

Effects of temperature and chemical addition on the formation of bromoorganic DBPs during ozonation

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Abstract

The effects of temperature and addition of OH radical scavengers/enhancers or HOBr scavenger on the formation of bromoorganic disinfection byproducts (DBPs) from ozonation of six raw waters were studied in true batch reactors. The formation of bromoorganic DBPs during ozonation generally increased with the increase of temperature, but might also decrease for the waters with somewhat higher values of specific UV absorbance (SUVA). The addition of hydrogen peroxide, ethanol, or ammonium dramatically decreased the formation of bromoorganic DBPs; *t*-butanol addition significantly increased the formation of bromoorganic DBPs; bicarbonate addition might increase or decrease bromoorganic DBP formation depending on the water source. For all the waters treated with the chemical addition, the level of total organic bromine (TOBr) varied with the same pace as that of ozone exposure (*CT*), which suggests that TOBr formed during ozonation may be used to estimate the *CT*, a measure for the achieved degree of disinfection. The results demonstrate that for each water, the correlation between TOBr and *CT* was less affected by the change of chemical composition of the water than that between BrO_3^- and *CT*; for a given chemical composition and temperature of a water, there generally were well-defined relationships between TOBr and *CT*, and bromoform and *CT* just as that between BrO_3^- and *CT*. The possible mechanisms behind the linear functions of TOBr or BrO_3^- versus *CT* were given. Further study is needed to examine whether the trends found in this research can be applicable for the high SUVA waters.

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1. Introduction

Ozone is an attractive drinking water disinfectant in inactivating highly resistant pathogenic microorganisms

such as *Cryptosporidium parvum* oocysts where conventional disinfectants do not work well. To inactivate these organisms, however, requires high ozone exposures, which may cause excessive disinfection byproducts (DBPs), in particular bromate, a probable human carcinogen. Bromate is formed in ozonation process from the oxidation of bromide through a combination of O_3 and $\cdot\text{OH}$ reactions, and bromate control strategies focus on minimizing concentrations of critical reactants, i.e. O_3 , $\cdot\text{OH}$, and HOBr/OBr^- (Krasner et al., 1993;

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Song et al., 1997). In order to minimize the formation of bromate, many water quality parameters and water treatment measures have been considered including pH, ozone dose, temperature, and addition of hydrogen peroxide, ethanol, *t*-butanol, bicarbonate or ammonium. Hydrogen peroxide is an $\cdot\text{OH}$ enhancer and an HOBr/OBr^- reductant, *t*-butanol and bicarbonate are $\cdot\text{OH}$ scavengers, and ammonium can convert HOBr/OBr^- to bromamines. Despite numerous documents on bromate control options by varying water quality/treatment parameters or chemical addition (von Gunten, 2003 and references therein), only few studies have been carried out on their effects on the formation of bromoorganic DBPs (Glaze et al., 1993; Siddiqui and Amy, 1993; Song et al., 1997). In this work, the effects of temperature and addition of $\cdot\text{OH}$ scavengers/enhancers or HOBr scavenger on the formation of bromoorganic DBPs during ozonation of six waters were examined and compared comprehensively. DBPs analyzed mainly included a collective parameter, total organic bromine (TOBr), and some individual species such as monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), bromoform and dibromoacetonitrile (DBAN).

To balance the disinfection and DBP formation from using ozone, a better assessment of disinfection efficiency is needed. Using indicator microorganisms works well provided that the undesired pathogens are inactivated at least as efficiently as the indicator microorganisms. The problem is that the inactivation of some viral and protozoan pathogens with ozone is much slower than that of conventional indicator microorganisms. Moreover, the analysis of indicator microorganisms requires great expenditure on time and labor. To get the better of this problem, a process-oriented approach can be based on an estimation of the ozone exposure (CT), which is calculated as the time-dependent ozone concentration (C) integrated for the time T of its action. Since the integral CT -value cannot be readily obtained in non-ideally behaving reactors during drinking water treatment, CT is generally calculated with a very conservative approach, which may lead to an underestimation of the integral CT in the reactor and excessive amounts of DBPs. Because of the above reasons, von Gunten et al. (2001) proposed a new concept that uses the undesired side effect of chemical water disinfection for a fast and reliable test of treatment efficiency. They have shown in laboratory systems that bromate formation during ozonation can be used to calculate the CT , which is a measure for the achieved degree of disinfection. Since bromoorganic DBPs are generated concurrently with bromate from using ozone, therefore, another goal of this work was to examine whether TOBr and individual DBP formation during ozonation can be used to better estimate the CT .

