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Comparison of ferrate and ozone pre-oxidation on disinfection byproduct formation from chlorination and chloramination

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ABSTRACT

This study investigated the effects of ferrate and ozone pre-oxidation on disinfection byproduct (DBP) formation from subsequent chlorination or chloramination. Two natural waters were treated at bench-scale under various scenarios (chlorine, chloramine, each with ferrate pre-oxidation, and each with pre-ozonation). The formation of brominated and iodinated DBPs in fortified natural waters was assessed. Results indicated ferrate and ozone pre-oxidation were comparable at molar equivalent doses for most DBPs. A net decrease in trihalomethanes (including iodinated forms), haloacetic acids (HAAs), dihaloacetonitrile, total organic chlorine, and total organic iodine was found with both pre-oxidants as compared to chlorination only. An increase in chloropicrin and minor changes in total organic bromine yield were caused by both pre-oxidants compared to chlorination only. However, ozone led to higher haloketone and chloropicrin formation potentials than ferrate.

The relative performance of ferrate versus ozone for DBP precursor removal was affected by water quality (e.g., nature of organic matter and bromide concentration) and oxidant dose, and varied by DBP species. Ferrate and ozone pre-oxidation also decreased DBP formation from chloramination under most conditions. However, some increases in THM and dihaloacetonitrile formation potentials were observed at elevated bromide levels.

Keywords: ferrate pre-oxidation; ozone pre-oxidation; organic matter, chlorine disinfection; chloramine disinfection; disinfection byproducts

1. Introduction

While crucial in the prevention of waterborne disease, drinking water disinfection with chlorine has caused concern as more than 600 disinfection byproducts (DBPs) with potential adverse health effects have been detected in chlorinated waters (Richardson et al., 2007). Among the known DBP species, trihalomethanes (THMs) and haloacetic acids (HAAs) are the two most prevalent groups formed in chlorinated water and have been regulated by the United States Environmental Protection Agency (Seidel et al., 2017). Other unregulated DBPs, e.g., iodinated THMs (I-THMs), haloacetonitriles (HANs), haloketones (HKs), and chloropicrin (CP), have raised attention due to higher toxicity, carcinogenicity and mutagenicity (Daniel et al., 1986; Plewa et al., 2004; Plewa et al., 2002; Robinson et al., 1989). The formation of brominated and iodinated DBPs in waters with elevated levels of bromide and iodide calls for increased focus because brominated and

iodinated DBPs are more toxic than their chlorinated analogues (Langsa et al., 2017; Plewa et al., 2004)

Many utilities have turned to chloramines, which produce only trace amounts of THMs and trihalogenated HAAs (THAAs), to control regulated DBP formation in finished water (Diehl et al., 2000). However, chloramines can cause other water quality and operational problems and their use has not always been viewed as the best option. Instead, many utilities have chosen to make process changes to improve the removal of DBP precursors, and use of pre-oxidation features prominently in these strategies. Application of oxidants (e.g. ozone) can help by partially oxidizing DBP precursors within natural organic matter (NOM), and by having a beneficial impact on subsequent processes that affect final DBP concentrations (Camel and Bermond, 1998).

The use of oxidants, and ozone in particular, for abatement of THM precursors was an early area of research even in advance of the 1979 THM rule. Many of these early studies were poorly documented (Rice, 1980; Rosen, 1980; Stevens and Symons, 1976) and as a result, it's difficult to draw quantitative conclusions from this work. Subsequent research on the role of radical scavengers and chlorination protocols (Reckhow et al., 1986) has led to better design of precursor oxidation studies. Most studies have shown increasing abatement of THM precursors with increasing transferred ozone dose when treating waters with SUVA values of 2 or greater. At an transferred ozone dose of 1 mg-O₃/mg-C, the typical percent abatement is 15-35%, when subsequent chlorination is at near neutral pH (Hu et al., 2010b; Hua and Reckhow, 2013; Reckhow et al., 1986; Xiong and Graham, 1992; Yang et al., 2012).

Ozone was found to destroy chlorination DBP precursors with the efficacy order of DHANs > THMs $\approx$ THAAs > DHAAs, and also decreased the yields of DHAAs and THMs from chloramination (Hua and Reckhow, 2013; Wert and Rosario-Ortiz, 2011). However, pre-ozonation followed by chlorination was found to increase CP formation by 2–10 times in different waters (Hoigné and Bader, 1988; Jacangelo et al., 1989).

Pre- or intermediate ozonation may affect the performance of downstream treatment processes and thereby further impact final DBP concentrations. Although studied by several groups, the many effects of pre-ozonation on coagulation is still not easy to characterize or predict (Becker and O'Melia, 1995; Edwards and Benjamin, 1992; Reckhow et al., 1986; Schneider and Tobiason, 2000). Perhaps most important are the impacts on granular media filtration, either due to changes in biodegradation or adsorption. It has long been known that precursors to many DBPs are subject to biological degradation on acclimated media filters (Tobiason et al., 1993). Accordingly, ozone has been shown to enhance precursor removal in subsequent filtration much as it does removal of bulk NOM (Speitel et al., 1993). This impact is substantial and it affects precursors to different DBPs differently (de Vera et al., 2016; Krasner et al., 2012).

Ferrate (Fe(VI)) has been proposed as an alternative pre-oxidant in drinking water treatment. In addition to being a powerful disinfectant (Hu et al., 2012; Jiang et al., 2007; Schink and Waite, 1980), ferrate can oxidize many aquatic pollutants (Goodwill et al., 2016; Jiang, 2007; Lee et al., 2003; Murmann and Robinson, 1974; Sharma, 2002) while producing fewer regulated halogenated byproducts as compared to other oxidants more commonly deployed in water treatment (Sharma, 2013, 2011, 2010). Also, ferric iron resulting from ferrate decomposition may support coagulation (Goodwill et al., 2015; Jiang

and Wang, 2003; Ma and Liu, 2002), and catalyze ferrate decomposition (Y. Jiang et al., 2015). For DBP precursor removal, ferrate oxidation has been found to decrease the THM, HAA, HAN, and HK formation from chlorination, and the I-THM and *N*-nitrosodimethylamine (NDMA) formation from chloramination (Gan et al., 2015; Jiang et al., 2016a; Lee et al., 2008; Yang et al., 2013; Zhang et al., 2015). The addition of ferrate to a small-scale drinking water treatment system showed positive impacts on finished water quality without negative impacts on downstream processes (Goodwill et al., 2016).

