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A balancing act: Optimizing free chlorine contact time to minimize iodo-DBPs, NDMA, and regulated DBPs in chloraminated drinking water ☆

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ABSTRACT

Many drinking water treatment plants in the U.S. have switched from chlorination to chloramination to lower levels of regulated trihalomethane (THM) and haloacetic acid (HAA) disinfection byproducts (DBPs) in drinking water and meet the current regulations. However, chloramination can also produce other highly toxic/carcinogenic, unregulated DBPs: iodo-acids, iodo-THMs, and N-nitrosodimethylamine (NDMA). In practice, chloramines are generated by the addition of chlorine with ammonia, and plants use varying amounts of free chlorine contact time prior to ammonia addition to effectively kill pathogens and meet DBP regulations. However, iodo-DBPs and nitrosamines are generally not considered in this balancing of free chlorine contact time. The goal of our work was to determine whether an optimal free chlorine contact time could be established in which iodo-DBPs and NDMA could be minimized, while keeping regulated THMs and HAAs below their regulatory limits. The effect of free chlorine contact time was evaluated for the formation of six iodo-trihalomethanes (iodo-THMs), six iodo-acids, and NDMA during the chloramination of drinking water. Ten different free chlorine contact times were examined for two source waters with different dissolved organic carbon (DOC) and bromide/iodide. For the low DOC water at pH 7 and 8, an optimized free chlorine contact time of up to 1 h could control regulated THMs and HAAs, as well as iodo-DBPs and NDMA. For the high DOC water, a free chlorine contact time of 5 min could control iodo-DBPs and NDMA at both pHs, but the regulated DBPs could exceed the regulations at pH 7.

☆ This manuscript is dedicated to Prof. Michael Plewa, whose innovative and pioneering research has been a catalyst for improving the safety of drinking water.

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Introduction

Iodo-acids, iodo-trihalomethanes (iodo-THMs), and nitrosamines are highly toxic disinfection byproducts (DBPs) that are maximized in drinking water with chloramination (Mitch et al., 2003; Krasner et al., 2006; Richardson et al., 2007, 2008; Boyd et al., 2011; Nawrocki and Andrzejewski, 2011; Russell et al., 2012; Wei et al., 2013; Krasner et al., 2013; Postigo and Zonja, 2018; Dong et al., 2019; Allen et al., 2022). For iodo-DBPs, iodide in natural waters reacts with monochloramine to form hypoiodous acid (HOI), which then reacts with natural organic matter (NOM) to form iodo-acids and iodo-THMs (Bichsel and von Gunten, 1999, 2000; Richardson et al., 2008). Competing reactions to form iodite and iodate are much slower with monochloramine than with chlorine, which causes the increased formation of iodo-DBPs with chloramination (Appendix A Fig. S1; Bichsel and von Gunten, 1999, 2000; Richardson et al., 2008).

Iodo-THMs have been known as DBPs since the 1970s, and have been measured in drinking water from the United States, Spain, China, and Australia (Brass et al., 1977; Glaze et al., 1975; Hanson et al., 1987; Krasner et al., 1989; Cancho et al., 2000; Weinberg et al., 2002; Krasner et al., 2006; Richardson et al., 2008; Shi et al., 2009; Criquet et al., 2012; Wei et al., 2013; Kristiana et al., 2017; Allen et al., 2017, 2022; Cuthbertson et al., 2019, 2020), sometimes at levels that are comparable to the regulated THMs (Krasner et al., 2006; Richardson et al., 2008). Iodo-acids were discovered as DBPs more recently in chloraminated drinking water from the U.S. Nationwide Occurrence Study (Plewa et al., 2004; Weinberg et al., 2002; Krasner et al., 2006). A subsequent 23-city occurrence study of chloraminated and chlorinated drinking waters in the United States and Canada revealed up to 10.2 μg/L and 1.7 μg/L for individual iodo-THMs and iodo-acids, respectively (Richardson et al., 2008).

Iodo-DBPs are highly genotoxic and cytotoxic, with iodoacetic acid (IAA) the most genotoxic DBP identified to-date (Richardson et al., 2008; Plewa et al., 2004; Wagner and Plewa, 2017). Human cell results on nontransformed small intestine epithelial cells (Attene-Ramos et al., 2010) and primary lymphocytes (Escobar-Hoyos et al., 2013) show similar genotoxicity potency, and a biological mechanism for HAAs (including IAA) has been reported, in which the mono-HAAs inhibit the activity of glyceraldehyde-3-phosphate dehydrogenase (GAPDH) (Pals et al., 2011). This concentration-dependent activity follows the order: iodo > bromo >> chloroacetic acid, the same order found in earlier mammalian toxicity results (Plewa et al., 2004), which also correlates with their alkylating potential (Pals et al., 2011). IAA is also now known to be tumorigenic in mice, such that N2H3T3 cells can be transformed by IAA *in vivo* into aggressive fibrosarcomas (Wei et al., 2013). IAA also causes developmental abnormalities in mouse embryos (Hunter and Tugman, 1995; Hunter et al., 1996).

The primary source of iodine in iodo-DBPs appears to be from natural iodide in source waters, such that higher natural iodide levels result in higher levels of iodo-DBPs (Richardson et al., 2008; Jones et al., 2011; Dong et al., 2019). However, anthropogenic contaminants like iodinated X-ray contrast media can also serve as sources of iodine in iodo-DBPs when reacted with chlorine or chloramines (Duirk et al., 2011; Ye et al., 2014), and point-of-use iodine treatment (e.g., iodine tincture, iodine tablets, and the Lifestraw®) can produce iodinated DBPs by the reaction of these forms of iodine with NOM (Smith et al., 2010). In addition, seawater used for toilet flushing is also recognized as a source of iodide in the formation of iodo-DBPs (Gong et al., 2013; Gong and Zhang, 2015), and the use of iodized salt in the preservation of seafood (Gong et al., 2018) and in cooking (Pan et al., 2016) can also be sources.

