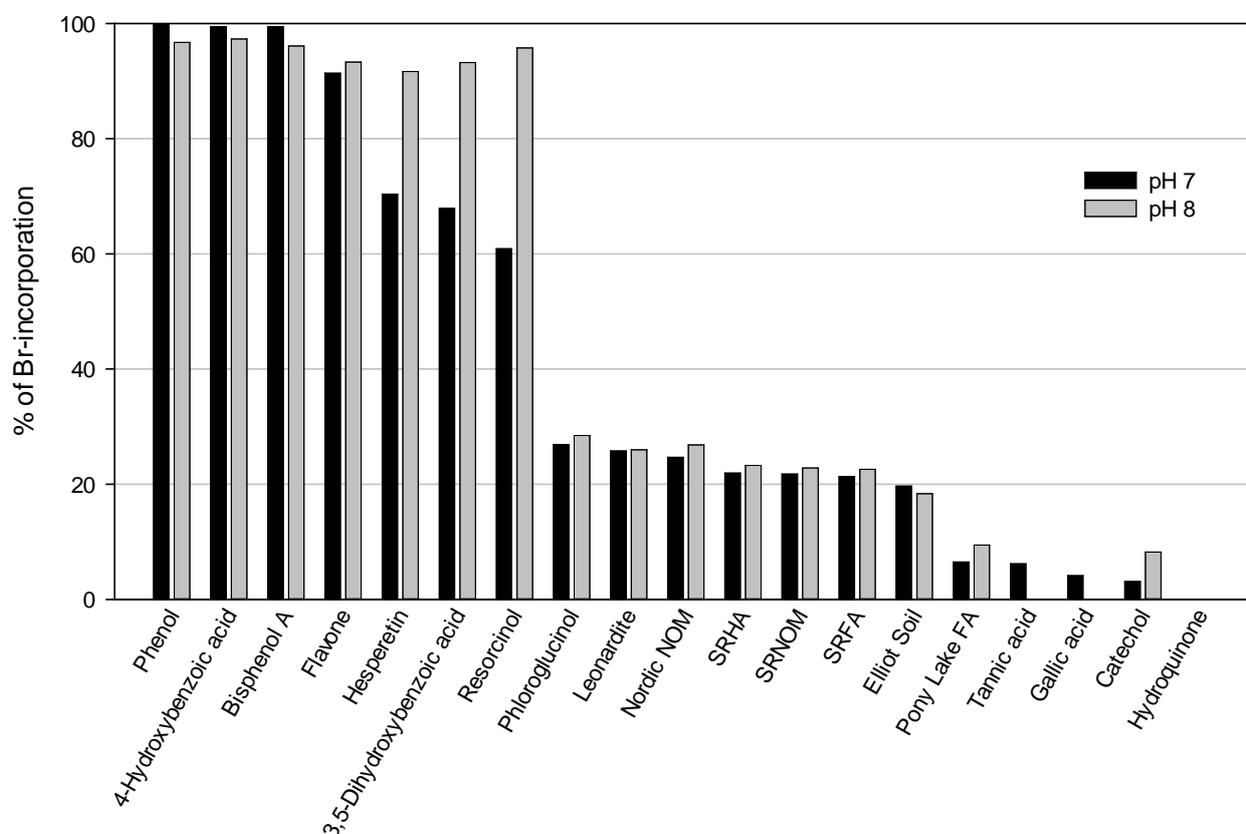


Figure 6: % Incorporation of bromine into phenolic compounds and natural organic matter observed at pH 7 and 8 after the reaction of bromine with an excess of the phenolic compound or natural organic matter extract. (No data available for tannic acid and hydroquinone at pH 8, otherwise no bar means no Br-incorporation observed) (adapted from Criquet *et al.*, submitted).

Moreover, the formation of a quinone structure is not desirable in water treatment applications, since haloquinones were previously predicted as DBPs of potential health concern (Bull *et al.* 2006). Based on the results of this study, to avoid the formation of a quinone, the ideal polyphenolic structure should be based on a phenol (i.e. one hydroxy group) or a resorcinol (1,3-dihydroxybenzene) structure where the hydroxy groups are *meta* to each other. Thus, future research will focus on the phenolic functionalities leading to 100% bromine incorporation as potential monomers for polyphenolic materials for bromide removal in drinking water treatment. For drinking water treatment application, the ratio between chlorination dose and bromide should be assessed. To reduce the risk of DBP formation (e.g. THMs), the phenolic moieties should be in excess compared to HOBr. The challenge and cost associated with synthesising or purchasing a polyphenolic material suitable for this application needs to be evaluated for large scale applications.

3.4 WP 3. Selective Oxidation of Iodide to Iodate.

Two processes based on the selective oxidation of iodide to iodate, the non-toxic and thus preferred sink for iodine, were investigated for mitigation of the formation of I-DBPs during disinfection with monochloramine. The first process was to use monochloramine as the disinfectant, with the monochloramine formed by addition of free chlorine followed by ammonia (chlorine/ammonia

process), rather than using preformed monochloramine. The second process involved selective oxidation of iodide to iodate using ozone as a pre-treatment process before final chloramination.

3.4.1 Pre-chlorination followed by ammonia addition for mitigation of I-organic DBPs in chloramination

A chloramination process, based on a free chlorine contact time followed by ammonia addition, instead of addition of preformed monochloramine, was investigated for reduction of I-organic DBP formation, since short exposure to free chlorine should promote the formation of non-toxic iodate, thereby minimising formation of I-DBPs. The subsequent addition of ammonia and the formation of monochloramine assists in mitigating the formation of other halogenated DBPs (Allard *et al.*, 2012b; Criquet *et al.*, 2012). The role of bromide in this process was also investigated for three different bromide concentrations. Figure 7 shows iodine incorporation into I-THMs (bars) and iodate yield (lines) for different prechlorination times and varying bromide concentrations for chloramination of a Western Australian river water. The free chlorine contact time was varied (0-20 min) such that the full range of conversion of iodide to iodate (from 0% up to nearly 90 %) was achieved and to allow the optimum conditions for minimal formation of I-THMs to be identified (Allard, *et al.*, 2012b; Criquet *et al.*, 2012). The formation of bromine (HOBr) through the oxidation of bromide by chlorine significantly enhanced the oxidation of iodide to iodate in a bromide-catalysed process, thereby decreasing the formation of highly iodinated THMs (Criquet *et al.*, 2012). After the free chlorine contact time, ammonia was immediately added to reduce the formation of bromo- and chloro-organic compounds. To assess the effectiveness of the pre-chlorination/ammonia addition process, the formation of the regulated THMs, as well as the formation of the iodo-THMs, was analysed after 24 hours to simulate contact times in distribution systems (Allard, *et al.*, 2012b; Criquet *et al.*, 2012). The formation and speciation of iodinated THMs was found to depend on the free chlorine contact time and the bromide concentration (Allard, *et al.*, 2012b; Criquet *et al.*, 2012). The chlorine dose was also an important parameter (results not shown) and the pre-chlorination time needs to be long enough to oxidise iodide to iodate. Since the formation of iodate was catalysed by the presence of bromide, a longer chlorine contact time was needed when the bromide concentration was lower. The concentrations of highly iodinated compounds, especially iodoform, were significantly reduced by this process, indicating that this is a valuable process option for mitigation of I-organic DBP formation (Criquet *et al.*, 2012). However, it needs to be noted that, the oxidation of iodide to iodate is also dependent on the type and concentration of the organic matter present in the water, therefore the oxidation of iodide to iodate may be much lower in waters containing high concentrations of organic matter (Criquet *et al.*, 2012).

