IMPACT OF BROMIDE AND IODIDE DURING DRINKING WATER DISINFECTION AND POTENTIAL TREATMENT PROCESSES FOR THEIR REMOVAL OR MITIGATION

A study to evaluate distributed water from two Western Australian drinking water sources

Y Gruchlik, J Tan, S Allard, A Heitz, M Bowman, D Halliwell, U von Gunten, J Criquet, C Joll

ABSTRACT

In this study, the impact of bromide and iodide on disinfected waters was examined and potential treatment technologies for their removal or mitigation were investigated. Distributed waters from two Western Australian drinking water sources were evaluated in terms of their bromide and iodide concentrations, disinfection by-product (DBP) formation, halogen-specific adsorbable organic halogen (AOX) formation and chlorinous odours after disinfection. In both systems, the brominated DBPs dominated the measured DBPs and, in both cases, the known DSPs accounted for only 30% of total organohalogens.

Chloramination with a sufficient free chlorine contact time followed by ammonia addition, rather than pre-formed monochloramine, may be a viable mitigation strategy for the minimisation of I-OBPs, since exposure to free chlorine should promote the conversion of iodide to iodate, a safe form of iodine. This study has shown that bromide plays an important role in this process, mainly by enhancing the preferred conversion of iodide to iodate.

Ozone pre-treatment selectively oxidised iodide to iodate and minimised the formation of I-DBPs. Complete conversion of iodide to iodate, while minimising the bromate formation to below the guideline value of 10 \( \mu \)g L\(^{-1}\), was achieved for a wide range of ozone concentrations in raw waters, including raw waters with high bromide concentrations.

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

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Keywords: bromide, iodide, disinfection by-products, halogen-specific AOX, ozonation, pre-chlorination.

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 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 that may appear in finished drinking water (Hansson et al., 1987). These compounds have low organoleptic threshold concentrations ranging from 0.03 to 8.9 \( \mu \)g L\(^{-1}\), with the lowest concentration being for CHI\(_3\) (Cancho et al., 2001).

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 (O₃) is used as the disinfectant, HOBr is further oxidised to bromate (BrO₃⁻), a potential human carcinogen; hence ozone application is often limited in bromide-containing waters (von Gunten, 2003b; Allard et al., 2013). Iodide also reacts quickly with free chlorine to form hypohalous 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 (IO₃⁻), a non-toxic, and thus preferred, sink for iodine (Bichsel and von Gunten, 1999; Allard et al., 2013). Unlike chlorine and ozone, monochloramine (NH₂Cl) is not able to oxidise HOI to iodate and thus formation of iodo-organic DBPs occurs during chloramination of iodide-containing waters (Bichsel and von Gunten, 1999).

Halogenated DBPs can be measured as individual species, e.g. trihalomethanes (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, AObBr and AOI) into known and unknown DBPs.

The formation of organic DBPs can be minimised by removal of their precursors (NOM and halides) and 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).

While there are several treatment processes for effective removal of NOM (e.g. Hammes et al., 2006; Watson 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 that 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). Electrochemical techniques 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).

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).

The aims of this study were to: (a) better understand the impact and occurrence of high concentrations of bromide and iodide in source waters on the quality of distributed waters; and (b) develop innovative water treatment processes for the removal/mitigation of both bromide and iodide in drinking water source waters. The potential technologies for the mitigation of bromide and/or iodide in source waters investigated in this study included: (i) chlorine followed by ammonia addition for chloramination and (ii) selective oxidation by ozone.

**METHODOLOGY**

**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 (regulated THMs (THM4), i-THMs, HAAs and HANs) and halogen-specific AOX, and for the presence of chlorinous odours.

**REAGENTS AND EXPERIMENTAL METHODS**

Experimental, reagent and analytical protocols were all rigorous and based on published sources, but space does not permit inclusion in this paper.