Compared to ozone, ferrate oxidation seems to produce lower levels of bromate due to the slow reaction rate between ferrate and bromide (Jiang et al., 2016b). Ferrate can be considered a simpler alternative to ozone, as it can be produced offsite without ancillary systems, or produced onsite using common water treatment inputs. In-situ electrochemical production is also possible (Dubrawski et al., 2018; Jiang et al., 2015; Villanueva-Rodríguez et al., 2012; Yates et al., 2014a). There are, of course, disadvantages of Fe(VI) as compared to O₃, including the handling of ferric iron solids (Yates et al., 2014b). Most Fe(VI) adaptation has been in treatment of industrial wastes, and utilization for drinking water treatment is limited (Cui et al., 2018; Goodwill et al., 2016), partly due to lack of information on performance, and extant research needs. No research has directly compared the effects of ferrate and ozone pre-oxidation on DBP formation from chlorination or chloramination, especially when there are elevated levels of bromide and iodide.

The reactions of strong oxidants like ozone with NOM and the ways in which these reactions propagate through subsequent treatment processes are difficult to study without simplifying the systems in some way. A reductionist approach has been commonly used whereby sub-components of full treatment system are been studied in isolation, and then

the pieces assembled to get a better picture for the complete system. This study represents a reductionist study of the direct impacts of pre-oxidation on DBP precursors.

The principal objectives of this research were (1) to investigate DBP formation under various oxidation scenarios (chlorine, chloramine, each with ferrate pre-oxidation, and each with pre-ozonation); (2) to compare the effectiveness of ferrate versus ozone pre-oxidation for DBP control; and (3) to determine the effect of oxidant dose, and bromide and iodide concentrations on DBP precursor transformation by ferrate and ozone.

2. Materials and methods

2.1 Chemicals and reagents

Potassium ferrate (K_2FeO_4 , 93%), potassium bromide (99.95%), potassium iodide (99.99%), and other reagents were purchased from Sigma-Aldrich (St. Louis, MO, US) or Fisher-Scientific (Fair Lawn, NJ, US). All aqueous solutions were prepared with ultrapure water produced by a Milli-Q system (Advantage A10, Millipore, Billerica, MA). The chlorine was sourced as a laboratory grade ~5.5% solution of sodium hypochlorite (Fisher-Scientific). The strength of chlorine stock solution was confirmed by titration each time before use.

2.2 Natural water samples

Two water samples were collected from the drinking water utilities in Gloucester (GL), Massachusetts (MA) and Norwalk (NW), Connecticut (CT). Table 1 shows the chemical characteristics of the raw waters. The dissolved organic carbon (DOC) concentration of the GL and NW waters were 4.0 and 3.2 mg/L, respectively. The nature of this DOC was characterized through specific ultra-violet absorbance (SUVA) (Edzwald, 1993; Edzwald

et al., 1985). In general, SUVA values > 4 indicate NOM comprised of a high fraction of aquatic humic matter, with high aromatic and hydrophobic character, and higher molecular weights (Van Benschoten and Edzwald, 1990). The GL water SUVA was 6.2, compared to 3.4 to NW, indicating a much different NOM character. The waters also contained low concentrations of bromide, 51.2 and 28.7 $\mu\text{g/L}$ for the GL and NW water, respectively. The iodide concentrations were not determined but expected to be at trace amount ($< 10 \mu\text{g/L}$) (von Gunten, 2003).

Table 1. Raw water characteristics

Sample Location	pH	Bromide ($\mu\text{g/L}$)	DOC (mg/L)	UV ₂₅₄ (cm^{-1})	SUVA (L/mg/m)	Carbonate alkalinity (mM)
Gloucester (GL), MA	6.0	51.2	4.0	0.24	6.0	0.3
Norwalk (NW), CT	7.2	28.7	3.2	0.11	3.4	NA*

NA*: Not Analyzed

2.3 Experimental methods

Raw waters were treated at bench scale under various oxidation scenarios (chlorine, chloramine, each with ferrate pre-oxidation, and each with pre-ozonation). All experiments were conducted just once, due to the large experimental matrix. As such, only larger ($> 10\%$) differences between conditions is discussed, supported by monotonic changes from multilevel tests. The pH was adjusted to 7.0 by dropwise addition of sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4) solutions as needed, prior to the preoxidation step. For each raw water, two typical doses of ferrate and ozone (low and high, see Table 2) were added under rapid mixing ($G \sim 350 \text{ sec}^{-1}$). The pH was monitored during preoxidation and only adjusted during rapid mixing if it deviated ± 0.1 from the set point, which occurred

infrequently, following a previously published procedure (Goodwill et al., 2016). The ferrate and ozone doses for the GL water were approximately 100% higher for those for the NW water due to the higher UV_{254} absorbance values of the GL water of the same proportion. Oxidant dosing was based on UV_{254} absorbance as a surrogate measurement for DBP precursors (Edzwald et al., 1985; Valade et al., 2009).

Ferrate oxidation was initiated by dosing K_2FeO_4 solids to the waters under rapid mixing at 20 °C. For pre-ozonation, an ozone stock solution was prepared using a previously published method (Lee et al., 2008; McCurry et al., 2016) involving bubbling an ozone and oxygen mixture through 2-L chilled (~6 degrees C) reactor filled with Milli-Q water. The Milli-Q water was made slightly acidic (Reckhow et al., 1986) to decrease potential decay of O_3 via the formation pathway of OH-radical (Staelin and Holgné, 1982) using ~50 μ L of 500 mM nitric acid, and also shielded from light.

Ozonation was conducted in a batch mode by adding a certain volume of the saturated ozone stock solution (c.a., 24 mg/L, spectrophotometrically determined using $\epsilon = 3200 \text{ M}^{-1}\text{cm}^{-1}$ at $\lambda = 260 \text{ nm}$, (von Sonntag and von Gunten, 2012)) to the raw water samples. Following oxidation, the samples were filtered (glass fiber filter (GF/F), effective size cutoff of 0.7 μ m, Whatman, Clifton, NJ) and saved for subsequent chlorination or chloramination.

Chlorination and chloramination were conducted on both raw water samples and pre-oxidized samples in 300-mL chlorine demand-free, glass-stoppered bottles. Chloramine pre-formed by mixing aqueous ammonium sulfate and sodium hypochlorite solutions at a Cl_2/N molar ratio of 0.8:1. The pH of both solutions was adjusted to 8.5 before mixing (Hua and Reckhow, 2007a). New solutions were made before each use. The same chlorine

or chloramine doses were applied to the raw water and pre-oxidized water for each sample. Chlorine and chloramine doses were determined based on preliminary demand testing of the raw waters. The target residuals were 0.5–1.5 mg Cl₂/L for both free chlorine and chloramine after a 72-h incubation time at 20 °C and pH 7.0 (5 mM phosphate buffer) in the dark. The samples were incubated headspace-free after being dosed. Residuals were quenched by sodium arsenite (Dodd et al., 2006; Kristiana et al., 2014) at the end of incubation at 120% of the required stoichiometric dose (Reckhow and Singer, 1990). Each water was also spiked with different concentrations of bromide (0, 0.15 or 0.8 mg/L) and iodide (0, 0.05 or 0.2 mg/L) before being treated by the above oxidation scenarios. Table 2 summarizes the experimental conditions used in this study. A resulting bromide concentration of 0.85 mg/L is high compared to more common values for surface water bodies in the United States (Amy et al., 1995); however, bromide concentrations may be elevated in some areas due to power generation facilities (Good and Vanbriesen, 2017), and Br⁻ concentrations of this order in ground and surface waters have been previously studied with respect to oxidation and DBPs (Allard et al., 2013).