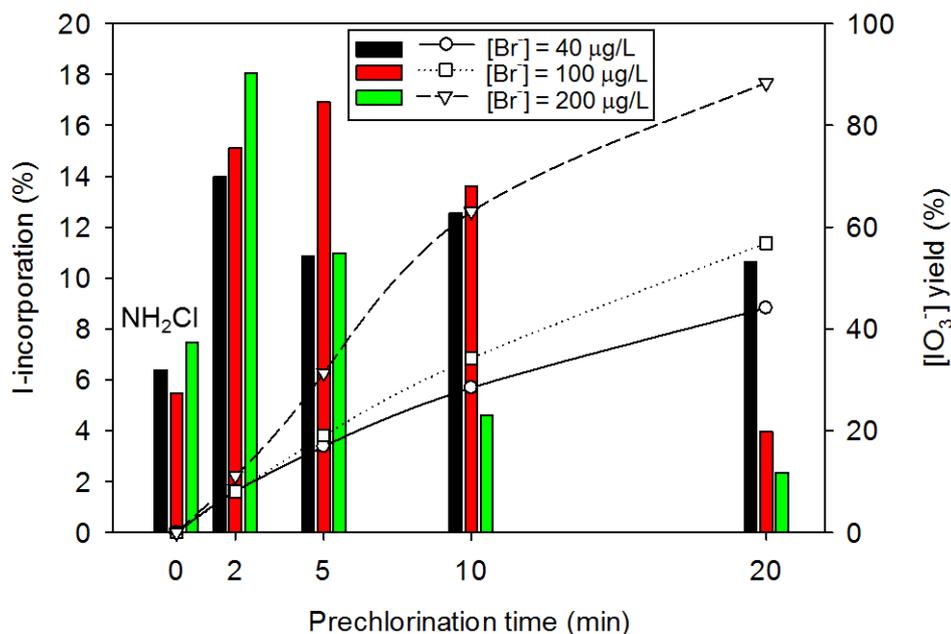


Figure 7. Iodine incorporation into I-THMs (bars) and iodate yield (lines) for different prechlorination times and varying bromide concentrations for chloramination of a Western Australian river water (initial concentrations after dilution and additions: $[I^-] = 50 \mu\text{g/L}$, pH 8, DOC = 1.2 mgC/L). Initial chlorine concentration: 1 mg Cl_2/L (15 μM); ammonia addition: 75 μM . $t = 0$ min, ammonia addition before the addition of chlorine. (Reprinted with permission from Criquet *et al.*, 2012. Copyright 2012 American Chemical Society.)

To further assess the applicability of the chlorine/ammonia process to drinking water treatment and to better understand the fate of iodine during this process, the influence of the major precursors (iodide, bromide and DOM) on the formation and speciation of I-THMs and iodate was investigated (Allard *et al.*, submitted). In this part of the study, DOM extracts from the International Humic Substances Society (IHSS) were used, rather than real waters, to avoid interferences from other constituents of the water matrix. The experiments were conducted using solutions containing iodide at a constant concentration (63 $\mu\text{g/L}$; 0.5 μM), bromide at varying concentrations (80 $\mu\text{g/L}$ to 2 mg/L; 1 to 25 μM) and different types and concentrations (1 to 4 mgC/L) of DOM. In this study, three different disinfection options were explored: (1) concurrent addition of HOCl and ammonia (chloramination); (2) pre-chlorination at different contact times followed by ammonia addition and (3) HOCl alone (Allard *et al.*, submitted). To ascertain whether the use of the chlorine/ammonia process was beneficial in terms of reduction in toxic DBPs, theoretical toxicities of the produced waters were calculated based on the THMs formed.

The experimental results from the chlorine/ammonia process showed that the pre-chlorination time, the bromide concentration and the type and concentration of DOM all played a significant role in the formation of I-THMs and iodate. For waters with low bromide concentrations, a short pre-chlorination time enhanced the formation of I-THMs and the overall toxicity compared to chloramination. In this case, a longer chlorine contact time was required to allow for the full conversion of iodide to iodate and to reduce formation of I-THMs (Allard *et al.*, submitted). However, for waters containing high bromide concentrations, the toxicity related to the formation of Br-DBPs outweighed the benefit of reduced formation of I-THMs when a high chlorine contact time was used. For highly reactive DOM (high SUVA_{254}), the decrease in the theoretical toxicity resulting from the conversion of iodide to iodate during the pre-chlorination step was off-set by the toxicity of the regulated THMs. Thus, the mitigation of I-DBPs was not beneficial in this case and NH_2Cl alone

would be recommended. For DOM with lower reactivity (low SUVA₂₅₄), pre-chlorination was beneficial, however, the chlorine contact time needs to be adjusted based on the concentrations of bromide and DOM to ensure full conversion of iodide to iodate for optimum mitigation of I-DBPs (Allard *et al.*, submitted). It should be noted that, although the theoretical toxicity of the waters in these experiments was based on the THMs formed, the formation of THMs is not representative of the *overall* toxicity. However, it appears that, in the presence of high concentrations of precursors (Br⁻ and DOM), as well as high oxidant exposure, the toxicity will be important and driven by the formation of chloro- and bromo-DBPs (Allard *et al.*, submitted). Although the chlorine/ammonia process may not be applicable to all waters, this process can still be valuable to water utilities for the mitigation of iodide-related problems if an appropriate pre-chlorination time is applied based on careful consideration of other parameters, such as the concentrations of DBP precursors (i.e. bromide and DOM).

3.4.2 Selective pre-oxidation of iodide to iodate using ozone for mitigation of formation of I-organic DBPs in subsequent chloramination

The oxidation of iodide to iodate by ozone, while keeping the bromate concentration below the Australian drinking water guideline value of 10 µg/L (NHMRC, 2011), was investigated (Allard *et al.*, 2012b; Allard *et al.*, 2013). To elucidate the factors affecting iodate and bromate formation, experiments were performed with various waters (Table 7) under different ozonation conditions.

Table 7. Key water quality parameters for the waters in ozonation experiments (adapted from Allard *et al.* (2013)).

	HR	DR	QR	JG
DOC (mgC/L)	2.8	12.0	20.0	3.5
SUVA ₂₅₄ (mgC/L/m)	1.7	4.1	4.9	2.6
Br ⁻ (µg/L)	170	410	400	940
I ⁻ (µg/L)	<LOD	<LOD	<LOD	15
pH	8.6	7.5	6	6.7
SO ₄ ²⁻ (mg/L)	12	20	17	82
Cl ⁻ (mg/L)	50	330	160	255
Ca ²⁺ (mg/L)	25	8	3.4	43
Mg ²⁺ (mg/L)	21	24	10	16
Alkalinity (mg/L CaCO ₃)	146	14	14	86

Ozone pre-treatment selectively oxidised iodide to iodate and minimised the formation of I-DBPs upon subsequent chloramination (Allard *et al.*, 2012b; Allard *et al.*, 2013). Complete conversion of iodide to iodate, while minimising the bromate formation to below 10 µg/L, was achieved for a wide range of initial ozone concentrations in several surface waters which are drinking water source waters (Figure 8). Iodide was completely oxidised to iodate for ozone concentrations of 8 – 14 µM (0.38 – 0.67 mg/L) depending on the water quality (Allard *et al.*, 2013). Bromate formation followed a different pattern, with no bromate formation for ozone concentrations below 14 µM, followed by a linear increase in bromate concentrations for increasing initial ozone concentrations (Figure 8) (Allard *et al.*, 2013). It was observed that, bromate formation increased as the alkalinity increased. As expected, since HOBr was the sole halogenating agent in the pre-ozonation step, the major THM formed during ozonation was bromoform, but traces of CHBr₂Cl and CHBr₂I were also detected (Allard *et al.*, 2013).

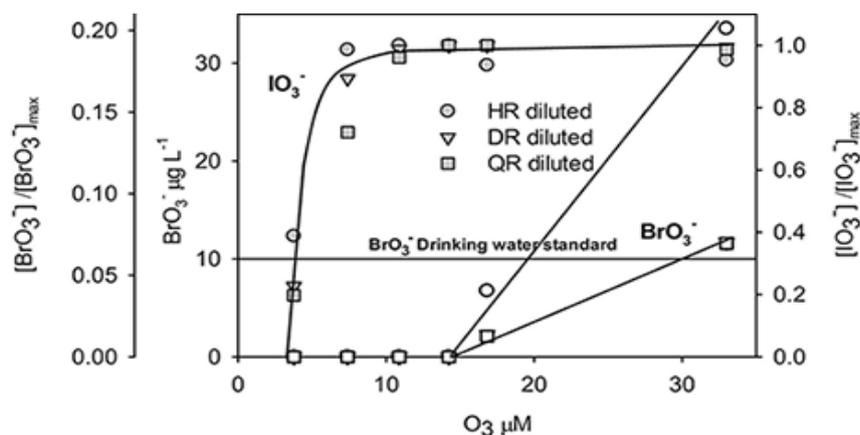


Figure 8. Iodate and bromate formation as a function of the initial ozone concentration for HR, DR and QR surface waters (see Table 7). Experimental conditions: $3.7 \mu\text{M} < [\text{O}_3] < 33 \mu\text{M}$, $[\text{DOC}] = 1.3 \text{ mgC/L}$, $[\text{I}^-] = 50 \mu\text{g/L}$, $[\text{Br}^-] = 100 \mu\text{g/L}$, $\text{pH } 8$ (1 mM phosphate buffer). Open symbols: bromate; filled symbols: iodate. (Reprinted with permission from Allard *et al.*, 2013. Copyright 2013 Elsevier.)