Chloramination forms nitrosamines through reactions of NOM with monochloramine (NH_2Cl, primary disinfectant of chloramines) or dichloramine ($NHCl_2$, a minor component of chloramines) (Schreiber and Mitch, 2006a; Krasner et al., 2013). Both chloramine species can give rise to nitrosamines, including N-nitrosodimethylamine (NDMA), but recent mechanistic studies have shown that $NHCl_2$ plays a more significant role (Schreiber and Mitch, 2006a). Nitrosamines were recognized as DBPs in 2002 and have been found in drinking waters in the United States, Canada, the United Kingdom, China, Japan, Australia, and Singapore (Mitch and Sedlak, 2002; Choi and Valentine, 2002; Zhao et al., 2006; Charrois et al., 2007; Tugulea et al., 2008; Dillon et al., 2008; Goslan et al., 2009; Asami et al., 2009; Templeton and Chen, 2010; Zhang et al., 2010; Boyd et al., 2011; Bond et al., 2011; Wang et al., 2011, 2016; Newcombe et al.. 2012; Luo et al., 2012; Bei et al., 2016, 2017; Kristiana et al., 2017; Qiu et al., 2020). The largest body of data for nitrosamines resulted from the U.S. EPA's Unregulated Contaminant Monitoring Rule-2 (UCMR-2), in which NDMA and 5 other nitrosamines were measured in ~1200 water treatment plants in the United States (U.S. EPA, 2010; Russell et al., 2012). In the UCMR-2, NDMA was detected in 34% of the chloraminated drinking waters and 3% of the chlorinated drinking waters. Typically, levels were 10 ng/L or less, but occasionally were higher, up to 630 ng/L at one location. Other nitrosamines—nitrosodiethylamine (NDEA), nitrosomethylethylamine (NMEA), nitrosopyrrolidine (NPYR), and nitrosobutylamine (NDBA) were also detected, but at lower levels and at much lower frequency than NDMA.

Chlorine can also produce nitrosamines through reactions with ammonia (Tugulea et al., 2008), nitrogen-containing pharmaceuticals and other anthropogenic contaminants (Kemper et al., 2010; Le Roux et al., 2011; Shen and Andrews, 2011), and with wastewater-impacted waters (Schreiber and Mitch 2006b; Krasner et al., 2009), as well as with coagulants (Wilczak et al., 2003; Park et al., 2009), ion-exchange resins (Singer and Flower, 2012), and activated carbon (Padhye et al., 2010) used in drinking water treatment. Swimming pools can also be a source of exposure to nitrosamines (Walse and Mitch, 2008; Soltermann et al., 2013).

Nitrosamines are animal carcinogens (Shank and Magee, 1981; U.S. EPA, 1987; Richardson et al., 2007), and NDMA is recognized as a probable human carcinogen, with a health reference level (HRL) for cancer of 0.7 ng/L (https://www.epa.gov/sites/default/files/2014-03/documents/ffrrofactsheet_contaminant_ndma_january2014_final.pdf). Several nitrosamines are recognized bladder carcinogens (International Agency for Research on Cancer (IARC), 1979; Shank and Magee, 1981), the cancer endpoint most commonly observed in human epidemiologic studies

(Villanueva et al., 2004). Research also shows that several nitrosamines are mutagenic in Salmonella (Ames test) and genotoxic in mammalian cells, with NDMA the most potent in both assays (Wagner et al., 2012).

In practice, chloramines are generated at drinking water plants by the addition of chlorine and ammonia. Because chlorine is a stronger disinfectant than chloramines, drinking water plants typically add chlorine first and allow a sufficient free chlorine contact time to more effectively kill pathogens before adding ammonia to form chloramines. Occasionally, preformed monochloramine has been used, and sometimes there is a significant amount of ammonia already present in source waters, such that plants that chlorinate these waters are essentially chloraminating (Tugulea et al., 2008). Chloramination has become a popular disinfectant because it can significantly reduce the levels of regulated THMs and haloacetic acids (HAAs) (Seidel et al., 2005; Chen et al., 2007; Krasner et al., 2013; Li et al., 2018), allowing plants with high NOM to more effectively meet the U.S. regulatory limits of 80 and 60 μg/L, respectively (U.S. EPA, 2006). Balancing the concentration-time (CT) of the disinfectant dose and time of reaction is key in assuring effective disinfection and compliance with DBP regulations. However, with shorter free chlorine contact times (and increased time of reaction with chloramines), both iodo-DBPs and nitrosamines will increase in formation. Therefore, it has been suggested that plants should optimize this free chlorine contact time, such that iodo-DBPs (Richardson et al., 2008; Jones et al., 2011) and nitrosamines (Charrois and Hrudey, 2007; Chen and Valentine, 2008; Shah et al., 2012; Li et al, 2018) are minimized, while also keeping the regulated DBPs below their maximum contaminant levels (MCLs).