2. Experimental methods

2.1. Materials

Sodium bromide, ammonium sulfate, sodium bicarbonate, sodium thiosulfate, ethanol, *t*-butanol were of analytical grade, hydrogen peroxide stock solution were of reagent grade, and purchased from Fisher. Formaldehyde and acetaldehyde were purchased from Aldrich. Standard stock solutions of haloacetic acids, trihalomethanes, and haloacetonitriles were purchased from Supelco. Milli-Q water was supplied by the Millipore MR3 water purifier system.

2.2. Raw water sources

Six raw waters used in laboratory experiments were from Northern Midwest municipal water supplies in the United States which cover a variety of natural organic matter (NOM) and bromide levels in both ground and surface waters. The three ground waters were the Teays Aquifer in Illinois (TYS), Minot in North Dakota (MIN), and Manhattan in Kansas (MAN). The three surface waters were Lake Decatur in Illinois (DEC), St. Paul Lake Vadnais in Minnesota (STP), and Sioux Falls River in South Dakota (SFR). The raw water characteristics, which were performed by triplicate measurements, were summarized in Table 1. All the six water sources tested are relatively low in specific ultraviolet absorbance (SUVA) values, ranging from 0.9 to $2.1 \text{ L mg}^{-1} \text{ m}^{-1}$, which indicate that NOMs in these waters are hydrophilic in character and contain relatively small amounts of aromatic moieties. Therefore, these waters may not represent the high SUVA waters. On the other hand, if a utility ozonates settled water rather than raw water, the SUVA of settled water—especially after enhanced coagulation—will often be approximately $2 \text{ L mg}^{-1} \text{ m}^{-1}$ or less, so in sense, the choice of studying low-humic raw waters in many ways is more representative of the ozonation of typical settled waters. The three groundwaters in this study were relatively high in dissolved organic carbon (DOC; $2.9\text{--}5.6 \text{ mg L}^{-1}$), and thereby were considered for using ozone for halogenated organic DBP control. All the raw waters were filtered by a $0.22\text{-}\mu\text{m}$ membrane prior to ozonation (Nanny and Minear, 1994).

2.3. Stock ozone solution

The daily preparation of a concentrated ozone solution was carried out by continuously bubbling ozone through Milli-Q water in a 500-mL gas washing bottle. Ozone was generated from dry ultra high pure oxygen gas by an OREC Model 03V10-0 ozone generator. The ozone gas from the generator was first washed by bubbling through 0.5M phosphate buffer

Table 1
Raw water characteristics

Source	DOC (mg L ⁻¹)	Br ⁻ (μg L ⁻¹)	Inorganic carbon (mg L ⁻¹)	NH ₃ -N (mg L ⁻¹)	SUVA at 254 nm (L mg ⁻¹ m ⁻¹)	Br ⁻ /DOC (μg mg ⁻¹)	Inorganic carbon ^a (mg L ⁻¹)
TYS	2.9	15	72	0.14	2.1	5.2	72
DEC	3.4	40	41	0.05	2.0	11.8	36
MIN	5.6	508	114	0.09	1.6	90.7	61
STP	12.8	18	29	0.05	1.1	1.4	7
SFR	10.5	442	47	0.09	1.1	42.1	13
MAN	2.9	126	63	0.17	0.9	43.4	63

^aThe resultant inorganic carbon for each water when diluted to a DOC of 3 mg/L.

(pH 6) in a 500-mL gas washing bottle to remove non-ozone oxidants, then the washed ozone gas was introduced to Milli-Q water in the gas washing bottle in an ice-water bath through a bubble diffuser. Ozone gas was introduced to the water for 2 h before reaching an equilibrium concentration. This method yielded an ozone aqueous solution of ~30 mg L⁻¹.

2.4. True batch ozonation

A matrix for the batch ozonation experiments was designed whereby one parameter was varied each time while all others were maintained at the designated “baseline condition” marked by “*”: NOM concentration, 3.0 mg L⁻¹* as DOC except for raw waters with less than 3.0 mg L⁻¹ as DOC (TYS and MAN, 2.9 mg L⁻¹* as DOC); pH, 7.5*; Bromide ion, Br⁻/DOC = 133 μg mg⁻¹*; Ozone dose, O₃/DOC = 1.0*, 0.67, 0.33 mg mg⁻¹; Temperature, 10, 22*, 33 °C; Hydrogen peroxide addition, H₂O₂/O₃ = 0* or 0.35 mg mg⁻¹; Ethanol addition, 0* or 1 mM; *t*-Butanol addition, 0* or 1 mM; Bicarbonate addition, 0* or 5 mM; Ammonium ion addition, NH₃-N/DOC = 0* or 0.33 mg mg⁻¹. For the baseline condition, 3 mg L⁻¹ of DOC was used to represent the typical DOC level for surface waters. A pH of 7.5 instead of an acidic pH was used to represent the typical pH in the US and to better study the impact of chemicals that scavenge •OH. A bromide level of 400 μg L⁻¹ (95th percentile of bromide occurrence in the US) was used to amplify and observe the possible reactions and brominated DBPs.

