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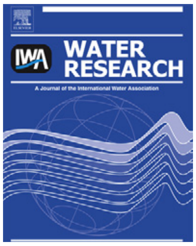

The impact of bromide/iodide concentration and ratio on iodinated trihalomethane formation and speciation

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ABSTRACT

The objective of this study was to evaluate the formation and speciation of iodinated trihalomethanes (I-THMs) from preformed chloramination of waters containing bromide (Br^-) and iodide (I^-) at a Br^-/I^- weight ratio of 10:1. The factors investigated were pH, iodide to dissolved organic carbon (I^-/DOC) ratio, and NOM characteristics, specifically $SUVA_{254}$. A Br^-/I^- ratio of 1:2 was also evaluated to determine the importance of Br^- and I^- concentrations and ratio on I-THM formation and speciation. Regulated triholamethanes (THMs) were measured alongside I-THMs for a more complete understanding of trihalomethane formation. The results showed that, in general, both I-THM and THM formation increased with decreased pH. Greater formation at lower pH was likely attributed to monochloramine decomposition and the formation of additional oxidants and substituting agents, most notably chlorine. For pH $\geq$ 7.5, I-THM yield increased with increasing I^-/DOC ratio and decreasing specific ultraviolet absorbance ($SUVA_{254}$) of the water. The Br^-/I^-, Br^-/DOC and I^-/DOC ratios were important factors for I-THM and THM speciation. At pH 6, dichloroiodomethane ($CHCl_2I$) and bromochloroiodomethane (CHBrClI) were the dominant species at the common bromide and iodide levels. For pH $\geq$ 7.5 and for elevated bromide and iodide levels, iodoform (CHI_3) was always the dominant specie regardless of the Br^-/I^- ratio. The results demonstrated that it is important to examine I-THM formation and speciation at typical Br^-/I^- ratios (~10) of natural waters, which have often been overlooked in previous investigations, in order to obtain practical and relevant results.

1. Introduction

Disinfection byproducts (DBPs) form in drinking waters as a result of reactions between oxidants and natural organic matter (NOM) (Rook, 1974). The NOM characteristics of the source water influence DBP formation and speciation (Kitis et al., 2001; Ates et al., 2007). The most commonly used oxidant in water treatment is chlorine. If bromide (Br^-) and iodide (I^-) are also present, they can react with oxidants and form halogenated DBPs, often measured as total organic halogen (TOX) (Krasner et al., 1989). Chlorine, bromine, and iodine may all substitute into NOM to form TOX. In terms of toxicity, it has been shown that iodinated DBPs, as a group, are more cyto- and genotoxic than brominated or chlorinated DBPs (Plewa et al., 2008). Trihalomethanes (THMs) and haloacetic acids (HAAs) include brominated and chlorinated DBP species that are currently regulated by the United States Environmental Agency (USEPA) (USEPA, 1998, 2006). However, iodinated DBPs are not currently regulated.

In order to comply with increasingly stringent THM and HAA regulations in the US, many water utilities have switched from chlorine to monochloramine practices (Seidel et al.,

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2005) because monochloramine forms fewer regulated THMs and HAAs (Hong et al., 2007). However, iodinated DBP formation is favorable during chloramination (Bichsel and von Gunten, 2000; Krasner et al., 2006; Hua and Reckhow, 2007a; Richardson et al., 2008). As a result, utilities that have converted to monochloramine to lower THM and HAA levels may form iodinated DBPs when treating source waters containing inorganic and organic iodine species.

Iodinated THM (I-THM) formation is favorable under chloramination conditions because of the competing kinetics of iodine oxidation and NOM substitution. First, monochloramine oxidizes I^- to HOI. Then, HOI can either react with NOM or be oxidized to IO_2^- and further to IO_3^-. However the oxidation pathway is extremely slow compared to the much faster reactions of HOI with NOM. Therefore, unlike ozone and chlorine, monochloramine does not considerably oxidize HOI to IO_3^-, a non-toxic end product for iodine (Bichsel and von Gunten, 1999, 2000). When comparing various treatment scenarios (ozone/chlorine, ozone/monochloramine, chlorine, monochloramine, and chlorine dioxide) of waters spiked with elevated concentrations of iodide (200 μg/L), it was confirmed that I-THM formation was greatest from monochloramine (Hua and Reckhow, 2007a).