In the present study, we examined the formation of both iodo-DBPs and nitrosamines (as represented by NDMA) in controlled chloramination laboratory studies using a low dissolved organic carbon (DOC)/low bromide-iodide source water and a high DOC/high bromide-iodide source water at two different pHs (7 and 8), using ten different free chlorine contact times (0, 5, 10, and 30 min; 1, 6, 12, 18, 24, and 48 hr). In the low DOC water experiments, bromide and iodide were spiked at levels realistic of high bromide/iodide source waters (500 and 50 μg/L, respectively) (Richardson et al., 2008). Our goal was to determine whether an optimal free chlorine contact time could be established in which the highly toxic/carcinogenic iodo-DBPs and NDMA could be minimized, while keeping regulated DBPs below their MCLs. In this way, drinking water treatment plants might be able to further improve drinking water quality and safety.

1. Materials and methods

1.1. Chemicals and reagents

Six iodo-THMs (dichloroiodomethane, bromochloroiodomethane, dibromoiodomethane, chlorodiiodomethane, bromodiiodomethane, and iodoform) and six iodoacids (iodoacetic acid, bromoiodoacetic acid, diiodoacetic acid, (*Z*)-3-bromo-3-iodo-propenoic acid, (*E*)-3-bromo-3-iodo-propenoic acid, and (*E*)-2-iodo-3-methylbutenedioic acid) were purchased at the highest level of purity from Orchid Cellmark (New Westminster, BC, Canada), CanSyn Chem. Corp. (Toronto, ON, Canada), and Sigma-Aldrich. Commercial 10%–13% sodium hypochlorite (NaOCl) was purchased from Sigma-Aldrich (Milwaukee, WI). All other organic and inorganic chemicals were certified ACS reagent grade and used without further purification.

Table 1 – Water quality data for source waters*.

	DOC (mg/L)	Br^- (μg/L)	I^- (μg/L)
Water 1 (spiked)	1.7	491	44
Water 2	6.1	473	32

* Water 1 was spiked with bromide and iodide due to low ambient levels (18.0 μg/L and non-detect, respectively); Water 2 bromide and iodide levels are ambient (unspiked).

1.2. Controlled laboratory reactions

Aqueous stock solutions and experiments utilized purified water (18 MΩ-cm) from a Barnstead ROPure Infinity™/NANOPure™ system (Barnstead-Thermolyne Corp., Dubuque, IA). The pH was monitored with an Orion 940 pH meter equipped with a Ross combination electrode (Thermo Scientific, Waltham, MA). Glassware and polytetrafluoroethylene (PTFE) septa were soaked in a concentrated free chlorine solution (6%) for 24 hr, rinsed with deionized water, followed by purified water and methanol, and dried prior to use. Source waters were obtained from drinking water treatment plants from two different states within the U.S.; one from a low DOC/low bromide surface water (Water 1), and one from a higher DOC/high bromide surface water (Water 2). Source water characteristics are shown in Table 1. These waters were filtered (using 5.0 and 0.45 μm filters, Millipore Corp., Billerica, MA) prior to use. For Water 1 (with low natural bromide and no natural iodide), sodium bromide and sodium iodide were spiked at 500 and 50 μg/L bromide and iodide, respectively, to achieve similar concentrations observed in high bromide/iodide source waters (Richardson et al., 2008). Aqueous chlorine solutions were diluted to 1000 mg/L and added to the source waters and buffer in a 6 L Erlenmeyer flask under rapid-mix conditions using a magnetic stir plate and a PTFE-coated stir bar. Appropriate chlorine doses were determined based on oxidant demand of the source waters, such that there was a free chlorine residual of approximately 1.0 mg/L after 24 hr. This resulted in a dose of 4 mg/L free chlorine for Water 1 and 9 mg/L free chlorine for Water 2, which had a higher TOC and exerted a higher oxidant demand.

Ammonium chloride was added to achieve a 0.7 Cl/N molar ratio) at different time points of free chlorine contact time (0 min, 5 min, 10 min, 30 min, 1 hr, 6 hr, 12 hr, 18 hr, 24 hr, and 48 hr) following initial dose of chlorine. The *N*,*N*-diethyl-*p*-phenylendiamine (DPD) titrimetric method was used to measure the free chlorine level at each time point so that an appropriate amount of ammonium chloride could be added to achieve the 0.7 Cl/N molar ratio for formation of monochloramine (Standard Methods, 1985). For the 0 min time point

(involving 0 min of free chlorine contact time, i.e., addition of preformed monochloramine), monochloramine solutions were prepared by mixing ammonium chloride with hypochlorous acid to achieve the desired 0.7 Cl/N molar ratio, and the solution was allowed to react and equilibrate for 30 min in 10 mmol/L buffer, prior to addition to the buffered source waters. Reactions were performed headspace-free in 125 and 250 mL amber reaction vessels with PTFE septa and stored in the dark at 25°C. The total reaction time for all experiments was 48 hr, and experiments were performed in duplicate unless otherwise stated. The pH was maintained using 10 mmol/L of phosphate buffer (for both pH 7.0 and 8.0) for Water 1 and 10 mmol/L of phosphate (pH 7.0) and 5 mmol/L of borate (pH 8.0) buffer for Water 2.

Samples were collected for iodo-THMs, iodo-acids, N-nitrosodimethylamine (NDMA), the four regulated THMs (THM4), and the nine chloro-bromo HAAs (HAA9) at the end of the 48 hr reaction time with monochloramine (post-NH_2Cl) following different free chlorine contact times. Residual oxidants were quenched with sodium sulfite (for THMs, iodo-THMs, and iodo-acids), ammonium chloride (for HAAs), and sodium thiosulfate (for NDMA). Samples were extracted immediately after quenching to eliminate the chance for potential degradation of iodo-DBPs. At the end of each 48 hr experiment, residual aqueous oxidant concentrations were determined using the DPD titrimetric method (Standard Methods, 1985).