Ozonation experiments were performed with the true-batch mode employed by Westerhoff et al. (1998). The batch reactors consisted of 1 L graduated cylinder with a sliding Teflon disk cover to prevent loss of ozone and DBPs by volatilization. Prior to each experiment, NaBr solution, phosphate buffer for pH adjustment, and other reactants and scavengers (if necessary) were added to certain volume of the tested water (i.e., a raw water, or a diluted raw water) in the reactor. The volumes of the water and reagents for each run were determined on the

stock ozone concentration and a given condition so that the expected reaction condition was achieved after dilution by the ozone stock solution. The concentration of phosphate buffer was 1 mM after the addition of the ozone stock solution. The stock ozone solution was transferred into the reactor with a 100-mL glass syringe with 50-cm Teflon tubing. At this point, the reaction time was set to zero min. The test solution was mixed with a magnetic stir bar throughout the experiment. Samples for aqueous ozone concentration measurement were collected to 10-mL beakers from a side port outlet at the bottom of the cylinder at 1, 2, 5, 10, 20, 30 and 60 min in order to obtain an ozone decay curve, and to estimate the ozone exposure. Also, samples for DBP measurement were collected into 60-mL glass vials with Teflon-lined screw caps after 2 h from the time point of ozone addition. Then after 24 h, ~4 μL of 0.1 M sodium thiosulfate solution, which was based on slight excess of stoichiometric requirement, was added to the sample vials for DBP analysis to quench the remaining active oxidants in the samples. Samples were stored at 4 °C for no more than 2 days prior to analysis.

2.5. Analytical methods

The indigo method was employed to measure aqueous ozone concentration of the samples. This method was essentially the same as the one which was described in the Standard Methods (APHA et al., 1995) except the reduced sample and reagent volumes (The total volume was 10 mL instead of 100 mL.) The concentration of the stock ozone solution was determined by directly measuring UV absorbance at 258 nm after the stock solution was diluted twice with Milli-Q water.

The analysis of total organic halogen (TOX) was performed with a Dohrman Model DX-20A TOX analyzer with an adsorption module (APHA et al., 1995). All the glassware was washed in an acid bath and rinsed with Milli-Q water to minimize its background level, and then was dried in an oven at 100 °C. Activated carbon, packing material, and packing tools were stored

in a desiccator under vacuum. Microcolumns were packed with activated carbon in a room with a relatively low organic background.

Gas chromatography with an electron capture detector was used for the determination of haloacetic acids, trihalomethanes and haloacetonitriles by using and slightly modifying EPA Methods 552.2, 551.1 and 501 (USEPA, 1990, 1992, 1995). With the modified procedures, three series of DBPs were well separated with the same DB-1701, fused silica capillary column (30 m × 0.32 mm i.d., 0.25 μm film thickness) under two different programs. The program for the analysis of haloacetic acids was: solvent, methyl tert-butyl ether; carrier gas, nitrogen; inlet pressure, 0.75 kg cm⁻²; 35 °C for 12 min, ramp to 135 °C at 5 °C min⁻¹, ramp to 220 °C at 20 °C min⁻¹. The program for the analysis of trihalomethanes and haloacetonitriles was: solvent, pentane; carrier gas, nitrogen; inlet pressure, 0.30 kg cm⁻²; 35 °C for 18 min, ramp to 145 °C at 5 °C min⁻¹, ramp to 220 °C at 20 °C min⁻¹.

The procedure for the determination of formaldehyde and acetaldehyde included derivatization of the aldehydes with *o*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride followed by extraction with hexane and analysis by gas chromatography with an electron capture detector using a DB-5, fused silica capillary column (Scimenti et al., 1990).

For all work, minimum replications of 15% on experimental procedures and 100% on analytical methods were performed. The minimum reporting levels of the DBPs analyzed were reported in the previous work (Zhang et al., 2000).