Table 2 Oxidation Conditions

Parameters		Conditions					
		GL Water			NW Water		
pH		7					
Bromide (mg/L)		0.05	0.2	0.85	0.03	0.18	0.83
Iodide (mg/L)		0	0.05	0.2	0	0.05	0.2
Ferrate dose (mg/L Fe) and [μM]	Low (L-Fe(VI))	2.8 [24]			1.4 [12]		
	High (H-Fe(VI))	5.6 [48]			2.8 [24]		
Ozone dose (mg/L) and [μM]	Low (L-O ₃)	2.2 [46]			1.2 [25]		
	High (H-O ₃)	4.0 [83]			2.3 [48]		
Oxidant exposure (mg/L*min) and [μM*min]	Low (L-Fe(VI))	7.6 [63]			9.1 [76]		
	High (H-Fe(VI))	13.1 [108]			14.1 [118]		
	Low (L-O ₃)	4.2 [88]			1.3 [27]		
	High (H-O ₃)	12.3 [256]			2.7 [56]		
Target residual (mg/L as Cl ₂)		0.5–1.5					
Disinfectant contact (hr)		72					
Temp. (C)		20					

2.4 Analytical methods

Analyzed DBPs included four chlorine- and bromine-containing THMs (THM4), nine chlorine- and bromine-containing HAAs (HAA9), three dihaloacetonitriles (DHANs) (dichloro-, bromochloro-, and dibromoacetonitriles), two haloketones (HKs) (dichloropropanone (DCP) and trichloropropanone (TCP)), and chloropicrin (CP). In addition, total organic chlorine (TOCl), total organic bromine (TOBr), and total organic iodine (TOI) were determined for bromide and iodide spiked samples. Six iodinated THMs (CHCl₂I, CHBr₂I, CHBrClI, CHClI₂, CHBrI₂, and CHI₃) were also analyzed in iodide-fortified samples. THM4, DHANs, HKs, and CP were determined by liquid/liquid extraction with pentane followed by gas chromatography and electron capture detection (GC/ECD) according to USEPA Method 551.1. Method detection limits for these compounds were in the range of 0.015-0.15 μg/L. HAA9 were quantified by liquid/liquid extraction with methyl-tertiary-butyl-ether (MtBE) followed by derivatization with acidic

methanol and by GC/ECD according to USEPA Method 552.2. Method detection limits for these compounds were in the range of 0.13-0.78 µg/L. Iodinated THMs (I-THMs) were analyzed by liquid/liquid extraction with pentane followed by GC/ECD, using 1,2-dibromopropane as an internal standard (Hua et al., 2006). Halogen-specific total organic halogen (TOX, including TOCl, TOBr, and TOI) were determined by high-temperature combustion and off-line ion chromatography (Hua and Reckhow, 2006). Method detection limits for TOX were in the range of 1.4-10.0 µg/L. The standard deviation of DBP measurements of 4.4% is estimated based on the worst-case central tendency of numerous replicates measured in parallel (see Text S1, Tables S1 – S4 and Figure S1 for additional information). Bromate was analyzed by an ultra-performance liquid chromatography–triple quadrupole mass spectrometer (UPLC–MS/MS; Waters Corp., Milford, MA) with an estimated detection limit of 0.05 µg/L.

2.5 Relative Toxicity Assessment

THMs resulting from each experimental matrix were assessed for relative toxicity using a previously published procedure (Allard et al., 2015; Smith et al., 2010), utilizing the same C50 values (i.e., the concentration of each individual THM inducing a 50% decrease in the density of Chinese Hamster Ovary cells treated for 72 h). Relative cytotoxicity assessments enable a comparison of cytotoxicity results from THMs from each experimental condition.

3. Results and discussion

3.1 Effect of ferrate and ozone pre-oxidation on the formation of THMs, THAAs, DHAAs, and DHANs from chlorination

Figure 1 shows speciation of THMs, DHAAs, THAAs, and DHANs at various bromide concentrations and oxidation scenarios for GL water with (NW results are shown in Figure S2). The GL water with higher DOC and SUVA values had higher DBPFPs than the NW water. Increasing the bromide concentration clearly shifted the formation of chlorinated to brominated DBPs. This is because chlorine can rapidly oxidize bromide to free bromine (Kumar and Margerum, 1987), and bromine reacts about 10 times faster with NOM isolates (Westerhoff et al., 2004). Without pre-oxidation, the total yield in each DBP class did not significantly change with the bromide concentration as the total number of reactive sites on NOM which can react with free chlorine and bromine is approximately constant. More DHANs were detected at higher bromide concentrations. Yu and Reckhow (2015) reported that the brominated DHANs were more stable than the chlorinated ones. Based on their estimation, the half-lives of dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) at pH 7 with 6–9 mg/L chlorine were about 3 days, 1 week, and 3 weeks, respectively. At 0 and 0.15 mg/L bromide, the dominant DHAN species was DCAN which might have partly degraded after three days of chlorination. Therefore, the total DHAN yields at different bromide concentrations would be similar if the degraded DCAN at lower bromide concentrations was taken into consideration.

In the GL water, ferrate generally exhibited slightly better performance in decreasing the DBPFPs than ozone. For example, the lower doses of ferrate and ozone decreased the formation of THMs by 17-31% and 16-22%, respectively. Other DPBs followed a similar trend. An exception was at 0.8 mg/L bromide where ferrate had lower removal of DHAA and THAA precursors than ozone. Both preoxidants decreased subsequent HAA formation to a lesser extent than THMs.