1.3. *Iodo-THM, iodo-acid, NDMA, iodide, and bromide measurements*

Iodo-THM measurements were carried out using liquid-liquid extraction and gas chromatography (GC) with electron ionization-MS; iodo-acid measurements were carried out using liquid-liquid extraction, diazomethane derivatization, and detection by GC-negative chemical ionization (NCI)-MS, according to previously published methods (Richardson et al., 2008; Duirk et al., 2011). NDMA measurements were carried out for Water 1 only using EPA Method 521, which uses solid phase extraction and analysis with GC-positive chemical ionization-MS/MS (U.S. EPA, 2004). Further details for iodo-DBP and NDMA analyses are available in Appendix A. Iodide and bromide were measured using high performance ion chromatography-tandem mass spectrometry (HPIC-MS/MS) (Xue et al., 2016).

1.4. *Total organic carbon measurements*

TOC was analyzed according to EPA Method 415.3 (Rev 1.1 http://www.epa.gov/nerlcwww/ordmeth.htm) utilizing a Shimadzu TOC-L combustion instrument with a reporting level of 0.1 mg-C/L.

2. Results and discussion

2.1. *Iodo-DBPs*

At pH 7 and 8, which are the pH values most relevant to drinking water treatment, iodo-THMs formed at much higher levels than iodo-acids, at relative ratios similar to those in the 23-city occurrence study (Richardson et al., 2008). Also, both iodo-THMs and iodo-acids maximized in formation at the lowest free chlorine contact times for both source waters, although a 5 min free chlorine contact time was not very different from a 0 min free chlorine contact time (preformed NH_2Cl) for iodo-acid formation from Water 2 (Figs. 1 and 2; Appendix A, Tables S1, S2, S6, S7).

Higher pH (pH 8 vs. pH 7) resulted in more iodine incorporation into iodo-THMs for both low DOC and high DOC waters (Water 1 and 2) (Figs. 1 and 2). For example, iodoform and chlorodiiodomethane were more dominant at pH 8 (for both Water 1 and 2), with their sum increasing from 13.9 to 30.6 nmol/L (Water 1) and from 11.9 to 37.0 nmol/L (Water 2) for pH 7 vs. pH 8. This is likely due to increased stability of NH_2Cl and HOI at pH 8 (Bichsel and von Gunten, 1999, 2000). Of the iodo-acids, iodoacetic acid was the predominant species formed in most of the reactions at shorter free chlorine contact times, followed by bromoiodoacetic acid and diiodoacetic acid (Figs. 1 and 2).

Decreasing levels of iodo-DBPs at longer free chlorine contact times can be explained by the rapid oxidation of iodide to HOI by HOCl, and further oxidation of HOI to form iodate (second-order rate constant of 8.2 $(mol/L)^{-1}$ sec^{-1}), whereas the addition of ammonia to form NH_2Cl hinders further oxidation of HOI to iodate (second-order rate constant of 2×10^{-3} $(mol/L)^{-1}$ sec^{-1}) (Bichsel and von Gunten 1999, 2000). In addition, high bromide increases the conversion of iodide to iodate with chlorine, such 50% of iodide is oxidized to iodate after 360, 35, and 13 min, for increasing bromide concentrations of 0, 0.5, and 2 μmol/L, respectively (Criquet et al., 2012).

Further, under high bromide conditions like the ones in these experiments, reactions with HOI will compete with those from HOBr, which are much faster and contribute to increased incorporation of bromine into the DBPs. HOBr is the predominant oxidant species relative to HOI in the presence of chlorine (Criquet et al., 2012; Jones et al., 2012).

The trend of increased iodo-DBPs at lowest free contact times is consistent with results from the 23-city survey in the U.S. and Canada (Richardson et al., 2008). In that study, iodo-THMs and iodo-acids were highest at plants with <1 min free chlorine contact time, and lowest at plants with >45 min free chlorine contact time. These results are also consistent with two other studies showing increased iodo-DBP formation from preformed NH_2Cl vs. HOCl (Hua and Reckhow, 2007a; Ding et al., 2009), as well as with reactions conducted on water with a low specific UV absorbance at 254 nm ($SUVA_{254}$) in a study that evaluated the formation of iodo-THMs at three free chlorine contact times (0, 5, and 20 min) and different Br/I ratios at pH 7.5 (Jones et al., 2011). In this study, iodine incorporation maximized with preformed NH_2Cl for a low $SUVA_{254}$ (2.5 L/(mg-m)) water. Low molecular weight, low $SUVA_{254}$ NOM has been shown to be more reactive with preformed NH_2Cl (Hua and Reckhow, 2007b).

However, reaction behavior can be complex, as iodo-DBP formation and NOM reactivity can vary dramatically with the type of NOM, dose of disinfectants, and concentration of bromide and iodide, as evidenced in a study of total organic iodine (TOI) produced by different NOM isolates when reacted with NH_2Cl or chlorine (Kristiana et al., 2009). For these NOM