3. Results and discussion

For all the ozonated samples, individual DBPs were analyzed including four trihalomethanes (chloroform, dichlorobromomethane, chlorodibromomethane, bromoform), nine haloacetic acids (mono-, di-, trichloroacetic acid, mono-, di-, tribromoacetic acid, bromochloroacetic acid, dibromochloroacetic acid, and bromodichloroacetic acid), and four haloacetonitriles (dichloro-, trichloro-, chlorobromo-, and dibromoacetonitrile). The concentrations of those chlorine-containing species were found to be close to or below detection limits. The earlier work has shown that no organochlorine compounds were present during ozonation (Glaze et al., 1993). This is confirmed by the kinetic studies that chloride is not oxidized by ozone and the oxidation of chloride to Cl radicals by OH radicals can be neglected under typical drinking water conditions (von Gunten, 2003). Typically, waters that are high in bromide should also have some significant level of iodide, but the reaction of HOI with NOM to form organoiodine compounds can be ruled out because in

contrast to aqueous bromine and chlorine, both HOI and OI⁻ are quickly further oxidized to iodate by ozone (von Gunten, 2003). Therefore, only bromine-containing species are significant, and the measured TOX is considered to be solely TOBr. It is of note that though MBAA and DBAA were produced at appreciable levels in most of the samples, tribromoacetic acid was not. This is mainly due to the analytical method limitation, i.e., the decomposition of tribromoacetic acid (Zhang and Minear, 2002) during the methylation at 50 °C for 2 h, resulting in a much higher minimum reporting level of tribromoacetic acid (1.6 μg L⁻¹) than that of MBAA (0.33 μg L⁻¹) or DBAA (0.16 μg L⁻¹) (Zhang et al., 2000).

3.1. Effect of temperature

Fig. 1 shows that the effect of temperature on the formation of bromoorganic DBPs. For the waters STP, SFR, MIN and MAN, TOBr and bromoform formation increased with increasing temperature. For the waters DEC and TYS, TOBr and bromoform formation first increased with increasing temperature from 10 to 22 °C, then decreased with increasing temperature from 22 to 33 °C. Because reaction rate generally increases with increasing temperature, it is not quite clear what caused the latter two waters to produce less bromoorganic DBPs at 33 °C. A possible explanation for these two waters is that as temperature increases from 22 to 33 °C, the reaction rates of competing reactions, such as NOM oxidation and bromate formation, increase faster than those of TOBr and bromoform formation. In fact, these two waters had a much different property from other waters. The SUVA values of these two waters (TYS 2.1 L mg⁻¹ m⁻¹, DEC 2.0 L mg⁻¹ m⁻¹) were higher than those of other waters (MIN 1.6 L mg⁻¹ m⁻¹, STP 1.1 L mg⁻¹ m⁻¹, SFR 1.1 L mg⁻¹ m⁻¹, MAN 0.9 L mg⁻¹ m⁻¹). A higher SUVA indicates more humic NOM, which means more ozone demand and, thus, less ozone available for TOBr formation. These two waters showed relatively fast ozone decay at 33 °C compared with other waters (data not presented). Fig. 2 shows the relationship between TOBr and SUVA. At a given temperature, lower TOBr levels generally were produced during ozonation of the waters with somewhat higher SUVA values. This general trend was not appreciable at lower temperatures (10 or 22 °C) but became remarkable at a higher temperature (33 °C).

Fig. 3 shows the correlation between individual DBPs and TOBr formed during ozonation of the six waters at three different temperatures. Data that were below detection limits are not plotted. While the differing temperatures and differing water sources contributed to scatter in the data, there was a good linear relationship between bromoform and TOBr ($R^2 = 0.871$), and a moderate linear relationship between DBAA and TOBr