In the NW water, ferrate and ozone exhibited comparable performance in decreasing the THM yield from chlorination. The lower doses of ferrate and ozone decreased the THM formation potentials (THMFPs) by 18–24% and 21–26%, and the higher doses of ferrate and ozone decreased the THMFPs by 40–47% and 36–43%, respectively. For DHAAs, ferrate led to similar or slightly larger decreases in DHAA yield than ozone at the higher doses, whereas ozone performed better at the lower doses. The lower doses of ferrate and ozone only slightly decreased the dihaloacetic acid formation potentials (DHAAPs), and the higher doses of ferrate and ozone decreased the formation of DHAAs by 23–29% and 18–26%, respectively. Ozone caused greater decreases in THAA and DHAN yields than ferrate under all NW water conditions (Fig. S2). The lower doses of ferrate did not significantly decrease the formation of THAAs, with lower doses of ozone decreasing approximately 25%. Both ferrate and ozone caused slight and similar changes to DHANs at lower dosages. More substantial changes were realized at the higher doses of ferrate and ozone. In addition, DHAA and THAA precursor removal by ferrate generally decreased in the presence of bromide, whereas for ozone at the higher dose, the percentage of decreases in DHAA and THAA yield was greater with bromide present compared to that without bromide fortified.

Figure 1. Speciation of THMs, DHAAs, THAAs, and DHANs at various bromide concentrations under different oxidation scenarios for the GL water.

The relative performance of ferrate versus ozone for DBP precursor removal was affected by water quality (e.g., nature of organic matter and bromide concentration) and oxidant dose and varied by DBP species. In the lower SUVA NW water, at 0 and 0.15 mg/L bromide, ferrate achieved greater THM and DHAA precursor abatement than ozone at the higher doses, whereas at the lower doses, ozone performed better than ferrate. At 0.8

mg/L bromide, ozone caused greater decreases in THM and DHAA yield than ferrate at both doses. It seems that in the NW water the ratio of oxidant dose to bromide concentration determined the better oxidant for THM and DHAA precursor removal. Ferrate performed better at the higher oxidant to bromide ratio, whereas ozone was more effective at the lower oxidant to bromide ratio. For THAAs and DHANs, ozone generally achieved higher precursor removal than ferrate under all conditions in the NW water.

Song et al. (2016) found ferrate preferentially oxidized hydrophobic/transphilic NOM fractions and high molecular weight (MW) molecules. This might explain the better performance of ferrate in the higher SUVA GL water for DBP precursor removal. In the NW water containing NOM with lower SUVA, incomplete oxidation/transformation (e.g. partial cleaving of larger organic molecules) of NOM at the lower ferrate dose might have produced new DBP precursors. For example, the formation potentials of DHAAs and THAAs at 0.15 and 0.8 mg/L bromide were increased by the lower dose of ferrate indicating the organic byproducts produced by the lower dose of ferrate were reactive with bromine and produced DHAAs and THAAs. Similarly, Hua and Reckhow (2013) reported that ozone increased the DHAA yield and had limited effects on the THM and THAA yields in low SUVA waters. In addition, ferrate and ozone generally decreased the yields of chlorinated species in each DBP class. However, due to the high reactivity of bromine for reactions with NOM, the formation of brominated DBPs was less affected by pre-oxidation. This less significant effect of pre-oxidation on brominated DBP formation was also indicated by the increased bromine substitution factor (BSF) (Hua et al., 2006) with pre-oxidation (see Figure S3). In addition, bromine is more reactive with hydrophilic and low MW precursors resulting in more THM and HAA formation (Hua and Reckhow,

2007b). The generally higher BSFs of the specific DBP classes for the NW water than those for the GL water are consistent with the difference in SUVA value between the two waters.

The effects of ferrate and ozone pre-oxidation on DBP precursor removal were also compared with previous studies. The impact of ozonation on DBPs has been extensively studied and rigorously reviewed (von Gunten, 2003). Reckhow et al. (1986) determined the removal of THM, DHAA, and THAA precursors by (primarily molecular) ozone at pH 7.0 and different carbonate concentrations in a fulvic acid solution extracted from Black Lake (BL, Elizabethtown, North Carolina (NC)). The impact of preozonation on HAA formation potential was found to decrease by approximately 50% using conditions similar to that in this study (Chin and Bérubé, 2005). Ferrate and ozone destroyed DBP precursors to extents similar to those observed for ozone in GL water at medium to high carbonate concentrations (see Figure S4).

Figure S5 shows the formation of bromate after ferrate and ozone oxidation (without chlorination) of the GL water at different bromide concentrations and pH 7.0. At equivalent doses, the bromate yields from ozonation were 2.5–4.5 times those from ferrate oxidation. The USEPA maximum contaminant level (MCL) of bromate in drinking water (10 µg/L) was exceeded when the water was oxidized by the higher dose of ozone (4 mg/L) at 0.8 mg/L bromide. The bromate yields from ferrate oxidation were below 4 µg/L under all conditions. These results generally agreed with a previous study that found bromate formation from ferrate oxidation decreased with increasing pH and the bromate yields from ferrate oxidation (2.8 mg/L) of a natural water in the presence of 1.0 mg/L bromide were 21.5 and 1.87 µg/L at pH 6.2 and 7.5, respectively (Jiang et al., 2016b). Bromate yields

from ozone preoxidation where consistently higher than ferrate preoxidation under all test conditions. In the GL water, with a maximum of approximately 10 µg/L (0.08 µM), the ozone dose normalized bromate yield was approximately 0.001 µM BrO₃/µM O₃, which is in agreement with prior bromate yield assessments and modeling efforts with varying NOM (Amy, 1997).

3.2 Effect of ferrate and ozone pre-oxidation on the formation of trichloropropanone (TCP) and chloropicrin (CP) from chlorination

Only the TCP formation potential (TCPFP) is shown for chlorination because TCP is the dominant HK species formed by chlorination and DCP was below detection limit. A previous study also found that free chlorine favored the formation of TCP over DCP (Hua and Reckhow, 2007a). Figure 2 shows that ozone led to higher TCPFP than ferrate under all conditions. At the lower doses, ferrate seemed to slightly increased the TCPFP for the GL and NW water, respectively, whereas at the higher doses, ferrate decreased the TCPFP in the GL water. Ferrate has been reported to have small and site-specific effects on HK formation potentials (Jiang et al., 2016a; Yang et al., 2013). In contrast, ozone pre-oxidation increased the TCPFP under all conditions. Low and high ozone dosages increased TCPFP by 17 and 23% for the GL water, and by 24 and 53% for the NW water. Ketones constitute a major class of organic byproducts of ozonation (Nawrochi et al., 2003).