**RESULTS AND DISCUSSION**

**SURVEY OF BROMIDE AND IODIDE CONCENTRATIONS IN WA DRINKING WATER SOURCE WATERS**

In a survey of the concentrations of bromide, iodide and DOC in many Western Australian drinking water source waters, the bromide concentrations were found to range from 400 µg L⁻¹ to 8450 µg L⁻¹, while the iodide concentrations ranged from less than 5 µg L⁻¹ to 593 µg L⁻¹ (Table 1). DOC concentrations ranged from 0.4 mg L⁻¹ to 16 mg L⁻¹ (Table 1).

Bromide concentrations of < 50 µg L⁻¹ 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⁻¹ (Ates et al., 2007). Bromide concentrations ranging from 76–540 µg L⁻¹ have been referred to as moderate to high (Boyer and Singer, 2005), and concentrations
around 700 μg L⁻¹ have been described as very high (Hansson et al., 1987).

Iodide concentrations in natural waters are generally fairly low (<10 μg L⁻¹) 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⁻¹ 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⁻¹ have previously been reported as high, while DOC concentrations of 5 mg L⁻¹ have been described as moderate (Fabris et al., 2008).

### Table 1. Concentrations of bromide, iodide and DOC in some Western Australian raw source waters

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bromide Concentration (μg L⁻¹)</th>
<th>Iodide Concentration (μg L⁻¹)</th>
<th>DOC Concentration (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>North-West Coastal GW</td>
<td>8,455</td>
<td>594</td>
<td>0.8</td>
</tr>
<tr>
<td>Great Southern SW1</td>
<td>847</td>
<td>17</td>
<td>10.2</td>
</tr>
<tr>
<td>South-East GW</td>
<td>754</td>
<td>72</td>
<td>1.2</td>
</tr>
<tr>
<td>North-West SW</td>
<td>448</td>
<td>31</td>
<td>4.3</td>
</tr>
<tr>
<td>South-West SW</td>
<td>400</td>
<td>90</td>
<td>3.5</td>
</tr>
<tr>
<td>Perth Metro GWTP raw water</td>
<td>743</td>
<td>31</td>
<td>7.6</td>
</tr>
<tr>
<td>Mid-West E GW bore</td>
<td>1,460</td>
<td>&lt; LOD</td>
<td>0.6</td>
</tr>
<tr>
<td>Goldfields GW bore 1</td>
<td>977</td>
<td>&lt; LOD</td>
<td>0.8</td>
</tr>
<tr>
<td>Goldfields GW bore 2</td>
<td>1,385</td>
<td>26</td>
<td>1.2</td>
</tr>
<tr>
<td>Goldfields GW bore 3</td>
<td>817</td>
<td>&lt; LOD</td>
<td>0.7</td>
</tr>
<tr>
<td>Goldfields GW bore 4</td>
<td>868</td>
<td>&lt; LOD</td>
<td>0.9</td>
</tr>
<tr>
<td>Goldfields GW bore 5</td>
<td>717</td>
<td>&lt; LOD</td>
<td>0.9</td>
</tr>
<tr>
<td>Perth South Coastal GW bore 1</td>
<td>1,483</td>
<td>23</td>
<td>1.0</td>
</tr>
<tr>
<td>Perth South Coastal GW bore 2</td>
<td>479</td>
<td>&lt; LOD</td>
<td>2.6</td>
</tr>
<tr>
<td>Perth South Coastal GW bore 3</td>
<td>1,307</td>
<td>25</td>
<td>1.2</td>
</tr>
<tr>
<td>Great Southern SW2</td>
<td>561</td>
<td>6</td>
<td>16.2</td>
</tr>
<tr>
<td>Mid-West W GW bore 1</td>
<td>2,249</td>
<td>215</td>
<td>0.5</td>
</tr>
<tr>
<td>Mid-West W GW bore 2</td>
<td>1,908</td>
<td>128</td>
<td>0.4</td>
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<tr>
<td>Mid-West W GW bore 3</td>
<td>2,807</td>
<td>493</td>
<td>0.6</td>
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<tr>
<td>Perth Northern GW bore</td>
<td>567</td>
<td>36</td>
<td>2.2</td>
</tr>
<tr>
<td>Perth Metro artesian GW</td>
<td>2,261</td>
<td>37</td>
<td>1.0</td>
</tr>
</tbody>
</table>