To investigate the behaviour of bromine and iodine species under more realistic conditions, ozonation experiments were performed with water samples collected from a Perth Metropolitan Water Treatment Plant (JG, Table 7) after a pre-chlorination step followed by coagulation, flocculation and clarification (i.e. post-clarifier). In these water samples, THMs were already present due to the pre-chlorination step. Decreasing the pH from 7.5 to 6.5 effectively reduced bromate formation and had no impact on the extent of iodate and bromoform formation (Allard *et al.*, 2013). Concentrations of most of the regular THMs were unaffected by the ozonation process, since these THMs do not react with ozone (von Gunten 2003a); however, the concentration of bromoform increased with increasing initial ozone concentration (Allard *et al.*, 2013). It was also demonstrated that all the I-THMs present in the water were efficiently oxidised during ozonation of chlorinated and post-clarified water (Figure 9). Thus, pre-ozonation provides several benefits for drinking water treatment of iodide-containing source waters, as it can selectively oxidise iodide to iodate, thereby minimising the formation of the more toxic I-DBPs in a subsequent disinfection step (chloramination), and it can also oxidise I-THMs if they are already present in the water. Furthermore, by carefully controlling the initial ozone concentration, it is possible to keep the bromate concentration below the Australian drinking water guideline ($10 \mu\text{g/L}$), even for source waters with high bromide concentrations (Allard *et al.*, 2013).

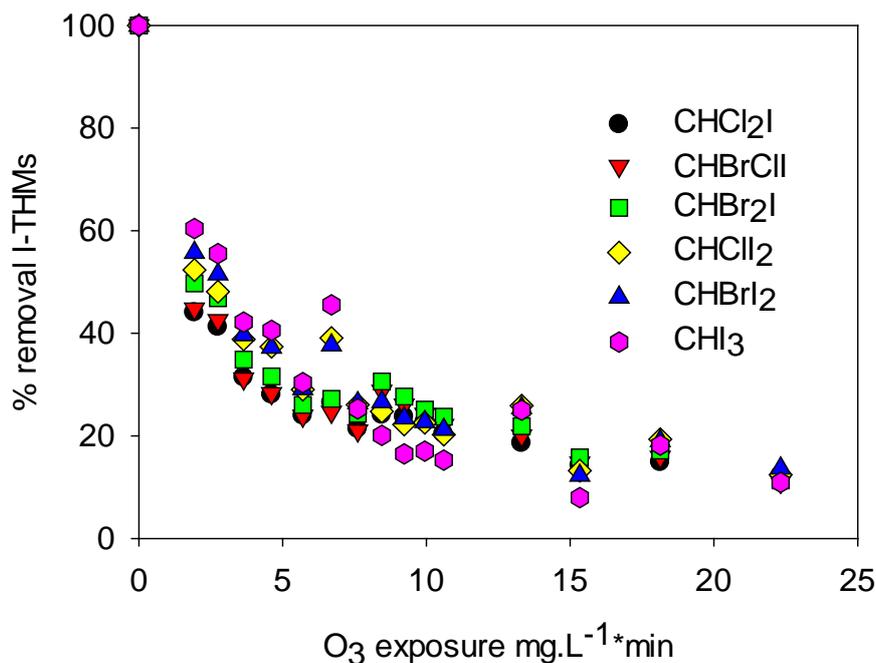


Figure 9. Oxidation of I-THMs during ozonation of chlorinated and post-clarified water. Experimental conditions: 2 $\mu\text{g/L}$ of each I-THM added, $[\text{I}^-] = 15 \mu\text{g/L}$, $[\text{Br}^-] = 940 \mu\text{g/L}$, $[\text{O}_3] = 104 \mu\text{M}$ (5 mg/L), $[\text{DOC}] = 3.5 \text{ mgC/L}$. (Reprinted with permission from Allard et al., 2013. Copyright 2013 Elsevier.)

3.5 WP 4. Comparison of the Novel Bromide and Iodide Removal Processes with Existing Methods.

The use of silver-based materials (WP 1, Section 3.2)) and polyphenolic materials (WP 2, Section 3.3) for the removal of bromide and/or iodide was investigated in this project, however both of these processes require further development. Table 8 shows a comparison between the halide removal capacities of the Ag-based materials studied in this project. The data was obtained by determining the adsorption isotherms for bromide and iodide, and applying the Langmuir equation to the adsorption equilibrium data (Sánchez-Polo and von Gunten, 2013, 2014).

Table 8. Comparison of selected Ag-based materials for halide removal in Milli-Q water (adapted from Sánchez-Polo and von Gunten, 2013; 2014).

Halide	Ag-cloth (mg/g)	Ag-aerogels (mg/g)	Ag-chitosan membranes (mg/g)
Bromide	1.2	1.38	0.95
Iodide	1.7	2.55	1.56

Based on the results in Table 8, Ag-aerogels showed the highest halide removal, while Ag-chitosan membranes had the lowest removal. A previously reported study comparing the adsorption of bromide by a commercial activated carbon and a silver-aerogel using water from Lake Zurich showed that the Ag-aerogel had a higher halide adsorption capacity than conventional activated carbon (Figure 10) (Sánchez-Polo, *et al.*, 2007a).

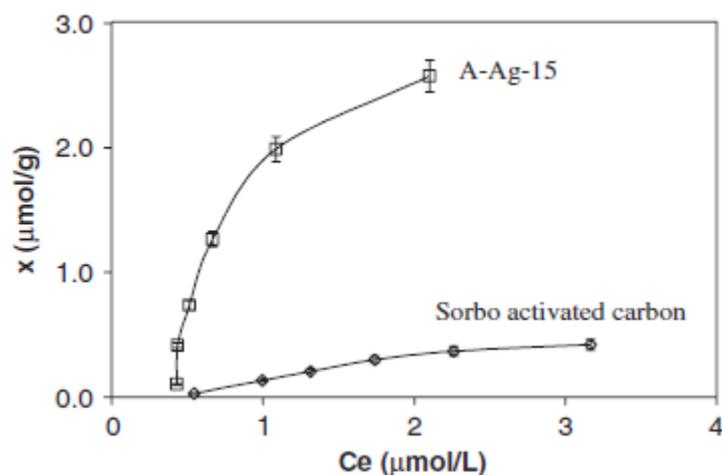


Figure 10. Comparison between capacities of Ag aerogels and Sorbo-activated carbon to remove bromide from Lake Zurich waters. $T = 25\text{ }^{\circ}\text{C}$, $\text{pH } 7$. Equilibration time 7 days: (□) Aerogel A-Ag-15 and (◇) Sorbo-activated carbon (adapted from Sánchez-Polo et al., 2007a).

Although the silver materials studied showed some promise for halide removal, it should be noted that water quality parameters such as pH, chloride and DOC reduced the removal capacity of all of the Ag-based materials studied in this project. In addition, at this stage, in all of these materials the fraction of silver available for halide binding is very small, which may make these processes not economically viable for large scale application.

For application of polyphenolic materials for the removal of bromide and/or iodide in drinking water treatment, the structure of the base phenolic compound was found to be the key factor in determining whether bromine incorporation, and hence bromide removal, or oxidation to the quinone will occur. Our experiments using model compounds have shown that, for best bromide removal, the ideal polyphenolic structure should be based on the phenol (i.e. one hydroxy group) structure or the resorcinol (1,3-dihydroxybenzene) structure where the hydroxy groups are *meta* to each other. However, further research is required to obtain or synthesise such polymers and to assess their viability for bromide removal on laboratory scale, before considering any large scale application.