Without pre-oxidation, CP formation potential (CPFP) was 0.7 and 0.8 µg/L for the GL and NW waters, respectively, well within the national range for CP (Richardson et al., 2007). Both ferrate and ozone increased CPFP, however, this increase was less for ferrate than ozone, especially at the higher dosages. With ozone, increases of 18 and 86% at the lower doses, and 230 and 830% at the higher doses were observed for the GL and NW

347 waters, respectively. CPFP greatly increased with increasing ozone dose but not with
348 ferrate dose. Jiang et al. (2016a) observed increases in CPFP up to 95% with ferrate pre-
349 oxidation, and pre-ozonation was reported to increase the CPFP by 2–10 times in different
350 waters (Hoigné and Bader, 1988; Hu et al., 2010b; Jacangelo et al., 1989).
351 Ozonation/chlorination treatment of lysine, glycine, and triethanolamine produced high CP
352 yields (Hoigné and Bader, 1988; Shan et al., 2012), and new CP precursors were formed
353 through oxidation of amine groups to nitro groups (Bond et al., 2014; McCurry et al., 2016).
354 It seems that ozone created more nitro groups than ferrate by oxidizing organic amines,
355 which might result from differences in oxidation kinetics between ozone and ferrate. Ozone
356 has a second order reaction rate constant 2 orders of magnitude faster than ferrate for the
357 oxidation of a second-degree amine (i.e. dimethylamine) at pH 7 (Lee and von Gunten,
358 2010). Also, the higher dose of ozone increased the CPFP of the NW water to a much
359 greater extent than the GL water, even though oxidant exposure were higher for NW water.
360 This is likely because the NW water contained more hydrophilic NOM than the GL water
361 and the hydrophilic fractions of NOM were determined as the major halonitromethane
362 precursors (Hu et al., 2010a). Jiang et al., 2016 determined the extent of ferrate
363 transformation of DBP precursors was independent of exposure, and ferrate pre-oxidation
364 at lower pH yielded the same or slightly greater transformation at lower pH (and lower
365 exposure values). Subsequent treatment, including biofiltration could impact precursors
366 resulting from preoxidation, as discussed previously (Tobiason et al., 1993).

Figure 2. Effect of ferrate and ozone pre-oxidation on the formation of TCP and CP from chlorination. Plots on the left read to the left axis and are in terms of µg/L. Plots on the right read to the right axis and are in terms of change in yield (%). Negative change in yield (%) indicates decrease in DBP yield, whereas positive change in yield (%) indicates increase in DBP yield. (TCP = trichloropropanone, CP = chloropicrin, GL = Gloucester, NW = Norwalk).

3.3 Effect of ferrate and ozone pre-oxidation on the formation of TOCl, TOBr, and TOX from chlorination

Figure 3 shows the formation of TOCl, TOBr, and TOX in the presence of different concentrations of bromide under each oxidation scenario. Without pre-oxidation, the total yield of TOX did not significantly change with the bromide concentration, attributed to the constant number of reactive sites on NOM to react with chlorine and bromine. Increasing

the bromide concentration decreased the TOCl but increased the TOBr yield. The fraction of chlorine incorporated into TOCl (TOCl concentration divided by the chlorine dose) for the GL and NW water decreased from 33 and 27% at 0 mg/L bromide, to 22 and 24% at 0.8 mg/L bromide, respectively. These chlorine incorporation ratios indicate that the reactive sites on NOM only reacted with a small fraction of added chlorine. The fraction of bromide incorporated into TOBr approached 100% for the raw water and the water fortified with 0.15 mg/L bromide, whereas the bromide incorporation ratio at 0.8 mg/L bromide ranged from 87 to 65% for the GL and NW waters, respectively. These bromide incorporation ratios suggest that the concentration of NOM reactive sites was sufficient for all bromine produced at 0.15 mg/L, but insufficient for the amount of bromine produced at 0.8 mg/L.

Ferrate and ozone pre-oxidation generally decreased the TOCl but did not appreciably change the TOBr yields. However, in NW water at 0.8 mg/L bromide, both oxidants decreased TOBr yield, with ozone to a greater extent. This decrease in TOBr can be attributed to a combination of increased bromate yield as a sink for bromine (e.g. HOBr/OBr⁻) and a decrease in NOM sites able to react to form bromo-organics, (Sulzberger et al., 1997). Increased bromate yield is expected in waters with lower NOM concentrations (Siddiqui et al., 1995) and with NOM comprised of lower molecular weights and hydrophobicity (Amy, 1997), as is the case in NW water compared to GL water. Additionally, for the higher SUVA GL, ferrate pre-oxidation (Gan et al., 2015; Graham et al., 2010; Song et al., 2016) and ozone pre-oxidation (Bose et al., 1994; Edwards and Benjamin, 1992; Westerhoff et al., 1999) likely caused fragmentation shifts from hydrophobic to hydrophilic NOM, some of which were still reactive with bromine. With

403 some reactive sites destroyed and new ones created, pre-oxidation did not significantly
404 change the TOBr yield. In contrast, for the NW water with lower SUVA value, pre-
405 oxidation may have destroyed the reactive sites with fewer new sites produced. Therefore,
406 the TOBr yield in the NW water was decreased by pre-oxidation at 0.8 mg/L bromide. No
407 significant decreases in TOBr yield were observed for the other two bromide
408 concentrations. This is because at 0 and 0.15 mg/L bromide, the remaining reactive sites
409 after pre-oxidation were still sufficient to react with all bromine despite of the decreased
410 concentration of reactive sites. This combination increased the bromate yield and increased
411 the destruction of reactive sites and likely contributed to lower TOBr at the highest bromide
412 situation for the NW water. For TOCl, chlorine was in excess of the reactive sites under all
413 conditions. Pre-oxidation likely destroyed the reactive sites on NOM and thus decreased
414 the TOCl yield. As TOX was dominated by TOCl, TOX showed similar trends as TOCl
415 and was decreased by pre-oxidation.

Figure 3. Effect of ferrate and ozone pre-oxidation on TOCl, TOBr, and TOX yields from chlorination at different bromide concentrations.

Figure 4. Correlations between the TOBr concentration and the bromine concentration in specific DBP groups.

Figure 4 shows that TOBr had linear relationships with the bromine concentration in each specific DBP class, demonstrating that the variation of bromine concentration in known DBP species can indicate the change in TOBr concentration under different oxidation scenarios. However, TOCl did not have good linear relationships with the chlorine concentration in each DBP class (see Figure 6S). Figure 5 shows that ferrate and ozone pre-oxidation decreased the unknown TOX (UTOX) yield under most conditions. Ferrate and ozone pre-oxidation generally did not change the UTOX/TOX ratio, due to the transformation of both known and unknown DBP precursors by pre-oxidation. Nevertheless, some increases in the UTOX/TOX ratio were observed, especially at high ozone doses.