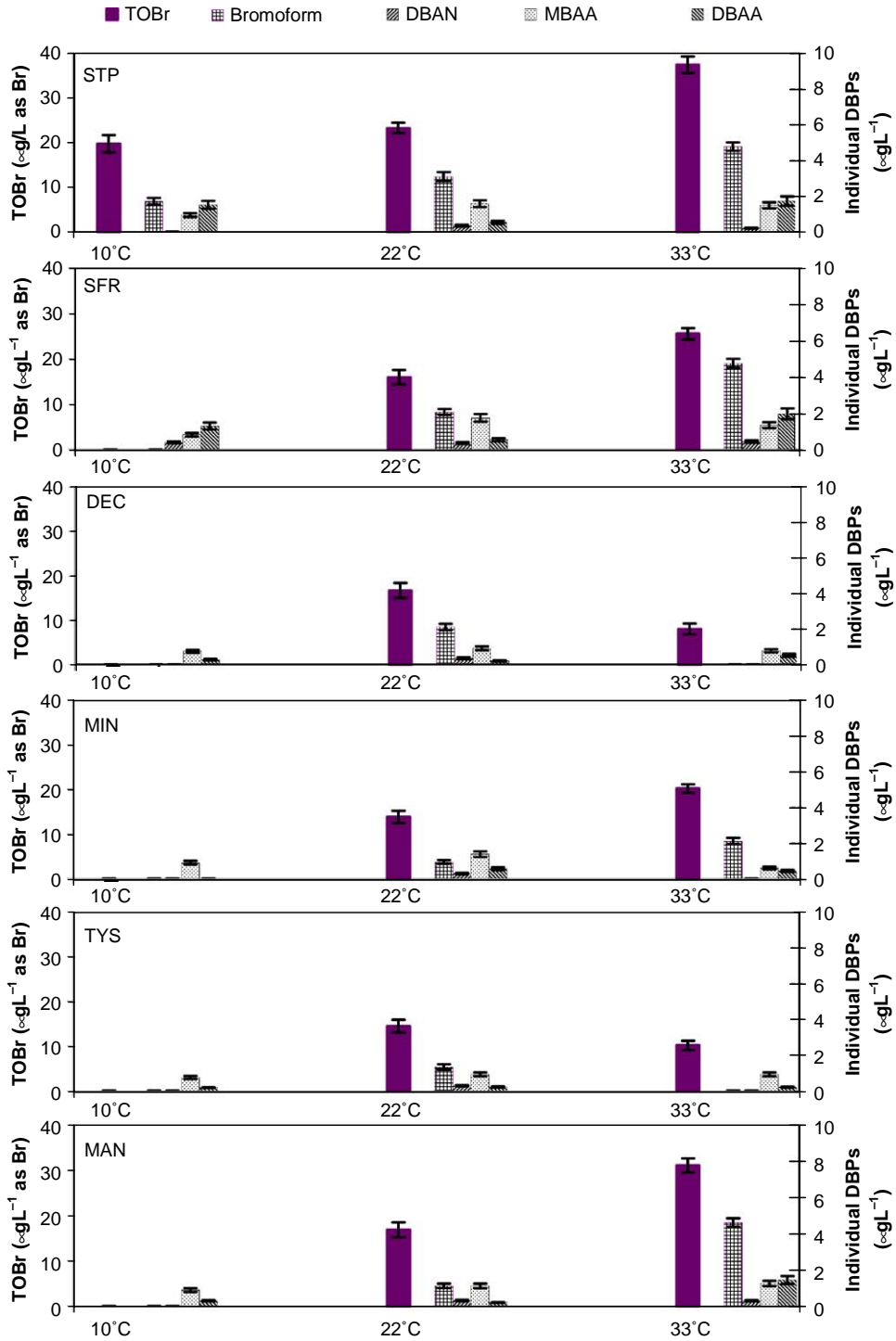


Fig. 1. Effect of temperature on the formation of bromoorganic DBPs during ozonation of the six waters. DOC \cong 3.0 mg L⁻¹, Br⁻ \cong 400 µg L⁻¹, ozone dose \cong 3.0 mg L⁻¹, pH = 7.5 with phosphate buffer.

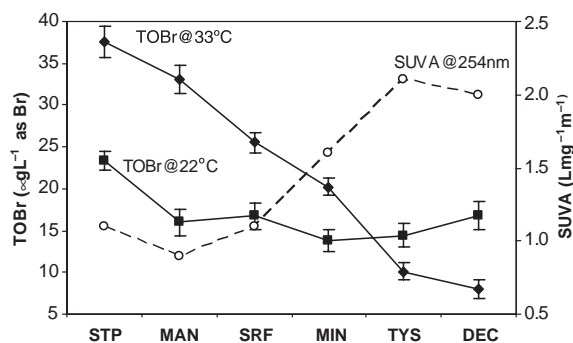


Fig. 2. Relationship between TOBr and SUVA at temperatures 22 and 33 °C. TOBr data at 10 °C are not plotted because most of them were below detection limit.

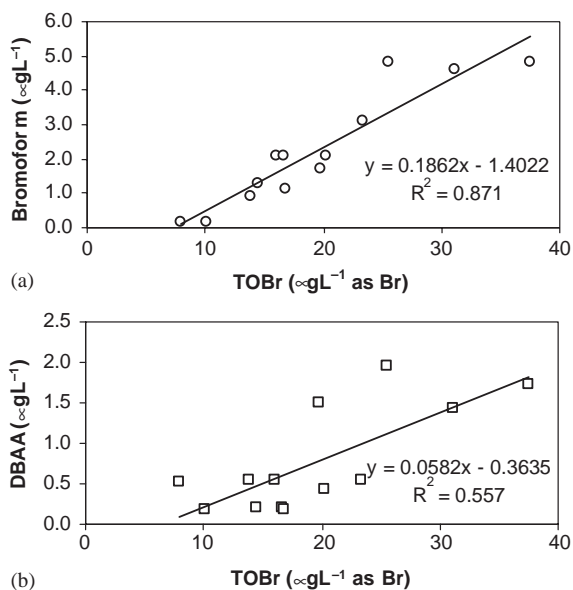


Fig. 3. Relationships of individual DBPs to TOBr formed during ozonation of the six waters. DOC \cong 3.0 mg L⁻¹, Br⁻ \cong 400 µg L⁻¹, ozone dose \cong 3.0 mg L⁻¹, pH = 7.5 with phosphate buffer. Variables include three different temperatures and six waters. TOBr values below detection limit were not plotted. (a) Bromoform versus TOBr, and (b) DBAA versus TOBr.