While bromide removal from source waters remains a challenge for water utilities, potential methods for minimising iodide-related issues have been developed. Our experiments have shown that in chlorinated systems, the majority of iodide present is oxidised to the safe product, iodate, with only minor formation of I-DBPs (Section 3.6). However, as the oxidation of iodide to iodate is dependent on the DOC concentration, thus the conversion of iodide to iodate may be significantly reduced in waters rich in organic matter (Section 3.4.1). Options for reducing iodide-related problems during chloramination have also been developed in this project (Section 3.4). Chloramination where chlorine is added first followed by ammonia, instead of addition of pre-formed monochloramine, was shown to be a viable process for the mitigation of iodide-related problems. However, application of this process needs to be based on careful consideration of water quality parameters, such as the concentration of precursors, specifically the concentration of bromide, as well as the type and concentration of DOM, so that an appropriate pre-chlorination time can be applied.

Incorporating an ozonation step prior to chloramination can also reduce occurrence of water quality issues resulting from source waters with high iodide concentrations. In this process, ozone oxidises iodide to iodate, thereby minimising the formation of I-DBPs. We have shown (Section 3.4.2) that, even for waters with high bromide concentrations, complete oxidation of iodide to iodate is possible

while maintaining the bromate concentration below the Australian drinking water guideline value of 10 µg/L, provided an appropriate ozone dose is used.

As discussed in Section 1.2, comparison of the developed halide removal methods with existing halide removal methods, including comparison of the treated waters in terms of taste and odour, DBP and AOX formation, was not achieved due to the lower ARC funding available and the challenges still remaining in bromide removal. Curtin Civil Engineering PhD student Babak Rajaeian's project, commenced in 2014, supervised by CIs Heitz and Joll, includes batch and column studies of the kinetics of adsorption and the adsorption capacity of halides on silver-impregnated activated carbon and layered double hydroxides (e.g. hydrotalcite), including the influence of water quality parameters on halide removal. Ion exchange resin studies will be conducted by Babak or an Honours student.

3.6 WP 5. Study of Source Waters in Terms of Bromide and Iodide Concentrations, and DBP Formation and Aesthetic Properties after Disinfection.

Distributed waters from selected high bromide and/or iodide water resources were examined in terms of their bromide and iodide concentrations, DBP formation, halogen-specific AOX formation and aesthetic properties after disinfection. To better understand the repartition of Cl-, Br- and I-DBPs, source waters with minimal treatment (i.e. disinfection only) prior to distribution were chosen. Two such source waters were selected for this study: a groundwater (GW) from the south-eastern region of Western Australia and a surface water (SW) in the south-western region of Western Australia. The key water quality parameters for raw and distributed waters are shown in Table 9. Both source waters were disinfected using chlorine prior to distribution. The sampling points for both source waters are shown in Figure 11, along with the chlorine contact times from the point of chlorine dosing to the reticulation sampling points. For the GW system, the raw water was sampled at the bore, while the distributed water was sampled at the town reticulation sampling point (GW Retic SP). For the SW system, there were two sampling points for the distributed water: one immediately downstream of dosing at the water treatment plant (WTP Outlet SP) and the second at the end of the distribution system (SW Retic SP).

Table 9. Key water quality parameters for raw and distributed waters for GW and SW.

Samples		pH	DOC (mg/L)	Bromide (µg/L)	Iodide (µg/L)
GW	Raw	7.9	1.2	750	70
	GW Retic SP		1.2	680*	<LOD*
SW	Raw	7.5	3.5	400	90
	WTP Outlet SP		3.5	70*	<LOD*
	Retic		3.5	60*	<LOD*

*The concentrations of bromide and iodide in the distributed waters were measured after quenching the free chlorine equivalent residual.

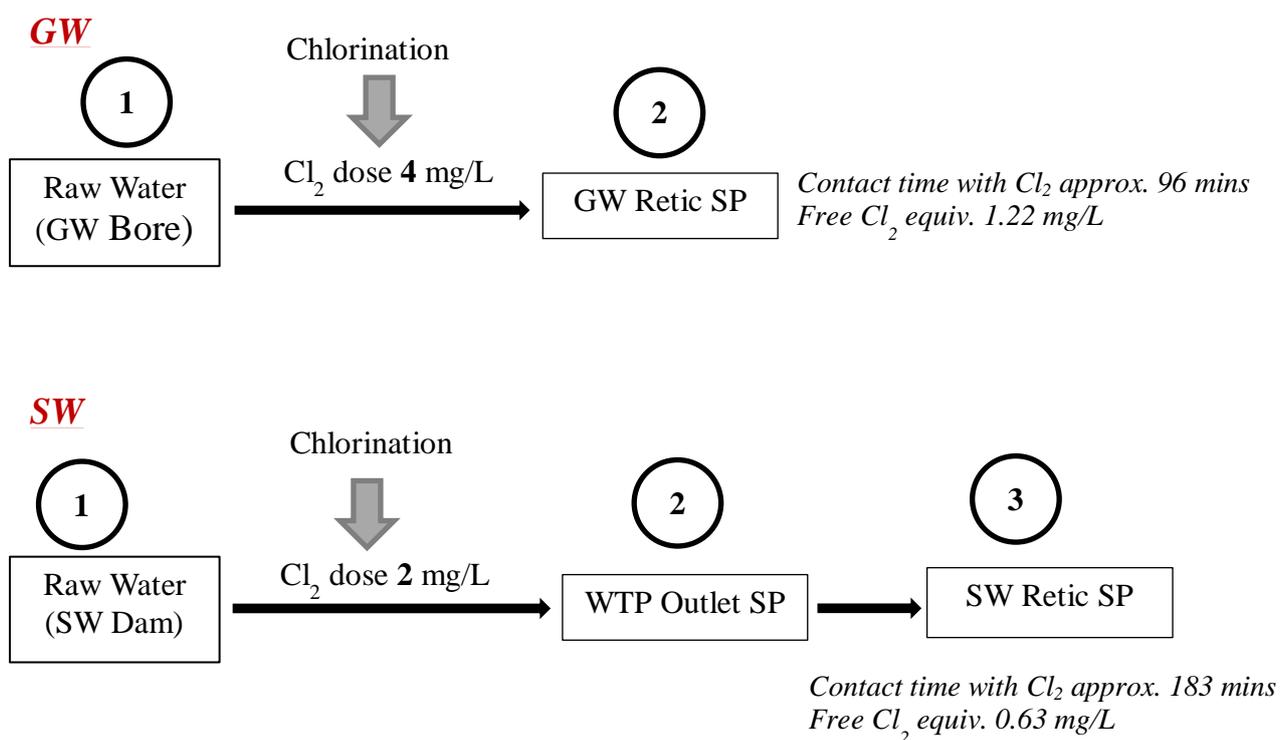


Figure 11. Sampling points for raw and distributed waters for GW and SW systems, showing the chlorine contact times from the point of chlorine dosing to the reticulation sampling points.

3.6.1 Formation of disinfection by-products (DBPs)

The concentrations of the measured DBPs are shown in Table 10. In both the GW and the SW systems, the brominated DBPs dominated the measured DBPs in the distribution system samples (Table 10 and Figures 12 and 13). This is mostly due to the higher rate of reaction with organic substances for HOBr compared to HOCl (Acero *et al.*, 2005; Westerhoff *et al.*, 2004), which can lead to higher yield of brominated DBPs than chlorinated DBPs, even though HOCl is present at a much higher concentration than HOBr. In terms of molar concentrations, the regulated THMs (33%) and HAAs (65%) were the dominant DBPs detected in the GW system, with only minor concentrations of HANs (1%) detected (Figure 12).

All 10 species of THMs (six I-THMs and four regulated Cl-Br-THMs) were detected in the SW distributed waters. In this distribution system, the regulated THMs and HAAs also formed the largest proportion of DBPs, followed by a small percentage of HANs and a minor quantity of I-THMs (Figure 13). Again, the brominated DBPs dominated the measured DBPs in the distribution system. In the SW system, the concentrations of most of the DBPs increased further into the distribution system, with slightly greater increases observed for Cl-DBPs due to the relatively low reactivity of chlorine, compared to bromine, with organics and the long contact time with chlorine. Although GW raw water contained higher bromide concentrations than SW raw water (Table 9), the concentrations of the measured Br-DBPs in the GW distribution system were lower than those found in the SW distribution system. This is most likely attributable to the higher DOC concentration found in SW raw water (Table 9). The majority of the initial iodide concentration present in the raw water was converted to iodate after chlorination (results not shown), with only low concentrations of I-THMs being detected in the SW distribution system. The regulated THMs and HAAs detected were all present at concentrations below the Australian Drinking Water Guidelines (250 µg/L for THM4, 100 µg/L for dichloro- and trichloro-acetic acids, and 150 µg/L for chloroacetic acid) (NHMRC, 2011) in both the GW and SW distribution systems.