Figure 5. Effect of ferrate and ozone pre-oxidation on UTOX and UTOX/TOX ratio following chlorination at different initial bromide concentrations

3.4 Effect of ferrate and ozone pre-oxidation on the formation of iodinated DBPs from chlorination

Figure 6 shows the I-THMs, TOI, unknown TOI (UTOI), and UTOI/TOI ratio under different oxidation scenarios in iodide fortified water. With chlorination only (no pre-oxidation), dichloriodomethane (CHCl_2I) was the dominant I-THM species. The fraction of iodide incorporated into TOI was 25 and 15% at 0.05 mg/L iodide, for the GL and NW waters, and less at 0.2 mg/L iodide. These low iodide incorporation ratios were due to the oxidation of iodide to iodate by free chlorine (Bichsel and Von Gunten, 1999; Hua and Reckhow, 2007a; Hua et al., 2006). Allard et al. (2015) demonstrated longer free chlorine contact times, such as the 72 hours used in this study, are recommend for more complete conversion of iodide to iodate. Hua and Reckhow (2007a) observed that

hydrophilic and low MW precursors produced more I-THMs, whereas hydrophobic and high MW precursors were more reactive with iodine in TOI and UTOI formation. Our results also showed that the specific TOI and UTOI yields (normalized to the DOC concentration) were higher for the GL water, whereas the specific I-THM yields were similar for the two waters. Without pre-oxidation, the UTOI/TOI ratio was also higher for the GL water, and decreased with the iodide concentration.

Pre-oxidation greatly decreased the formation potential of CHCl_2I and the total I-THM yield. Other I-THM species, e.g., CHClBrI and CHBr_2I , accounted for larger fractions of the total I-THMs as a result of pre-oxidation. Ferrate and ozone can oxidize iodide to iodate, leaving less iodide to be oxidized to active iodine during chlorination, which decreased the formation of iodinated DBPs (Bichsel and Von Gunten, 1999; Zhang et al., 2015). It is clear that the application of ozone can mitigate some iodine-derived water issues (Allard et al., 2013). Shin et al. (2018) reported that ferrate can completely oxidize I^- to IO_3^- in pure water at near-neutral pHs within a minute and the half-life of HOI treated by ferrate is estimated to be only a few seconds and comparable to ozone, predicting low I-DBP formation with ferrate pretreatment of real waters similar to ozonation. Table 3 shows that for I-THM precursor removal, ozone performed slightly better than ferrate in the GL water, whereas ferrate achieved greater decreases in I-THM yield in the NW water. Ozone led to lower TOI formation from chlorination than ferrate in both waters. The UTOI yield was decreased by ferrate and ozone pre-oxidation at 0.05 mg/L iodide, whereas some increases were observed at 0.2 mg/L iodide (see Figure 6). The UTOI/TOI ratio generally increased by pre-oxidation, which was due to the greater decreases in I-THM yield than the TOI yield

471 caused by pre-oxidation. Ferrate pre-oxidation led to slightly higher UTOI/TOI ratio than
 472 ozone.

473
 474 Figure 6. Effect of ferrate and ozone pre-oxidation on I-THMs, TOI, UTOI, and
 475 UTOI/TOI at different iodide concentrations with chlorination. I-THM results for the 0.2
 476 mg/L I⁻ condition read to the right axis

Table 3. The percentage of decreases in I-THM and TOI yield by ferrate and ozone pre-oxidation with chlorination.

Iodide (mg/L)			Decrease in I-THM yield* (%)		Decrease in TOI yield (%)	
		Dose	GL	NW	GL	NW
0.05	Ferrate	Low	49	45	34	43
		High	68	70	48	53
	Ozone	Low	50	37	59	55
		High	71	54	60	56
0.2	Ferrate	Low	53	49	24	4
		High	86	81	25	20
	Ozone	Low	74	40	33	20
		High	89	75	59	37

* I-THM yield was calculated by adding up the mass-based concentrations of the six I-THM species.

3.5 Effect of ferrate and ozone pre-oxidation on the formation of THMs, DHAAs, and DHANs from chloramination

Figure 7 includes speciation of THMs, DHAAs, and DHANs at various bromide concentrations under different oxidation scenarios. Generally, the DBPFPs with chloramination were much lower than those with chlorination. The results for THAAs are not shown because chloramine produced little THAAs, and DHAAs were the most abundant DBP species detected for chloramination. Without pre-oxidation, increasing the bromide concentration shifted the formation of chlorinated DBPs to brominated DBPs, similar to chlorination. Other studies found bromide increased the formation of brominated DBPs during chloramination (Diehl et al., 2000; Yang et al., 2007). Bromide can react with chloramine forming bromochloramine (Luh and Mariñas, 2014), and the bromine atom of bromochloramine is very labile and reactive (Valentine, 1986). Therefore, bromochloramine may play important roles in DBP formation and the products are similar

to those produced by free bromine (Diehl et al., 2000). This formation of reactive bromochloramine might also have caused the higher DBPFPs at elevated bromide levels in the NW water (see Figure S7).

Figure S8 shows the change in yield of THM, DHAA, and DHAN derived by pre-oxidation compared to chloramination only (see Figure 7 for concentrations in GL water). Yields were calculated by adding up the molar concentrations of all species in each group. The magnitude of decreases in THM yield by pre-oxidation diminished with added bromide. At 0 and 0.15 mg/L bromide, different doses of ferrate and ozone decreased the THMFPs of the two waters by 4–36 and 24–53%, respectively. However, at 0.8 mg/L bromide, increases in THM yield were observed for both pre-oxidants. Ferrate pre-oxidation increased the THMFP for all conditions, while ozone decreased the THMFP of the GL water, but increased the THMFP of the NW water by 12 and 32% at the low and high doses, respectively. These increases in THMFP at elevated bromide level can be attributed to two aspects: First, ferrate and ozone are able to oxidize bromide forming free bromine (Haag and Holgné, 1983; Jiang et al., 2016b), that can react with NOM to directly or indirectly form DBPs. Secondly, pre-oxidation might have changed NOM into forms that reacted with bromochloramine more readily and produced THMs; however, this was not directly confirmed in this work. Therefore, brominated NOM could have contributed to the increased THMFPs at 0.8 mg/L bromide. The reason for the decreases in THMFPs at 0 and 0.15 mg/L bromide might be that little free bromine or bromochloramine was produced at low bromide levels and pre-oxidation partly destroyed THM precursors, the balanced effect of which was an overall decrease in THMFPs. To demonstrate the effects observed at elevated bromide levels, the reactivity of NOM after pre-oxidation with

chloramine and bromochloramine requires further investigation. More work is required to examine the reactivity of pre-oxidized NOM with chloramine and bromochloramine and to determine DBP formation after direct ozonation of natural waters with elevated levels of bromide and assess the contribution of free bromine. TOBr following preoxidation with the high ferrate dose in the high bromide fortified GL water was 0.33 μM .