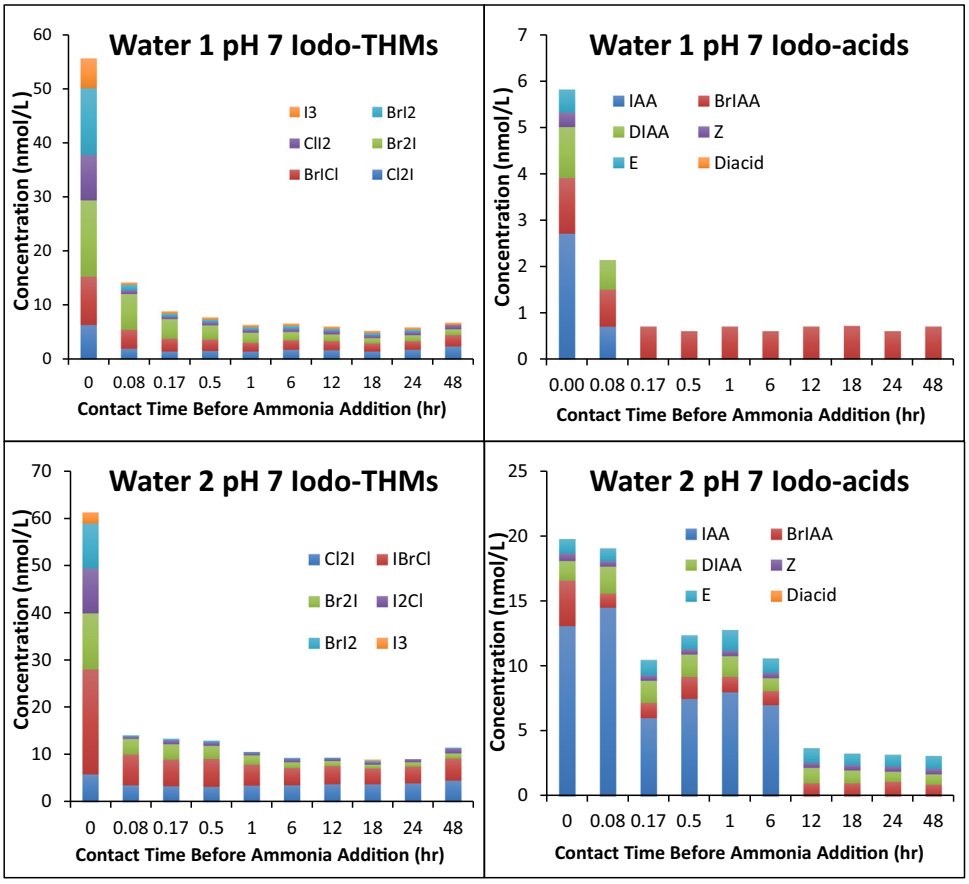

Fig. 1 – Effect of free chlorine contact time on iodo-THMs and iodo-acids at pH 7. Cl2I = dichloroiodomethane, BrClI = bromochloroiodomethane, Br2I = dibromoiodomethane, ClI2 = chlorodiiodomethane, BrI2 = bromodiiodomethane, I3 = iodoform, IAA = iodoacetic acid, BrIAA = bromoiodoacetic acid, DIAA = diiodoacetic acid, Z = (Z)-3-bromo-3-iodopropenoic acid, E = (E)-3-bromo-3-iodopropenoic acid, Diacid = (E)-2-iodo-3-methylbutenedioic acid. Data are the mean of 2 replicates. See Appendix A Tables S1 and S3 for individual DBP concentrations and standard error.

isolates collected from the United States and France, percent aromatic carbon varied from 9% to 26% and iodine incorporation into DBPs varied from 8% to 64%. Aromatic carbon was determined to be a major reaction site for the production of TOI with chloramination. The importance of aromatic composition in NOM in the formation of iodo-DBPs was also noted in an earlier study which found that phenolic moieties could account for the observed reactivity of HOI with NOM (Bichsel and von Gunten, 2000). Differences in NOM reactivity were also evident in the Jones et al. (2011) study, where a higher $SUVA_{254}$ water sometimes formed higher levels of iodo-THMs with prechlorination (prior to chloramination), compared to reactions with preformed NH_2Cl.

Further, while the concentration of NH_2Cl may have a minimal effect on the formation of TOI, the concentration of chlorine can significantly impact the amount of TOI formed, such that in the NOM isolate experiments cited above, TOI was formed only when chlorine doses were <10 mg/L (Kristiana et al., 2009). The effect of chlorine dose was also noted in the Jones et al. study, which found that doubling the HOCl dose and adding 15 more minutes of free chlorine contact time decreased iodo-THM formation (Jones et al., 2011). At higher doses of chlorine and CT, chlorine is more effectively able to oxidize iodide to iodate and reduce the competing reactions of HOI with NOM. Further, in chloraminated water, the formation of bromamines, which are not as reactive with NOM as HOBr, can compete favorably with HOBr in high bromide waters, such that TOCl (representing chlorine-containing DBPs) is higher than TOBr (representing bromine-containing DBPs) (Kristiana et al., 2009). Thus, the formation of these DBPs is a complex interplay of NOM chemical structure (e.g., aromatic composition), dose of disinfectant, reaction time, and relative levels of iodide and bromide, and is influenced by the competing reactions of different oxidant species produced.

2.2. NDMA

As expected, preformed chloramine (zero free chlorine contact time) maximized NDMA formation at both pHs for Water 1 (Fig. 3; Appendix A Table S5), in keeping with previous studies that have shown that NDMA formation is favored for chloramine vs. chlorine (Russell et al., 2012). Because bromide can catalyze the formation of NDMA during chloramination (Le Roux et al., 2012; Luh and Marinas, 2012), the relatively higher NDMA levels observed here vs. those previously reported in