Table 10. Concentrations of disinfection by-products formed in distributed water samples from the GW and SW schemes.

Sampling location		GW Retic SP	SW WTP Outlet SP	SW Retic SP
<i>DBPs</i>	Units			
<i>Trihalomethanes (THMs/I-THMs)</i>				
Chloroform	µg/L	0.1	2	5
Bromodichloromethane	µg/L	0.6	9	19
Chlorodibromomethane	µg/L	4	25	45
Bromoform	µg/L	22	13	19
Dichloroiodomethane	ng/L	<LOD*	71	113
Bromochloroiodomethane	ng/L	<LOD	255	328
Dibromoiodomethane	ng/L	12	338	299
Chlorodiiodomethane	ng/L	<LOD	67	90
Bromodiiodomethane	ng/L	<LOD	73	46
Iodoform	ng/L	<LOD	23	8
<i>Haloacetic Acids (HAAs)</i>				
Bromochloroacetic acid	µg/L	6	10	15
Dibromoacetic acid	µg/L	28	16	22
Bromoacetic acid	µg/L	<LOD	3	4
Dichloroacetic acid	µg/L	<LOD	4	6
Trichloroacetic acid	µg/L	<LOD	2	4
Bromodichloroacetic acid	µg/L	<LOD	7	14
Chlorodibromoacetic acid	µg/L	<LOD	<LOD	38
<i>Haloacetonitriles (HANs)</i>				
Dichloroacetonitrile	µg/L	<LOD	0.4	0.7
Bromoacetonitrile	µg/L	<LOD	0.3	0.4
Dibromoacetonitrile	µg/L	0.2	2	3
Bromochloroacetonitrile	µg/L	0.4	1	2
*LOD = Limit of detection				

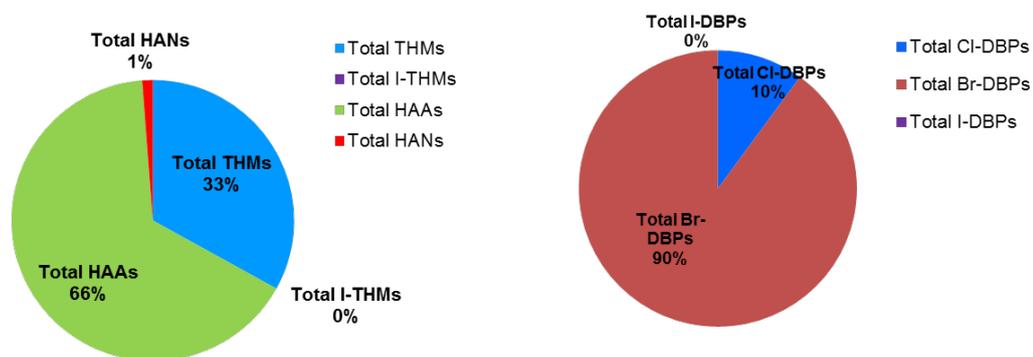


Figure 12. Distribution and speciation of the measured DBPs in the GW distribution system, reported as % of the total molar concentrations.

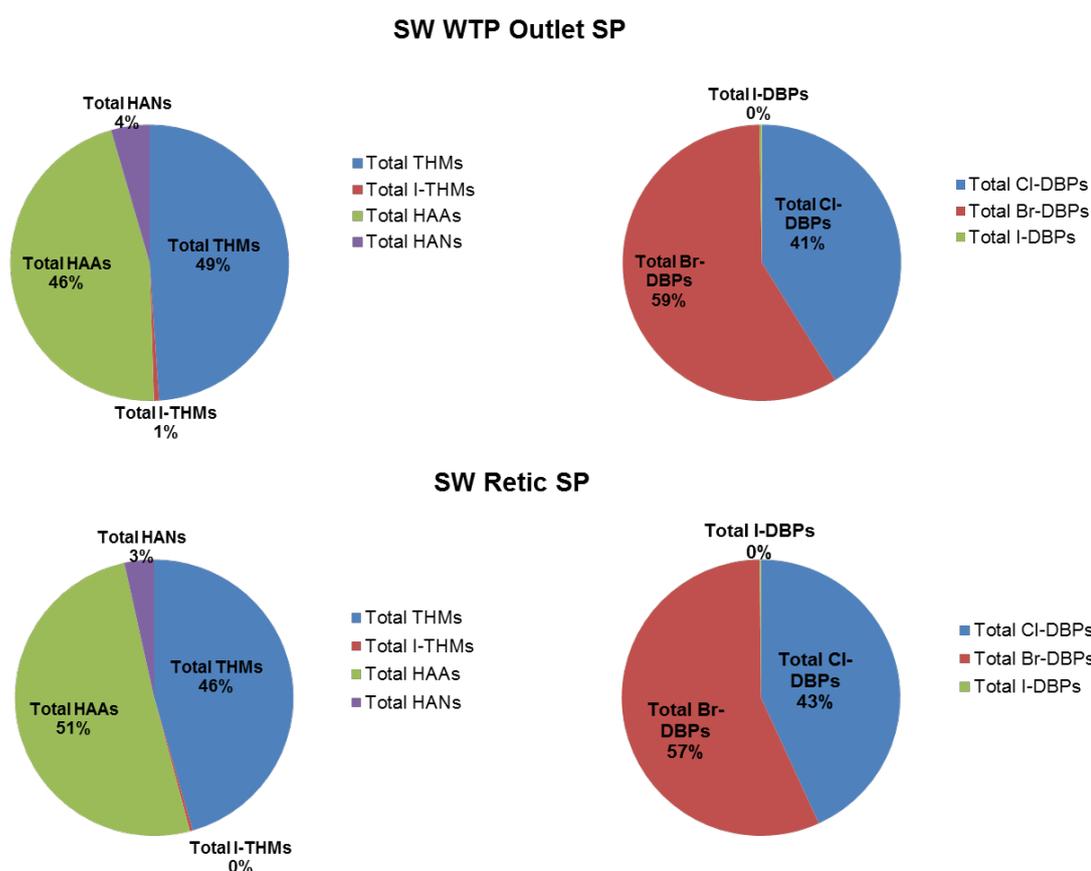


Figure 13. Distribution and speciation of the measured DBPs in the SW distribution system, reported as % of the total molar concentrations.

3.6.2 Halogen-specific AOX formation

The halogen-specific AOX was determined for the chlorinated GW and SW distribution system samples, with AOB_r dominating the formation of total AOX in both systems, forming approximately 50 – 60% of the total AOX (Figure 14). In both distribution systems, the known AOX (sum of halogen incorporation into the measured THMs, HAAs and HANs) only accounted for approximately 30% of the total AOX (Figure 15), illustrating the importance of AOX measurements in understanding the full formation of halogenated DBPs.

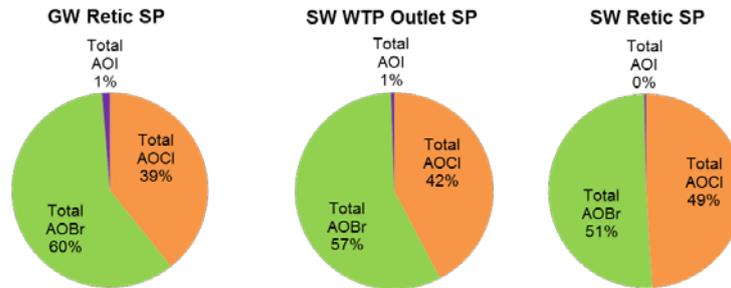


Figure 14. Specific AOX formation (AOCl, AOBr and AOI) in GW and SW distributed waters.