Ferrate and ozone decreased the DHAA formation potentials (DHAAPs) almost under all conditions, however, the decreases from lower doses of ferrate and ozone were minor. The higher doses of ferrate and ozone decreased the DHAAPs by 18–36 and 15–40%, respectively. These decreases in DHAAP indicated the abatement of DHAA precursors by pre-oxidation exceeded the newly produced precursors, if any, which can react with chloramine or bromochloramine forming DHAAs. The decreases in DHAA yield by pre-oxidation were the lowest at 0.8 mg/L bromide.

Ferrate pre-oxidation generally led to lower DHAN formation potentials (DHANFPs) than ozone; however, net increases in DHANFPs were observed for both pre-oxidants, especially in the GL water. The reason for the increased DHAN yield with pre-oxidation should be similar to that for enhanced THM formation, either due to the formation of free bromine or increased reactivity of NOM toward bromochloramine or chloramine. Figure S8 shows that different doses of ferrate and ozone increased the DHANFP for the GL water, and decreased the DHANFP in the NW water at the higher dosages. These large differences between the two waters indicated that the effect of pre-oxidation on DHAN formation from chloramination was also greatly affected by water quality. Hua and Reckhow (2013) also found that DHAN precursor removal was site-specific, and the ability of ozone to destroy DHAN precursors depends on water quality and precursor properties. Ferrate and ozone

pre-oxidation also increased the BSFs of THMs, DHAAs, and DHANs with chloramination (see Figure S9).

Figure 7. Effect of ferrate and ozone pre-oxidation on the formation of THMs, DHAAs, and DHANs from chloramination at different bromide concentrations for the GL water.

3.6 Effect of ferrate and ozone pre-oxidation on the formation of DCP and CP from chloramination

The dominant HK species with chloramination was DCP, differing from the chlorination result. TCP was below detection limit due to the inability of chloramine to produce trihalogenated byproducts (Hua and Reckhow, 2007a). Figure 8 shows that for DCP, the lower doses of ferrate slightly increased the DCP formation potential (DCFP). DCFP

decreased with increasing ferrate dose. In contrast, the DCPFP was increased by ozone pre-oxidation under all conditions. The lower doses of ozone increased the DCPFP by 34 and 74%, and the higher doses of ozone increased the DCPFP by 54 and 130% for the GL and NW waters, respectively. These results indicate that the byproducts from oxidation, e.g. ketones, might be able to react with chloramine forming DCP. Ozone led to higher DCPFP than ferrate under all conditions.

Similar to chlorination, the CP formation from chloramination was also increased by both pre-oxidants. Ozone pre-oxidation generally led to higher CP yields than ferrate. The CP formation potential (CPFP) of the GL water without pre-oxidation was below detection limit. Ferrate and ozone pre-oxidation followed by chloramination produced CP of 0.19 and 0.13 $\mu\text{g/L}$ at the lower doses, and 0.25 and 0.33 $\mu\text{g/L}$ at the higher doses, respectively. For the NW water, both the low and high oxidant doses yielded increased CPFP. CP yield for ozone was higher than that of ferrate, with the high ozone dose more than doubling the CP yield.

Figure 8. Effect of ferrate and ozone pre-oxidation on DCP and CP formation from chloramination.

3.7 Effect of ferrate and ozone pre-oxidation on the formation of iodinated DBPs from chloramination

Figure 9 shows the I-THMs, TOI, UTOI, and UTOI/TOI ratio at different iodide concentrations under different oxidation scenarios. Chloramine (without pre-oxidation) produced some amounts of iodoform (CHI_3), which was not detected with chlorination (see Figure 6). Total I-THM yields for the GL were slightly lower with chloramination than with chlorination, whereas chloramine produced more I-THMs than chlorine in the NW water (compare Figures 6 and 9). Chloramine oxidized iodide to iodine and did not further oxidize iodine to iodate (Hua and Reckhow, 2007a; Kumar et al., 1986). In contrast, free

chlorine was able to partially oxidize iodide to iodate and thus decrease the I-DBPFP. Iodinated THMs could form during chlorination, especially when there was significant competition from NOM for iodine (Hua and Reckhow, 2007b). Therefore, no consistent trend regarding whether chlorine or chloramine produced more I-THMs was observed. In contrast, the TOI yields were much higher with chloramination than with chlorination for both waters, attributable to the greater oxidation of iodide to iodate by chlorine than chloramines (Allard et al., 2015; Hua and Reckhow, 2007a; Jones et al., 2011). At 0.05 and 0.2 mg/L iodide, the percentages of iodide incorporated into TOI with chloramination were greater for the GL water, than for the NW water. As previously noted, hydrophobic and high MW precursors are more reactive with iodine in TOI and UTOI formation. Therefore, the specific TOI and UTOI yields with chloramination were also higher in the high SUVA GL water than the NW water.

Ferrate and ozone greatly decreased the formation potential of I-THMs, UTOI, and TOI, by oxidizing iodide to iodate. For I-THMs, the formation of CHCl_2I was decreased by pre-oxidation, whereas some increases in CHBr_2I yield were observed. Table 4 and Figure 9 indicate that ferrate decreased the I-THM yield more than ozone in most cases, whereas ozone generally led to lower UTOI and TOI yields than ferrate. Under different conditions, both ferrate and ozone decreased the yields for I-THMs, UTOI and TOI, with ozone achieving a larger change. Without pre-oxidation, the UTOI/TOI ratios ranged from 72–98%, indicating that I-THMs only constituted a small fraction of TOI. Pre-oxidation generally did not significantly change the UTOI/TOI ratio.

Figure 9. Effect of ferrate and ozone pre-oxidation on I-THMs, TOI, UTOI, and UTOI/TOI at different iodide concentrations with chloramination.

Table 4. The percentage of decreases in I-THM and TOI yield by ferrate and ozone pre-oxidation with chloramination.

Iodide (mg/L)	Dose	Decrease in I-THM yield* (%)		Decrease in TOI yield (%)	
		GL	NW	GL	NW
0.05	Ferrate	Low	86	69	67
		High	86	76	85
	Ozone	Low	71	49	80
		High	80	77	93
0.2	Ferrate	Low	84	93	73
		High	96	98	89
	Ozone	Low	86	77	84
		High	92	97	92

* I-THM yield was calculated by adding up the mass-based concentrations of the six I-THM species.

3.8 Effect of ozone and ferrate on relative cytotoxicity of trihalomethanes

The relative cytotoxicity resulting from Fe(VI) and O₃ generally followed a similar pattern (see Figure S10) proportional to the concentration of each DBP. Toxicity of regulated THMs (e.g. THM4) and iodinated THMs following chlorination were decreased by increasing dosages of both ozone and ferrate. THM4 following chlorination was much lower following chloramination, however, preoxidation with both O₃ and Fe(VI) increased relative cytotoxicity in the high bromide fortified NW water. The high Fe(VI) dose condition also increased toxicity in the high bromide fortified GL water in a way O₃ preoxidation did not. Relative cytotoxicity was highest for iodinated THMs in the chloramination condition, attributed to the lack of iodate formation in the absence of free chlorine. Under these conditions, both Fe(VI) and O₃ pre-oxidation decreased relative toxicity orders of magnitude in the high iodide fortified waters.