An occurrence study conducted in the US that investigated 12 water treatment plants with “challenged” source waters (i.e., comparatively high TOC, high Br^- concentrations) found that the highest I-THM formation was observed at a monochloramine plant that added chlorine and ammonia at the same location in the plant (i.e., little to no free chlorine contact time) (Krasner et al., 2006). The sum of six I-THM species was 81% of the mass of 4 regulated THM species at this particular plant. Additionally, during this study, iodo-acids were also found in drinking waters for the first time. The higher formation of I-DBPs during chloramination prompted a follow up study of chloramination plants in 23 cities (Richardson et al., 2008). The source waters had different bromide and iodide concentrations, and the utilities practiced varying chlorine contact times prior to ammonia addition. The researchers found that I-THM formation (2 of 6 I-THM species measured) was greater for plants with shorter free chlorine contact times (<1 min) than plants with longer free chlorine contact times (>45 min). The same occurrence study demonstrated that iodide levels generally varied between 0.4 and 104 μg/L with a median of 10 μg/L, while the bromide concentration varied from 24 to 1120 μg/L with a median of 109 μg/L in these source waters.

It is only under extreme circumstances that iodide can be higher than 100 μg/L. For example, the iodide concentration in the Rio Grande in Brownsville, TX was previously recorded as 212 μg/L (Moran et al., 2002). Iodide concentrations can be higher in arid watersheds such as the American Southwest where irrigation is prevalent, and transpiration dominates. Therefore, salts may concentrate in the soil, and agricultural runoff can transport iodide to the rivers. However, this scenario is rare and most of the time, the iodide concentrations are much lower. For confined groundwaters, iodide generally varies between 0.01 and 20 μg/L (Ali-Mohamed and Jamali, 1989). However, if salt water intrusion is occurring, or if the groundwater is adjacent to halide rocks or brines, iodide concentrations can exceed 50 μg/L (Muramatsu and Wedepohl, 1998; Cancho et al., 2000).

Similar to the concentrations of bromide and iodide, the Br^-/I^- ratio may also vary in source waters. However, the bromide level is almost always higher than the iodide level. In the Richardson et al. (2008) study, the Br^-/I^- ratio varied widely from 3/1 to 238/1 with an average of 13/1. Such large variations in the Br^-/I^- ratio in freshwater are probably due to many factors such as salt water intrusion, various salt deposits containing different levels of bromine and iodine, anthropogenic influences, and slightly greater oxidation potential and biological cycling of iodide compared to bromide (Whitehead, 1984; Fuge and Johnson, 1986; Neal et al., 1990; Muramatsu and Wedepohl, 1998; von Gunten, 2003; Steinberg et al., 2008).

Bromide and iodide concentrations will likely play an important role in I-THM formation and speciation. Kristiana et al. (2009) showed that the formation of total organic iodine (TOI) from chloramination of the hydrophobic acid fraction from the Loire River, Australia increased linearly with increasing iodide concentration (50–300 μg/L). The bromide level was held constant at 300 μg/L, so varying Br^-/I^- ratios were evaluated. Since I-THMs were not measured, it is unknown if I-THM formation would follow the same linear trend as TOI formation.

Hua and Reckhow (2008) investigated the effect of pH on I-THM formation from preformed monochloramine. A source water was spiked with very high concentrations of iodide (1900 μg/L). No bromide was added, and the ambient level of bromide was much lower (78 μg/L); as a result, the Br^-/I^- ratio of the spiked source water was 1:25. This was much lower than a more typical Br^-/I^- mass ratio of 13:1 in natural waters (Richardson et al., 2008). The results showed that (i) I-THM formation increased with pH from 5 to 9, and (ii) iodoform (CHI_3) was the most important I-THM specie for all pH values.

The NOM characteristics of the source water are also important in iodinated DBP formation. Kristiana et al. (2009) quantified iodine incorporation into different NOM fractions (hydrophobic (HPO), hydrophobic acid (HPOA), and transphilic (TPI)) for multiple source waters at varying iodide levels (50–300 μg/L) and bromide at 300 μg/L. Iodine incorporation varied from 10 to 64% and depended on iodide concentration and the NOM isolate. However, I-THMs were not distinguished from TOI. Hua and Reckhow (2007b) suggested that bromine and iodine were more reactive with low specific ultraviolet absorbance (low-$SUVA_{254}$) and low molecular weight (MW) NOM to form I-THMs than high-SUVA, high MW NOM. However, this was not necessarily true for all iodinated DBPs (I-DBPs) because high MW components seemed to contain more TOI precursors than low MW NOM. It is unclear if the I-DBPs formed were of high or low MW. While this study evaluated the effects of NOM characteristics, specifically SUVA and MW distribution, the concentrations of iodide were elevated (250 and 500 μg/L), while the corresponding bromide levels were much lower (<10 and 85 μg/L). Therefore, the results may not be applicable for the conditions encountered in natural waters.

Since the occurrence of iodide and typical bromide to iodide ratios in natural waters have not been extensively characterized until recently, previous research studies have investigated I-THM formation and speciation at very high iodide concentrations (i.e., in excess of 100 μg/L) and without