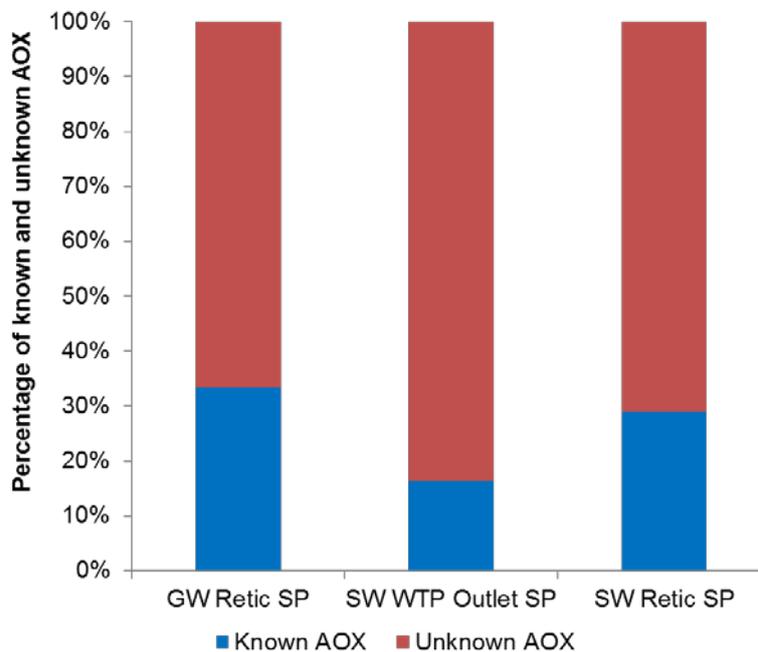


Figure 15. Proportion of known and unknown AOX in GW and SW distributed waters.

The formation of AOX and all classes of DBPs measured in this study was driven by bromine due to faster reaction kinetics for bromination, compared to chlorination, even though chlorine was present at much higher concentration.

3.6.3 Aesthetic properties

A chlorinous odour was detected by more than 50% of the panellists in all distributed waters when the measured free chlorine equivalent concentration was above the odour threshold concentration (OTC) for free chlorine (0.1 mg/L) (Figures 16a and 17a). When the free chlorine equivalent concentration was below the OTC for free chlorine, a chlorinous odour was still detected in the GW distributed water and in the distributed water from the WTP outlet sampling point (WTP Outlet SP) of the SW distribution system (Figures 16b and 17b). Both GW and SW are source waters with high bromide concentrations and we have proposed previously that bromine (produced when bromide reacts with chlorine) could be the cause of chlorinous odours when the free chlorine equivalent concentration is below the OTC for free chlorine in these types of waters upon disinfection

(McDonald *et al.*, 2009; McDonald *et al.*, 2013). Thus, the chlorinous odour detected when the free chlorine equivalent concentration was below the OTC for free chlorine in these distributed waters could be caused by the presence of bromine. In addition, all distributed waters were perceived to have an earthy/musty/mouldy odour by the panellists when the free chlorine equivalent concentration was below the OTC for free chlorine (Figures 16b and 17b). In the case of the SW samples, it is possible that the earthy/musty/mouldy odours were initially masked by the chlorinous odour when the free chlorine equivalent concentrations were above the OTC for free chlorine, as the earthy/musty/mouldy odour was also found to be significant in the raw water from SW (Figure 17). No medicinal odours were detected by the panellists, corresponding to all the iodo-THMs being present below their OTCs.

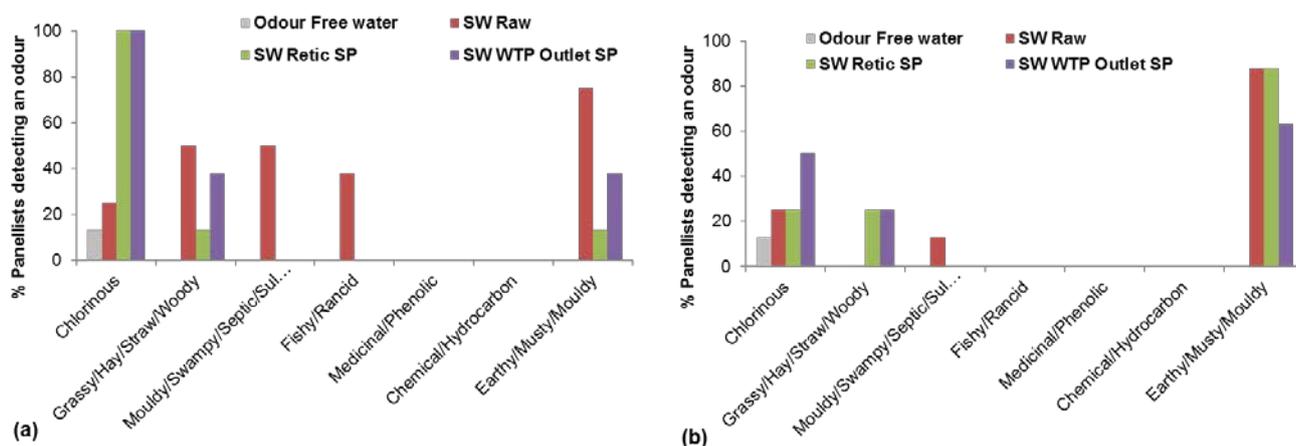


Figure 16. Odour descriptors for samples with free chlorine equivalent concentrations above (a) and below (b) the OTC for free chlorine for GW raw and distributed waters.

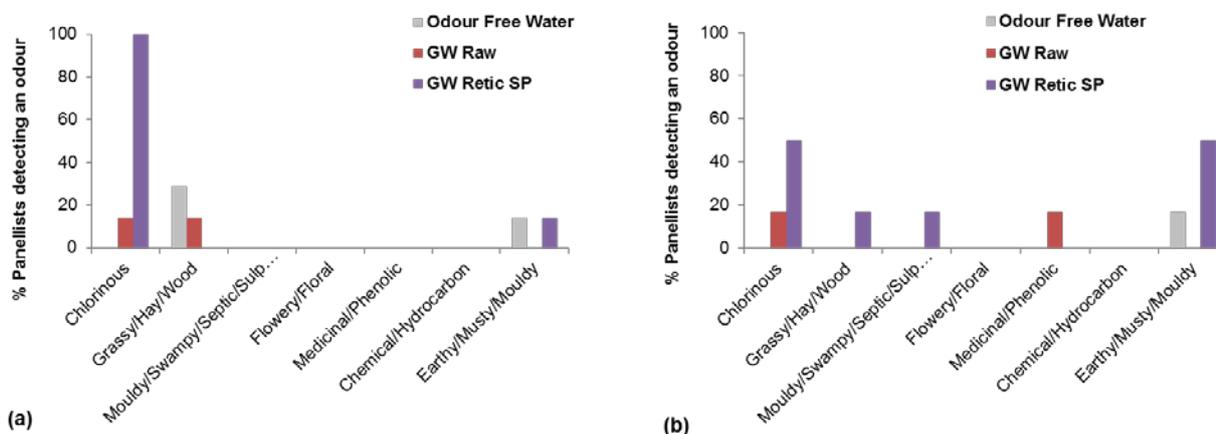


Figure 17. Odour descriptors for samples with free chlorine equivalent concentrations above (a) and below (b) the OTC for free chlorine for SW raw and distributed waters.

4.0 Summary and Conclusions

A survey of the concentrations of bromide, iodide and DOC in many Western Australian drinking water sources was conducted. The bromide concentrations were found to be high to very high, ranging from 400 $\mu\text{g/L}$ to 8450 $\mu\text{g/L}$, while iodide concentrations were often also found to be high, ranging from less than 5 $\mu\text{g/L}$ to 593 $\mu\text{g/L}$. This survey demonstrated the significant concentrations of the disinfection by-product (DBP) precursors, bromide and iodide, in many Western Australian source waters, challenging the production of drinking water meeting the Australian Drinking Water Guidelines for DBPs.

The impact of high bromide and iodide concentrations on distributed waters from two Western Australian drinking water source waters was then investigated. In both systems, the brominated DBPs dominated the measured DBPs (THM4, I-THMs, HAAs and HANs). However, in both distribution systems, the measured DBPs accounted for only 30% of total organohalogens, demonstrating that AOX measurements are important in providing an understanding of the full formation of halogenated DBPs in drinking water. The primary fate of iodide after chlorination was conversion to iodate, the non-toxic sink for iodine, with only minor concentrations of iodo-THMs formed, highlighting a benefit of using chlorine as the disinfectant when the source water contains iodide.