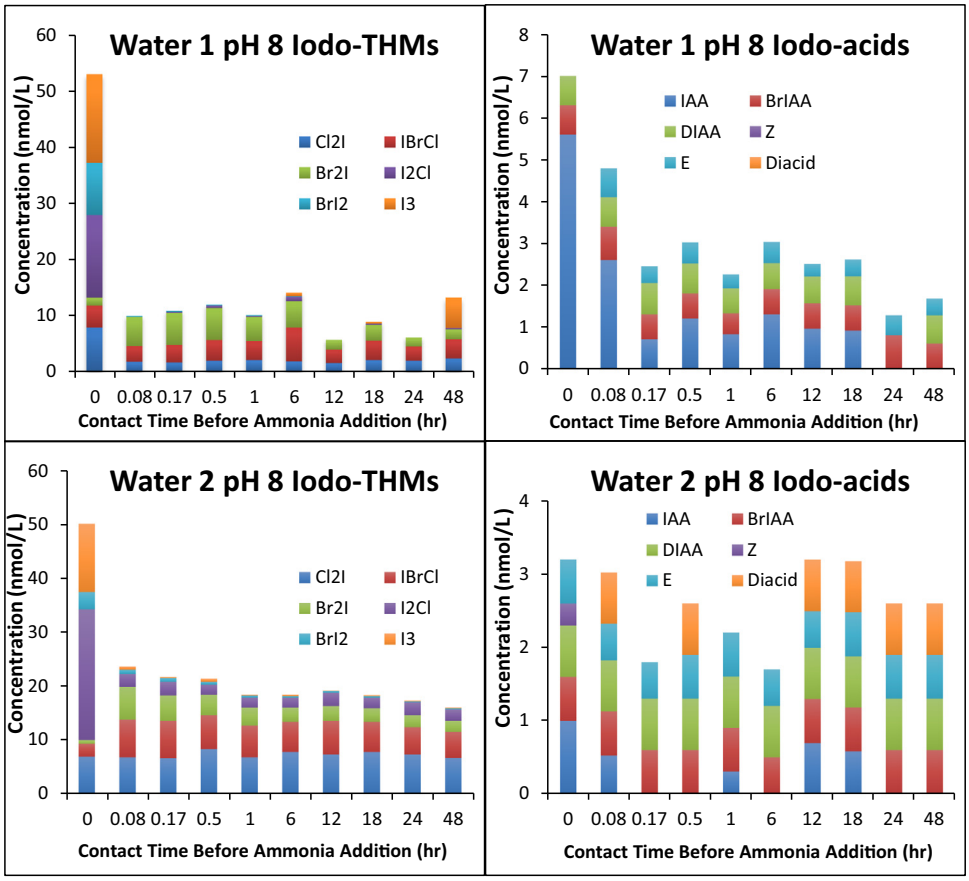

Fig. 2 – Effect of free chlorine contact time on iodo-THMs and iodo-acids at pH 8. Cl2I = dichloroiodomethane, BrClI = bromochloroiodomethane, Br2I = dibromoiodomethane, ClI2 = chlorodiiodomethane, BrI2 = bromodiiodomethane, I3 = iodoform, IAA = iodoacetic acid, BrIAA = bromoiodoacetic acid, DIAA = diiodoacetic acid, Z = (Z)-3-bromo-3-iodopropenoic acid, E = (E)-3-bromo-3-iodopropenoic acid, Diacid = (E)-2-iodo-3-methylbutenedioic acid. Data are the mean of 2 replicates. See Appendix A Tables S2 and S4 for individual DBP concentrations and standard error.

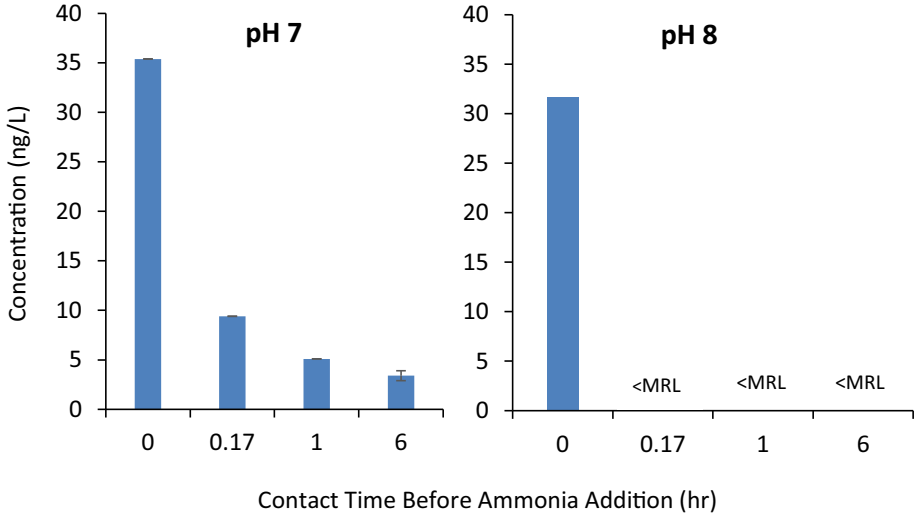

Fig. 3 – Effect of free chlorine contact time on NDMA at pH 7 and 8 (Water 1). Error-bars represent the standard error of duplicate experiments when replicate experiments were run and values were greater than the estimated MRL of 2.0 ng/L.