($R^2 = 0.557$). MBAA and DBAN did not correlate well linearly with TOBr, with a correlation coefficient of 0.192 and 0.069, respectively, most likely in that the occurrence of MBAA and DBAN was closer to their minimum reporting levels, which are in a region of higher analytical errors. The poor correlation between DBAN and TOBr could also be due to the significantly different decomposition rates of DBAN at different temperatures. Since the decomposition rate constant of DBAN at 21 and 35 °C was 0.004 and 0.031 h⁻¹,

respectively (Nikolaou et al., 2000), DBAN formed mainly in the first 2 h could decompose approximately 9% and 54% in the followed 24 h at 22 and 33 °C, respectively, thus the different reaction temperatures would dramatically contribute to scatter in the data provided that the decomposition rates of TOBr at the different temperatures are relatively small and do not differ significantly. Fig. 3 also shows a non-zero x -intercept for each correlation, which means that there was a lag phase for the formation of bromoform or DBAA during ozonation in comparison to the formation of TOBr. Li et al. (2000) found that chloroform and haloacetic acids were produced a little later than TOX during chlorination, and they interpreted this as indicating that the initial substitution of Cl into NOM forms relatively high molecular weight chlorinated compounds and that smaller compounds such as chloroform and haloacetic acids are not split from the parent molecule until a substantial amount of Cl has been incorporated. A similar process is believed to happen in the incorporation of HOBr to NOM during ozonation.

It is noteworthy that the amount of bromoform, MBAA and DBAA formed during ozonation was very low compared to the maximum contaminant levels in the US (USEPA, 1998), but these DBPs could only account for a small percentage of TOBr. According to the DBP data from ozonation of the six waters at three different temperatures, the four individual DBPs including bromoform, DBAN, MBAA and DBAA could only represent 8.0–27.9% of TOBr. Recent research has identified new brominated DBPs, e.g., brominated halonitromethanes (Plewa et al., 2004), that appear to be of higher health concern than the regulated ones. Although the emerging DBPs were not measured in this study, the formation of a high percentage of unidentified TOBr suggests that some of the emerging DBPs of higher health concern may have formed.

3.2. Effect of chemical addition

The addition of hydrogen peroxide (0.35 mg H₂O₂/mg O₃) almost completely prevented the formation of bromoorganic DBPs (Fig. 4). Except for a low µg L⁻¹ level of MBAA observed in one water (TYS), the levels of TOBr, bromoform, DBAN and DBAA in all the other waters were reduced to below detection limits. Cooper et al. (1986) also found that hydrogen peroxide addition significantly decreased the formation of bromoorganic DBPs. It is known that hydrogen peroxide enhances the OH radical chain reaction with ozone, which results in a rapid consumption of ozone. The ozone decay curves confirm this. According to the tests, ozone exposures of the six waters under the baseline conditions were in the range of 7.6–47.1 mg L⁻¹ min, but after addition of hydrogen peroxide, ozone exposures