4. Conclusions

Ferrate and ozone pre-oxidation were generally comparable at equivalent doses for the abatement of numerous DBP precursors, following both chlorination and chloramination. The estimated relative cytotoxicity of THM4 and I-THMs resulting from Fe(VI) and O₃ followed similar trends. For both pre-oxidants, TOBr had linear relationships with the bromine concentration in each specific DBP class, suggesting variation of bromine concentration in known DBP species can indicate the change in TOBr concentration.

Key differences in performance between the two pre-oxidants were also found. O₃ increased the HK, CP and DHAN yields to greater extents than Fe(VI). Bromate yields from O₃ preoxidation were consistently higher than Fe(VI) under all test conditions. In contrast, O₃ led to lower TOI values than Fe(VI) in the higher I⁻ fortified conditions with both chlorination and chloramination. The relative performance of Fe(VI) versus O₃ pre-oxidation for DBP precursor abatement depended on water quality. In general, Fe(VI) led to lower DBPs in high SUVA water with lower bromide concentrations.

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Supplementary Information

Text S1. HAA and THM analyses were conventional, following USEPA 552.2 and 551.1. These methods are well established with typical method detection limits and limits of quantification well below the concentrations measured in this study (see Tables S1 through Tables S3, and Figure S1. Standard deviations are commensurate with the method detection limits. Figure S1 includes additional bromodichloromethane measurements collected during this reported research and the linear relationship used to approximate measurement standard deviation (SD) (4.4%). The (SD) of other DBP measurements reported in this study were assessed in the same manner, with bromodichloromethane representing the highest (e.g. worst-case) SD.

Table S1. Method Detection Limits for Volatile Extractables

Commercial Mix	Analyte	Molecular Formula	MDL (µg/L)	
			Analyst 1	Analyst 2
EPA 551A	Chloroform (TCM)	CHCl ₃	0.065	0.15
	Bromodichloromethane (BDCM)	CHCl ₂ Br	0.077	0.020
	Chlorodibromomethane (CDBM)	CHClBr ₂	0.018	0.024
	Bromoform (TBM)	CHBr ₃	0.033	0.069
EPA 551B	Trichloroacetonitrile (TCAN)	C ₂ Cl ₃ N		0.043
	Dichloroacetonitrile (DCAN)	C ₂ HCl ₂ N	0.025	0.015
	Dibromoacetonitrile (DBAN)	C ₂ HBr ₂ N	0.017	0.034
	Bromochloroacetonitrile (BCAN)	C ₂ HClBrN	0.014	0.039
	1,1-dichloropropanone (DCP)	C ₃ H ₆ Cl ₂	0.016	0.027
	1,1,1-trichloropropanone (TCP)	C ₃ H ₃ Cl ₃	0.004	0.016
	Chloropicrin (TCNM)	CCl ₃ NO ₂	0.006	0.018

941 Table S2. Method Detection Limits for HAA

Analyte	Molecular Formula	MDL (µg/L)
Monochloroacetic Acid (MCAA)	CH ₂ ClCOOH	0.25
Monobromoacetic Acid (MBAA)	CH ₂ BrCOOH	0.21
Dichloroacetic Acid (DCAA)	CHCl ₂ COOH	0.29
Bromochloroacetic Acid (BCAA)	CHBrClCOOH	0.39
Dibromoacetic Acid (DBAA)	CHBr ₂ COOH	0.13
Trichloroacetic Acid (TCAA)	CCl ₃ COOH	0.13
Bromodichloroacetic Acid (BDCAA)	CBrCl ₂ COOH	0.20
Chlorodibromoacetic Acid (CDBAA)	CBr ₂ ClCOOH	0.34
Tribromoacetic Acid (TBAA)	CBr ₃ COOH	0.78

942

943 Table S3. Method Detection Limits for TOX

Analyte	Method detection limit (mg/L)	
	Analyst 1	Analyst 2
Total organic chloride (TOCl)	0.0014	0.010
Total organic bromide (TOBr)	0.0023	0.0044
Total organic bromide (TOI)	0.0035	

944

945 Table S4. Method Detection Limits for Iodinated THMs

Analyte	Molecular Formula	MDL (µg/L)
Dichloroiodomethane (DCIM)	CHCl ₂ I	0.106
Bromochloroiodomethane (BCIM)	CHClBrI	0.086
Dibromoiodomethane (DBIM)	CHBr ₂ I	0.074
Chlorodiiodomethane (CDIM)	CHClI ₂	0.056
Bromodiiodomethane (BDIM)	CHBrI ₂	0.023
Triiodomethane (TIM)	CHI ₃	0.063

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947

948 Figure S1. Linear relationship between mean concentration and standard deviation for
 949 replicate bromodichloromethane measurements.

Figure S2. Speciation of THMs, DHAAs, THAAs, and DHANs at various bromide concentrations under different oxidation scenarios for the NW water.

954

955 Figure S3. Effect of ferrate and ozone pre-oxidation on the BSF of THMs, THAAs,

956 DHAAs, and DHANs at different bromide concentrations with chlorination.

957

958 Figure S4. THM, DHAA, and THAA precursor removal by ferrate and ozone in GL and
 959 NW waters (this study) and precursor removal by ozone in Black Lake water (Reckhow et
 960 al., 1986) at different carbonate concentrations and pH 7.0.

Figure S5. Effect of ferrate and ozone pre-oxidation on bromate formation at different bromide concentrations. Experimental condition: pH = 7.0

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966

967 Figure S6. Correlations between the TOCl concentration and the chloride concentration
 968 in specific DBP groups.

969

Figure S7. Effect of ferrate and ozone pre-oxidation on the formation of THMs, DHAAs, and DHANs from chloramination at different bromide concentrations for the NW water.

974

975 Figure S8. The percentage of change of THM, DHAA, and DHAN yields from
 976 chloramination caused by ferrate and ozone pre-oxidation. Negative change in yield (%)
 977 indicates decrease in DBP yield, whereas positive change in yield (%) indicates increase
 978 in DBP yield.

Figure S9. Effect of ferrate and ozone pre-oxidation on the BSF of THMs, DHAAs, and DHANs at different bromide concentrations with chloramination.

984 Figure S10. Calculated total relative cytotoxicity resulting from THM concentrations in
985 each experimental condition.

Author Version