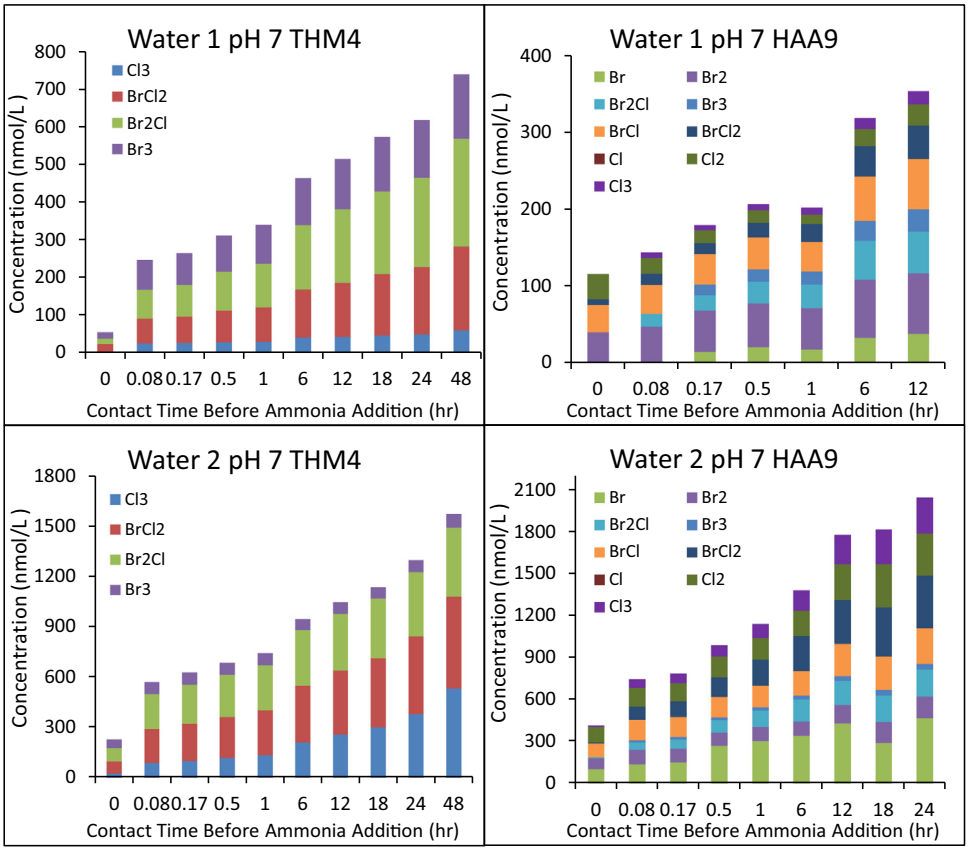

Fig. 4 – Effect of free chlorine contact time on THM4 and HAA9 at pH 7.

other studies are likely due to the relatively high bromide level (e.g., 491 µg/L). From these data, it is also clear that, for this source water, a free chlorine contact time of 10 min (0.17 hr) substantially reduces NDMA formation to levels that would meet NDMA regulations in Canada (40 ng/L) and the California notification level of 10 ng/L.

2.3. *Regulated THM and HAA formation*

As expected, longer reaction times with free chlorine resulted in higher levels of the chloro/bromo THMs and HAAs at both pHs (Figs. 4 and 5; Appendix A Tables S6-S9). Higher THMs were generally formed at higher pH and higher HAAs formed at lower pH. For Water 1, the THM4 regulatory limit (MCL of 80 µg/L) was exceeded at a free chlorine contact time of 6 hr at both pHs. However, for Water 2 (with high DOC), THM MCL levels were exceeded after only very short free chlorine contact times of 5–10 min. For HAA5, Water 1 did not exceed the HAA5 MCL of 60 µg/L at pH 7 and 8, even for 12 hr of free chlorine contact time. For Water 2, the MCL was exceeded at 5 min and 6 hr, for pH 7 and 8, respectively. The initial concentration of bromide in both these waters is quite high (but representative of real source waters), and we expect a high degree of bromine incorporation into both THM and HAAs, leading to higher mass-based concentrations. However, unlike THMs where enhanced bromine incorporation will lead to higher THM4 concentrations, greater bromine incorporation in the HAA class can lead to increased formation of HAA species 6–9 (bromochloro-, bromodichloro-, dibromochloro-, and tribromoacetic acid) at the expense of HAA5. Hence, the lack of HAA5 MCL exceedance for Water 1 is likely due to shifts to the non-regulated, brominated species.

2.4. *Balancing the formation of iodo-DBPs and NDMA vs. regulated THMs and HAAs*

Results from this study revealed that the range of free chlorine contact time to minimize the formation of iodo-DBPs and NDMA, while still maintaining regulated THMs and HAAs below their MCLs, can vary with the water and pH. For the low DOC water (Water 1) at pH 7 and 8, an optimized free chlorine contact time of up to 1 hr could control regulated THMs (THM4) and HAAs (HAA5) to their MCLs of 80 and 60 µg/L, respectively (Appendix A Tables S6-S9), as well as iodo-DBPs and NDMA. For the high DOC water (Water 2), a free chlorine contact time of 5 min could control iodo-DBPs and NDMA at both pHs, but the regulated THMs and HAAs would exceed the regulatory limits at pH 7.

However, it is also important that the disinfectant concentration-time (CT) is adequate to achieve sufficient inactivation of pathogens in the water. To that end, we estimated Giardia inactivation for each free chlorine reaction phase and used a conservative assumption for the effective chlorine concentration with residual chlorine measured at the end of the free chlorine phase. Log-inactivation estimates were made using the above times (1 hr and 5 min) and residual assumptions