The use of silver impregnated materials and the feasibility of using polyphenolic materials for halide (bromide and iodide) removal were examined. The silver-doped materials showed promise and are currently under further investigation. For the potential application of polyphenolic materials for the removal of bromide and/or iodide in drinking water treatment, the structure of the base phenolic compound is the key factor in determining whether bromine incorporation or oxidation to the quinone will occur. The formation of a quinone structure is not desirable in water treatment applications, since haloquinones were previously predicted as DBPs of potential health concern. Thus, future research will focus on the phenolic functionalities leading to 100% bromine incorporation, as potential monomers for polyphenolic materials for bromide removal in drinking water treatment. For drinking water treatment application, the ratio between chlorination dose and bromide should be assessed. In order to reduce the risk of DBP formation (e.g. THMs), the phenolic moieties should be in excess compared to HOBr.

Two processes based on the selective oxidation of iodide to iodate, the non-toxic and thus preferred sink for iodine, were investigated for the mitigation of I-DBP formation in iodide-containing waters. The first process was based on the chlorine/ammonia process. The second process involved a pre-ozonation step before chloramination. In the chlorine/ammonia process, free chlorine was added first, since it oxidised iodide to iodate, the non-toxic sink for iodine, with the presence of bromine catalysing this reaction. This was followed by ammonia addition to quench the chlorine residual and form monochloramine in order to mitigate the formation of regulated DBPs. This is beneficial compared to preformed monochloramine (NH_2Cl), since during chloramination iodide can not be oxidised to iodate and therefore I-organic DBP formation occurs. This process reduced the formation of iodo-organic DBPs, provided that the free chlorine contact time was sufficient for full conversion of iodide to iodate. Additional experiments were conducted to evaluate the applicability of the chlorine/ammonia process to drinking water treatment and to understand the influence of iodide, bromide and DOM on the formation and speciation of I-THMs and iodate. The results indicated that, depending on the water quality, the chlorine/ammonia process was not always favourable over preformed monochloramine and, in certain cases, the formation of I-organic precursors was enhanced during chlorination and therefore I-THM formation during chlorination could exceed I-THM formation during chloramination. In these cases, the use of preformed monochloramine alone was the preferred option. For example, for highly reactive DOM, pre-chlorination was not beneficial and the use of preformed NH_2Cl alone was recommended, even though the formation of I-THMs is favoured. For DOM with lower reactivity, the chlorine/ammonia process was beneficial if the

chlorine contact time was adjusted according to the bromide and DOM concentration to allow for the complete oxidation of iodide to iodate for maximum reduction of I-DBPs. Thus, the chlorine/ammonia process is valuable to water utilities for minimisation of iodide-related issues provided that an appropriate pre-chlorination time is used based on careful consideration of the type of precursors and their concentration (e.g. bromide and DOM).

Selective oxidation of iodide to iodate, without significant bromate formation, was achieved over a large range of ozonation conditions, confirming that ozonation is a viable pretreatment option for mitigation of I-organic DBPs. In addition to reducing the formation of the more toxic I-DBPs, ozone can also oxidise I-THMs if they are already present in the water.

While potential solutions for mitigation of I-organic DBP formation are now available, options for efficient and cost effective removal of bromide from source waters need further investigation and development. Research is continuing on the use of silver-impregnated activated carbon and layered double hydroxides for bromide removal. Future CWQRC-Water Corporation projects (PA-005 and ARC LP150101161, respectively) will also investigate (a) pre-oxidation, to reduce the concentration of DBP precursors with DOM, as an alternative strategy for minimisation of the formation of Br-DBPs, and (b) the influence of bromide in chloraminated distribution systems, in terms of the stability of the disinfectant residual and the formation of Br-DBPs.

5.0 References

- Acero, J. L., Piriou, P. and von Gunten, U. (2005) Kinetics and mechanisms of formation of bromophenols during drinking water chlorination: Assessment of taste and odour development. *Water Research*, **39**(13), 2979-2993.
- Agus, E., N. Voutchkov, and D. Sedlak. (2009). Disinfection by-products and their potential impact on the quality of water produced by desalination systems: A literature review. *Desalination*, **237**(1-3), 214-237.
- Allard, S., Tan, J., Joll, C. A. and von Gunten, U. (submitted) The chlorine/ammonia process: A mechanistic study on the formation of Cl-/Br-/I-containing disinfection by-products combined with a theoretical cytotoxicity evaluation. *Environmental Science and Technology*
- Allard, S., Nottle, C.E., Chan, A., Joll, C., von Gunten, U. (2013) Ozonation of iodide-containing waters: Selective oxidation of iodide to iodate with simultaneous minimization of bromate and I-THMs. *Water Research*, **47**(6), 1953-1960.
- Allard, S., Charrois, J. W. A., Joll, C. A. and Heitz, A. (2012a) Simultaneous analysis of 10 trihalomethanes at nanogram per liter levels in water using solid-phase microextraction and gas chromatography mass spectrometry. *Journal of Chromatography, A*, **1238**, 15-21.
- Allard, S., Criquet, J., Heitz, A., Joll, C. and von Gunten, U. (2012b) Selective Oxidation of Iodide to Iodate – A report prepared as an outcome of ARC Linkage Project 100100285. *CWQRC Report No: CWQRC-2012-004*, (8 pages)
- Ates, N., Yetis, U., and Kitis, M., (2007). Effects of bromide ion and natural organic matter fractions on the formation and speciation of chlorination by-products. *Journal of Environmental Engineering – ASCE*, **133** (10), 947-954.
- Bichsel, Y. and von Gunten, U. (1999). Oxidation of iodide and hypiodous acid in the disinfection of natural waters. *Environmental Science and Technology*, **33**(22), 4040-4045.
- Bichsel, Y. and von Gunten, U. (2000) Formation of iodo-trihalomethanes during disinfection and oxidation of iodide-containing waters. *Environmental Science and Technology*, **34**(13), 2784-2791.
- Boyer, T.H., and Singer, P.C., (2005). Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. *Water Research*, **39**(7), 1265-1276.
- Brooke, E. S. and Collins, M. R. (2011) Assessing post-treatment aeration variables to reduce disinfection by-products (THMs) for small systems. Presentation from New England Water Treatment Technology Assistance Centre, University of New Hampshire, Durham, New Hampshire. [http://www.unh.edu/wttac/Presentations/Ethan%20Brooke,%20Assessing%20Post%20Treatment%20DBP%20\(THM\)%20Aeration%20Variables.pdf](http://www.unh.edu/wttac/Presentations/Ethan%20Brooke,%20Assessing%20Post%20Treatment%20DBP%20(THM)%20Aeration%20Variables.pdf)
- Bull, R. J.; Reckhow, D. A.; Rotello, V.; Bull, O. M.; Kim, J. (2006) *Use of toxicological and chemical models to prioritize DBP research*. Project 2867. Report to the Awwa Research Foundation, Denver, Colorado.
- Cancho, B.; Fabrellas, C.; Diaz, A.; Ventura, F. (2001). Determination of the odour threshold concentrations of iodinated trihalomethanes in drinking water. *Journal of Agriculture and Food Chemistry*, **49**, 1881-1884.

Criquet, J., Rodriguez, E. M., Allard, S., Wellauer, S., Salhi, E., Joll, C. and von Gunten, U. (submitted) Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts – electrophilic aromatic substitution and oxidation. *Water Research*.

Criquet, J., Allard, S., Sahli, E., Joll, C. A., Heitz, A. and von Gunten, U. (2012). Iodate and iodo-trihalomethanes formation during chlorination of iodide-containing waters. Role of Bromide. *Environmental Science and Technology*, **46**(13), 7350-7357.

Fabris, R., Chowa, C.W.K., Drikas, M. and Eikebrokk, B. (2008). Comparison of NOM character in selected Australian and Norwegian drinking waters. *Water Research*, **42**(15), 4188-4196.

Gillogly, T., Najm, I., Minear, R., Marinas, B., Urban, M., Kim, J.H., Echigo, S., Amy, G., Douville, C., Daw, B., Andrews, R., Hofman, R., and Croue, J.P., (2001). Bromate formation and control during ozonation of low bromide waters. AWWA Research Foundation (Now Water Research Foundation), CO, USA.