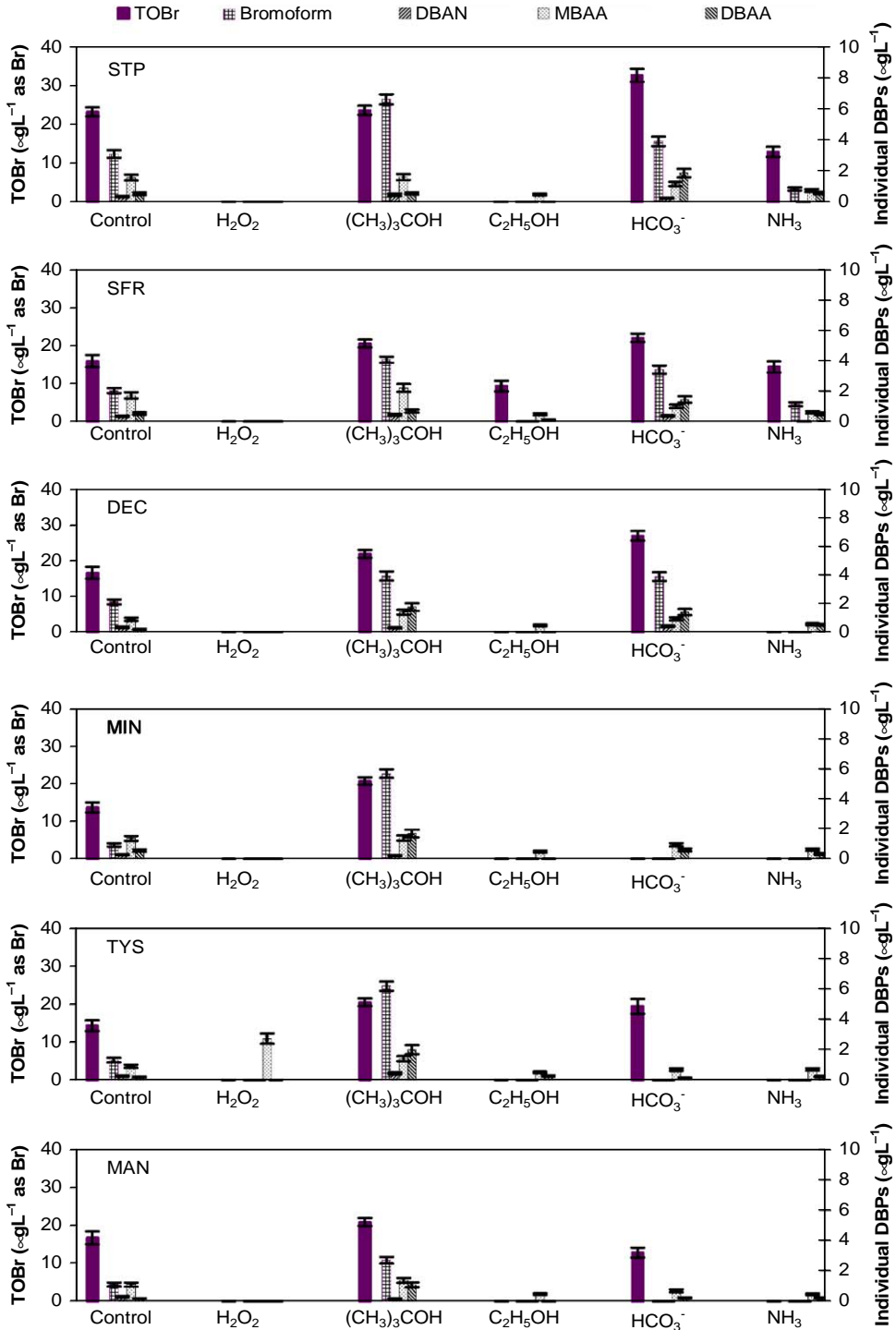


Fig. 4. Effect of chemical addition on the formation of bromoorganic DBPs during ozonation of the six waters. $\text{DOC} \cong 3.0 \text{ mg L}^{-1}$, $\text{Br}^- \cong 400 \mu\text{g L}^{-1}$, ozone dose $\cong 3.0 \text{ mg L}^{-1}$, $\text{pH} = 7.5$ with phosphate buffer, temperature = 22°C .

became very small ($0.7\text{--}3.6\text{ mg L}^{-1}\text{ min}$). Another reason is that hydrogen peroxide can reduce HOBr rapidly back to Br^- (von Gunten and Hoigné, 1994).

Compared to the baseline condition, the addition of ethanol (1 mM) greatly inhibited the formation of bromoorganic DBPs (Fig. 4). TOBr level in the water SFR decreased about 41%, and TOBr levels in other waters were reduced to below detection limits. Only trace amounts ($0.47\text{--}0.50\text{ }\mu\text{g L}^{-1}$) of MBAA were observed in all the waters, and $0.28\text{ }\mu\text{g L}^{-1}$ of DBAA was observed in one water (TYS). Meanwhile, the addition of ethanol greatly increased the production of acetaldehyde, from $15.8\text{--}28.1\text{ }\mu\text{g L}^{-1}$ under the baseline condition to $399\text{--}452\text{ }\mu\text{g L}^{-1}$ after the ethanol addition, which means that 0.87–0.96% of ethanol added ended up as acetaldehyde. Similar to the addition of hydrogen peroxide, the addition of ethanol greatly enhanced the ozone decay. This rapid ozone decay may be due to: reaction of ethanol with molecular ozone (Hoigné and Bader, 1979); reaction of acetaldehyde, the product from the oxidation of ethanol, with molecular ozone; and the production of hydrogen peroxide from the oxidation of ethanol, which enhances the radical chain reaction with ozone. Based on the tests, ozone exposures of the six waters were reduced to $1.6\text{--}6.0\text{ mg L}^{-1}\text{ min}$ after ethanol addition compared to $7.6\text{--}47.1\text{ mg L}^{-1}\text{ min}$ under the baseline condition. It appears that molecular ozone is the main reason for the oxidation of Br^- to OBr^-/HOBr , which then reacts with NOM to form bromoorganic DBPs. It needs mentioning that a utility would not add ethanol to the water as a treatment chemical; instead it is used only in bench-scale experiments as a means of probing the mechanism of DBP formation.