*Limit of detection (LOD) = 5 μg L⁻¹

#### THE IMPACT OF HIGH BROMIDE AND IODIDE CONCENTRATIONS ON DISINFECTED WATERS

A preliminary study to understand the impact of high bromide and iodide concentrations in drinking water source waters on disinfected waters was conducted. Distributed waters from selected water resources were examined in terms of their bromide and iodide concentrations, DBP formation, AOX formation and chlorinous odours after disinfection.

To minimise precursor removal and understand the process of DBP formation, source waters with minimal treatment (i.e. disinfection only) prior to distribution were chosen. Two such source waters were selected for this study. The first source water was a groundwater (GW) containing high bromide (750 μg L⁻¹) and iodide (70 μg L⁻¹) concentrations and a relatively low DOC (1.2 mg L⁻¹) concentration. The second water was a surface water (SW) containing a moderate DOC (3.5 mg L⁻¹) concentration and high bromide (400 μg L⁻¹) and iodide (90 μg L⁻¹) concentrations. Both source waters were disinfected using chlorine prior to distribution.

#### Formation of disinfection by-products (DBPs)

In both the GW and the SW systems, the more toxic brominated DBPs dominated the measured DBPs in the distribution system samples, as bromine is more reactive than chlorine, and thus can lead to higher formation of brominated DBPs than chlorinated DBPs, even when the chlorine concentration is much higher than the bromine concentration.

Most of the DBPs detected in the GW system were the regulated THMs (33%) and HAAs (65%), with only minor concentrations of HANs (1%) detected. All 10 species of THMs were detected in the SW distributed waters. In this distribution system, the regulated THMs and HAAs also formed the largest proportion of DBPs (46% and 51%, respectively) followed by a small percentage of HANs (3%) and a minor quantity of T-THMs (less than 1%). The DBPs detected are reported as a percentage of the total molar concentrations.

In the SW system, the concentrations of most of the DBPs increased further into the distribution system, with greater increases observed for the...
concentrations of Cl-DBPs due to a longer contact time with chlorine. The bulk of the initial iodide concentration present in the raw water appeared to be converted to iodate after chlorination, with only low concentrations of I-THMs being detected in the SW distribution system. The regulated THMs and HAAs detected were present at concentrations below the Australian Drinking Water Guidelines (250 \( \mu \)g L\(^{-1}\) for THM\(_4\), 100 \( \mu \)g L\(^{-1}\) for dichloro- and trichloroacetic acids, and 150 \( \mu \)g L\(^{-1}\) for chloroacetic acid) (NHMRC, 2011) in both the GW and SW distribution systems.

Halogen-specific adsorbable organic halogen (AOX) formation

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

Chlorinous odours

A chlorinous odour was detected by more than 50% of the panellists in all distributed waters when the free chlorine equivalent concentration was above the odour threshold concentration (OTC) of 0.1 mg L\(^{-1}\) for free chlorine. When the free chlorine equivalent concentration was below the OTC for free chlorine, a chlorinous odour was still detected in both the GW and SW distributed waters. The chlorinous odour detected when the free chlorine equivalent concentration was below the OTC for free chlorine in these distributed waters could have been caused by the presence of bromine (McDonald et al., 2013), highlighting the occurrence of potential aesthetic issues due to the presence of bromide in source waters.

INVESTIGATION OF POTENTIAL TECHNOLOGIES FOR THE MITIGATION OF HALOGENATED DBPS

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 pre-formed monochloramine, was investigated for reduction of I-organic DBP formation, since exposure to free chlorine should promote the formation of non-toxic iodate, thereby minimising formation of I-DBPs (Criquet et al., 2012). The role of bromine in this process was also investigated.