Gruchlik, Y., Heitz, A., Joll, C. and von Gunten, U. (2011a) Bromide and Iodide Concentrations in Western Australian Waters – A Summary of Results Collected Over the Past Few Years. *CWQRC Report No CWQRC-2011-002*, (48 pages).

Gruchlik, Y., Heitz, A., Joll, C. McDonald, S. and Breckler, L. (2011b) Bromide and Iodide Concentrations in Some Western Australian Source Waters. *CWQRC Report No: CWQRC-2011-007*, (19 pages).

Hammes, F., Salhi, E., Koster, O., Kaiser, H. P., Egli, T. and von Gunten, U. (2006) Mechanistic and kinetic evaluation of organic disinfection by-product and assimilable organic carbon (AOC) formation during the ozonation of drinking water, *Water Research*, **40**(12), 2275-2286.

Hansson, R.C., Henderson, M.J., Jack, P., and Taylor, R.D. (1987) Iodoform taste complaints in chloramination. *Water Research*, **21**(10), 1265-1271.

Hua, G. and Yeats, S. (2010) Control of trihalomethanes in wastewater treatment. *Florida Water Resources Journal*, **April 2010**, 6-12.

Hua, G. and Reckhow, D. A. (2007) Comparison of disinfection by-product formation from chlorine and alternative disinfectants. *Water Research*, **41**(8), 1667-1678.

Kristiana, I., Joll, C. and Heitz, A. (2012). Analysis of halonitriles in drinking water using solid-phase microextraction and gas chromatography-mass spectrometry. *Journal of Chromatography A*, **1225**, 45-54.

Kristiana, I., McDonald, S., Tan, J., Joll, C. and Heitz, A. (2015) Analysis of halogen-specific TOX revisited: Method improvement and application. *Talanta*, **139**, 104-110.

Lee, Y., Yoon, J. and von Gunten, U. (2005) Kinetics of the oxidation of phenols and phenolic endocrine disruptors during water treatment with ferrate (Fe(VI)) *Environmental Science and Technology*, **39**(22), 8978-8984.

Magara, Y., Aizawa, T., Kunikane, S., Itoh, M., Kohki, M., Kawasaki, M. and Takeuti, H. (1996) The behavior of inorganic constituents and disinfection by products in reverse osmosis water desalination process. *Water Science and Technology*, **34**, 141-148.

- McDonald, S., Joll, C.A., Lethorn, A., Loi, C. and A. Heitz (2013) Drinking water: the problem of chlorinous odours. *Journal of Water Supply: Research and Technology AQUA*, **62**(2), 86-96.
- McDonald, S., Lethorn, A., Loi, C., Joll, C., Driessen, H. and Heitz, A. (2009) Determination of odour threshold concentration ranges for some disinfectants and disinfection by-products for an Australian panel. *Water Science and Technology*, **60** (10), 2493-2506.
- Neale, P. A., Antony, A., Bartkow, M. E., Farré, M. J., Heitz, A., Kristiana, I., Tang, J. Y. M., and Escher, B. I. (2012) Bioanalytical assessment of the formation of disinfection by-products in a drinking water treatment plant. *Environmental Science and Technology*, **46**(18), 10317-10325.
- NHMRC (2011). Australian Drinking Water Guidelines, National Health and Medical Research Council (NHMRC), National Resource Management Ministerial Council, Australian Government, Australia.
https://www.nhmrc.gov.au/files/nhmrc/publications/attachments/eh52_aust_drinking_water_guidelines_update_131216.pdf
- Pressman, J.G., Richardson, S.D., Speth, T.F., Miltner, R.J., Narotsky, M.G., Hunter, E.S., III, Rice, G.E., Teuschler, L.K., McDonald, A., Parvez, S., Krasner, S.W., Weinberg, H.S., McKague, A.B., Parrett, C.J., Bodin, N., Chinn, R., Lee, C.-F.T. and Simmons, J.E. (2010) *Environmental Science and Technology*, **44**(19), 7184-7192.
- Richardson, S.D. (2011) Disinfection by-products: formation and occurrence in drinking water. In: J.O. Nriagu (Ed.), *The Encyclopedia of Environmental Health*, Vol. 2, Elsevier, Burlington, 110-136.
- Richardson, S. D., Fasano, F., Ellington, J. J., Crumley, G. F., Buettner, K. M., Evans, J. J., Blount, B. C., Silva, L. K., Waite, T. J., Luther, G. W., McKague, B. A., Miltner, R. J., Wagner, E. D., Plewa, M. J. (2008) Occurrence and mammalian cell toxicity of iodinated disinfection by-products in drinking water. *Environmental Science and Technology*, **42**(22), 8330-8338.
- Salhi, E. and von Gunten, U. (1999). Simultaneous determination of bromide, bromate and nitrite in low µg/L levels by ion chromatography without sample pre-treatment. *Water Research*, **33**(15), 3239-3244.
- Sánchez-Polo, M.; Rivera-Utrilla, J.; Salhi, E.; von Gunten, U. (2006) Removal of bromide and iodide anions from drinking water by silver-activated carbon aerogels. *Journal of Colloid and Interface Science*, **300**(1), 437-441.
- Sánchez-Polo, M.; Rivera-Utrilla, J.; Salhi, E.; von Gunten, U. (2007a) Ag-doped carbon aerogels for removing halide ions in water treatment. *Water Research*, **41**(5), 1031-1037.
- Sánchez-Polo, M.; Rivera-Utrilla, J.; von Gunten, U. (2007b) Bromide and iodide removal from waters under dynamic conditions by Ag-doped aerogels. *Journal of Colloid and Interface Science*, **306**(1), 183-186.
- Sánchez-Polo, M. and von Gunten, U. (2013) Novel silver-based materials for halide removal. *Presentation at Project Technology Transfer Workshop*, Water Corporation of Western Australia, Leederville, 26 September 2013.
- Sánchez-Polo, M. and von Gunten, U. (2014) Novel materials for halide removal from drinking water. *Research report prepared as part of ARC LP100100285*. (19 pages).

Symons, J. M., Stevens, A. A., Clark, R. M., Geldreich, E. E., Love, T. O. JR. and DeMarco, J. (1981) Treatment techniques for controlling trihalomethanes in drinking water. *US EPA Report, EPA/600/2-81/156*, Office of Research and Development, United States Environmental Protection Agency, Washington, DC, USA.

Trolio, R., Walker, R., McNeil, S., Hunyh, T. and Jismi, N. (2007) Trihalomethane management in drinking water: A novel approach. *Water, Journal of the Australian Water Association*, **34**(3), 77-81.

US-EPA, 2004. Statistical Protocol for the Determination of the Single-laboratory Lowest Concentration Minimum Reporting Level (LCMRL) and Validation of Laboratory Performance at or Below the Minimum Reporting Level (MRL). United States Environmental Protection Agency. http://www.epa.gov/ogwdw/methods/pdfs/methods/methods_lcmrl.pdf.

US-EPA, 1995. US EPA Method 552.2: Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Extraction, Derivatisation and Gas Chromatography with Electron Capture Detection - Revision 1.0 in *Methods for the Determination of Organic Compounds in Drinking Water Supplement III (EPA/600/R-95-131)*, United States Environmental Protection Agency.

von Gunten, U. (2003a) Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water research*, **37**(7), 1443-1467.

von Gunten, U. (2003b) Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. *Water research*, **37**(7), 1469-1487.

Warton, B., Heitz, A., Zappia, L. R., Franzmann, P. D., Masters, D., Joll C. A., Alessandrino, M., Allpike, B., O'Leary, B. and Kagi, R. I. (2007) Magnetic ion exchange drinking water treatment in a large-scale facility. *Journal American Water Works Association*, **99**(1), 89-101.

Watson, K., Farré, M. J. and Knight, N. (2012) Strategies for the removal of halides from drinking water sources, and their applicability in disinfection by-product formation: A critical review. *Journal of Environmental Management*, **110**, 276-298.

Westerhoff, P., Chao, P. and Mash, H. (2004) Reactivity of natural organic matter with aqueous chlorine and bromine. *Water Research* **38**(6), 1502-1513.

Xu, P., Drewes, J.E. and Heil, D. (2008) Beneficial use of co-produced water through membrane treatment: technical-economic assessment. *Desalination*, **225**(1-3), 139-155.