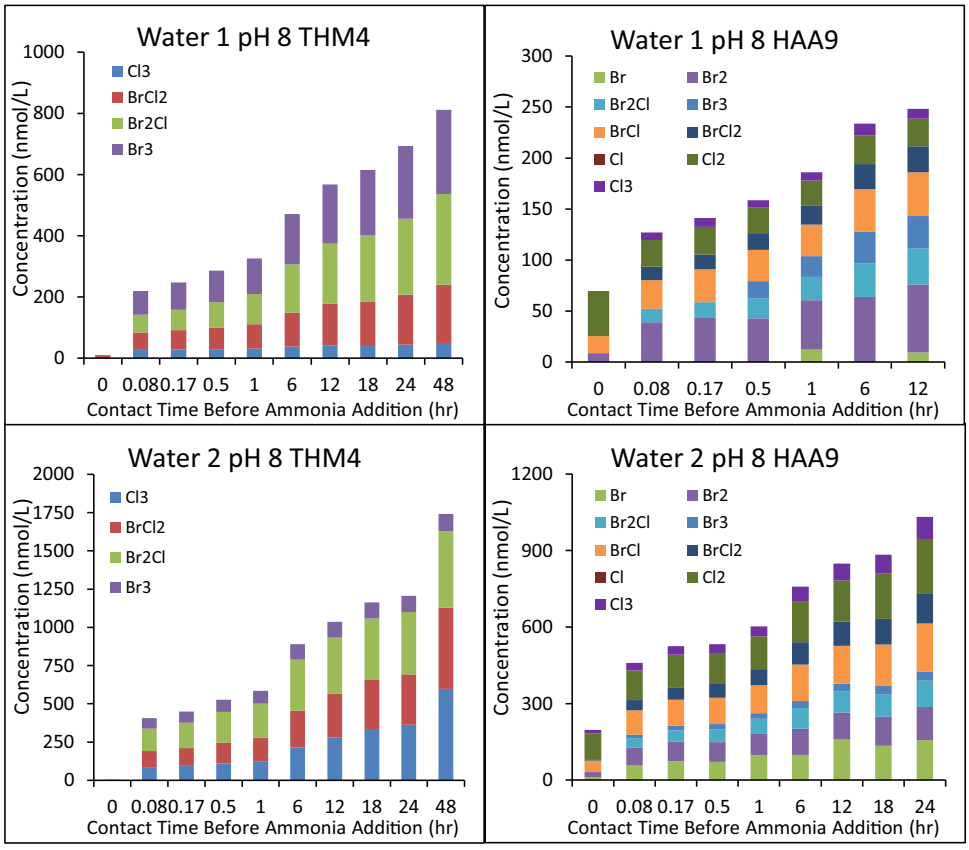

Fig. 5 – Effect of free chlorine contact time on THM4 and HAA9 at pH 8.

with a Giardia inactivation equation (Eq. (1)), which takes into account temperature and pH (U.S. EPA, 2020).

$$\text{Log reduction} = \frac{CT}{\left[0.2828 \times pH^{2.69} \times (Cl_2\ \text{residual})^{0.15} \times 0.933^{(\text{Temperature}-5)}\right]} \quad (1)$$

where CT is in the units of (mg·min)/L, Cl_2 residual in the units of mg/L (as Cl_2) and temperature is assumed to be 20°C. Calculations indicate that 1 hr of free chlorine contact time for Water 1 is likely sufficient to achieve 3-logs removal of Giardia, but 5 min of free chlorine contact time for Water 2 may not be sufficient. Therefore, before free chlorine contact times are established, sufficient pathogen inactivation needs to be tested with the specific water. Future research should also explore free chlorine contact times less than 5 min. While these two waters represent very different source water characteristics (low/high DOC), for application at a drinking water treatment plant, it is recommended to test the specific source waters because of the tremendous variation in NOM structure and reactivity. Moreover, drinking water treatment plants with high DOC commonly employ enhanced coagulation to remove some of the DOC, which should lower DBP concentrations compared to results shown here (where coagulation was not used). In addition, as outlined earlier, CT values are important to assure effective disinfection of drinking water.

Finally, it should be noted that maximum total iodo-DBPs measured in this study represent only 32% incorporation of iodide. Kristiana et al. (2009) showed that up to 60% of initial iodide can be incorporated into TOI formed with chloramination. Thus, while iodo-THMs and iodo-acids appear to be the dominant low molecular weight DBPs formed when chloramine is used to treat high-iodide waters (Richardson et al., 2008), it is almost certain that there are other iodinated compounds not accounted for here. To this point, new iodo-DBPs were discovered recently, including iodoacetaldehyde, iodoacetonitrile, chloroiodoacetonitrile, iodoacetamide, chloroiodoacetamide, diiodoacetamide, chloroiodomethane, trichloroiodomethane, iodo-phenols, and iodo-peptides (Dong et al., 2019; Postigo and Zonja, 2018; Allen et al., 2022). In addition, a previous study by Zhu and Zhang (2016) developed a kinetic model for the formation of TOCl, TOBr, and TOI during chlorination and chloramination, and investigated impacts of free chlorine contact time on the overall predicted toxicity. Their model indicated that increasing the free chlorine contact time from 0 to 5 min causes TOCl, TOBr, and TOI levels to vary dramatically, with estimated toxicity risk first decreasing, then increasing, with increasing free chlorine contact time. The minimum predicted toxicity occurred at 1 min (which was lower than what we found in the current study). This illustrates that other iodo- and bromo-DBPs that are part of the missing TOI and TOBr may play an important role in overall toxicity of the treated water.

Moreover, results from Dai and Mitch (2013) revealed that the measurable nitrosamines represent only ~5% of the total nitrosamines formed in chloraminated drinking water. Therefore, the measurement of NDMA is only a small part of the

complete nitrosamine picture. Given the toxicity of iodinated DBPs and nitrosamines, future research should focus on the unidentified TOI and nitrosamines and ensure that these recommended free chlorine contact times minimize all their toxic forms.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.05.024. This includes additional information on experimental methods and additional figure and tables.

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