The formation and the speciation of iodinated THMs was found to depend on the free chlorine contact time and the bromine concentration (Criquet et al., 2012). The presence of bromide was found to be beneficial, favouring the formation of iodate and decreasing the formation of highly iodinated THMs (Criquet et al., 2012).

Figure 3 shows iodine incorporation into I-THMs (bars) and iodate yield (lines) for different pre-chlorination times and varying bromide concentrations for chloramination of a Western Australian river water (initial concentrations after dilution and additions: [I\(^-\)] = 50 \( \mu \)g L\(^{-1}\), pH 8, DOC = 1.2 mg C L\(^{-1}\), initial chlorine concentration was 1 mg Cl\(^-\), L\(^{-1}\) (15 \( \mu \)M); ammonia addition: 75 \( \mu \)M. At t = 0 min, ammonia was added before the addition of chlorine. I-THMs were analysed after 24 h to simulate contact times in distribution systems. The chlorine concentration was an important parameter and the pre-chlorination time needs to be long enough to transform the iodide to iodate. 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).

Selective pre-oxidation of iodide to iodate using ozone with mitigation of I-organic DBP formation in post-chloramination

The possibility of oxidising iodide to iodate by ozone, while keeping the bromate concentration below the Australian drinking water guideline value of 10 \( \mu \)g L\(^{-1}\) (NHMRC, 2011), was investigated (Allard et al., 2013). To elucidate the factors affecting iodate and bromate formation, experiments were performed with various waters under different ozonation conditions.

Ozone pre-treatment selectively oxidised iodide to iodate and minimised the formation of I-DBPs (Allard et al., 2013). Complete conversion of iodide to iodate, while minimising the bromate formation to below 10 \( \mu \)g L\(^{-1}\), was achieved for a wide range of initial ozone concentrations in several source waters (Figure 4). Iodide was completely oxidised to iodate for ozone doses of 8–14 \( \mu \)M (0.38–0.67 mg L\(^{-1}\)) depending on the water quality (Allard et al., 2013). Bromate formation followed a different pattern, with no bromate formation for ozone doses below 14 \( \mu \)M, followed by a linear increase in bromate concentrations for increasing ozone doses (Figure 4) (Allard et al., 2013).

Bromate formation increased as the alkalinity increased and the consumption of ozone increased with the aromaticity...
of the NOM. 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 CHBrCl and CHBrJ were also detected (Allard et al., 2013).

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 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 concentration of bromoform increased with increasing ozone dose (Allard et al., 2013). It was also demonstrated that all the I-THMs present in the water were efficiently oxidised during ozonation (Figure 5) of chlorinated and post-clarified water. Experimental conditions: 2 μg L⁻¹ of each I-THM added, [I⁻] = 15 μg L⁻¹, [Br⁻] = 940 μg L⁻¹, [O₃] = 104 μM (5 mg L⁻¹), [DOC] = 3.5 mgC L⁻¹ (Allard et al., 2013).

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, and it can also oxidise I-THMs if they are already present in the water. Furthermore, by carefully controlling the ozone dose, it is possible to keep the bromate concentration below the Australian drinking water guideline (10 μg L⁻¹), even for source waters with high bromide concentrations.

CONCLUSIONS

The impact of high bromide and iodide concentrations on distributed waters from two Western Australian drinking water source waters was 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 a conversion to iodate, with only minor concentrations of iodo-THMs formed.

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 post-chloramination. The first process was based on using chloramination with addition of free chlorine, followed by ammonia, while the second process involved a pre-ozonation step before chloramination. Bromide was found to play an important role in the chlorination/ammonia addition process by promoting the preferred conversion of iodide to iodate.

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. Selective oxidation of iodide to iodate without significant bromate formation was achieved under certain ozonation conditions, confirming that ozonation is a viable pre-treatment option for mitigation of I-organic DBP formation in post-chloramination.

While potential solutions for the mitigation of I-organic DBP formation during chloramination are now available, options for actual removal of bromide and iodide from source waters need further investigation and development. The use of silver-based materials and polyphenolic materials for the removal of bromide and/or iodide is currently under investigation.
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**REFERENCES**