The addition of *t*-butanol (1 mM) significantly increased the formation of bromoorganic DBPs (Fig. 4). For the six waters tested, TOBr levels increased 2–51%, bromoform levels increased 0.90–5.3 fold, MBAA levels increased 2–55%, and DBAA levels increased 0.02–9.1 fold. As a strong OH radical scavenger, it is believed that *t*-butanol greatly shuts down the chain reaction of OH radical with ozone, and increases the lifetime of molecular ozone (Song, 1996). Among the six waters tested, ozone exposures increased to $21.0\text{--}55.0\text{ mg L}^{-1}\text{ min}$ after the addition of *t*-butanol in comparison to $7.6\text{--}47.1\text{ mg L}^{-1}\text{ min}$ under the baseline condition. This further confirms that it is molecular ozone that determines the formation of bromoorganic DBPs. Similar to ethanol, *t*-butanol is a bench-scale probe, not a full-scale treatment chemical.

It is of interest that the addition of bicarbonate (5 mM) had different effects for different waters (Fig. 4): it significantly increased the formation of TOBr and individual DBPs in waters STP, SFR, DEC and YYS, but significantly decreased the formation of TOBr and individual DBPs in waters MIN and MAN. The trend of TOBr level changes was consistent with that of ozone

exposure changes. For the first four waters, ozone exposures increased from $7.6\text{--}47.1\text{ mg L}^{-1}\text{ min}$ under the baseline condition to $10.5\text{--}51.2\text{ mg L}^{-1}\text{ min}$ after the bicarbonate addition. For other two waters, ozone exposures decreased a little from $19.5\text{--}27.7\text{ mg L}^{-1}\text{ min}$ under the baseline condition to $19.4\text{--}25.9\text{ mg L}^{-1}\text{ min}$ after the bicarbonate addition. It also seems to support the point that molecular ozone makes a greater contribution to the oxidation of Br^- to OBr^-/HOBr than OH radical. It is known that bicarbonate can scavenge OH radical to form bicarbonate radical, which may lead to slower ozone decay rate and larger ozone exposure. What caused the small decrease of ozone exposure in waters MIN and MAN after the bicarbonate addition is not clear. It is possible that bicarbonate radical can react with some species in these two waters to form some active radical, which then reacts with ozone.

The addition of ammonia ($0.33\text{ mg NH}_3\text{-N/mg DOC}$) dramatically decreased the formation of bromoorganic DBPs (Fig. 4). TOBr and bromoform levels in the waters DEC, MIN, YYS and MAN were reduced to below detection limits, and these levels in the waters of STP and SFR were reduced 9.4–44.6%. DBAN levels in all the waters were reduced to below detection limit. MBAA and DBAA levels were also reduced to some extent. Bromoform was better controlled than DBAA. These effects were expected because ammonium efficiently converts HOBr to NH_2Br (the reverse reaction is slow), presumably making HOBr unavailable for reaction with natural organics (Pinkernell and von Gunten, 2001). For waters STP, MIN and MAN, ozone exposure decreased appreciably from $19.5\text{--}47.1\text{ mg L}^{-1}\text{ min}$ under the baseline condition to $10.2\text{--}19.3\text{ mg L}^{-1}\text{ min}$ after the ammonia addition. For the other waters, ozone exposures did not vary appreciably after the ammonia addition. Ammonia addition generally does not alter the ozone stability and therefore, oxidation and disinfection processes remain unchanged. The decrease of ozone exposures for the three waters, however, is most likely due to the reaction of ozone with excessive amount of ammonia to form nitrate (von Gunten and Hoigné, 1994) in the three waters. One thing that deserves concern with the addition of ammonium is that due to the high levels of formaldehyde in these ozonated waters ($52\text{--}86\text{ }\mu\text{g L}^{-1}$), it may react with bromamines to form significant amounts of cyanogen bromide according to Lei et al. (2000).

3.3. Correlation between DBPs and CT

Correlations of TOBr and CT during ozonation of raw waters are shown in Fig. 5. Fortunately, Echigo (2002) analyzed the concentrations of BrO_3^- in the same batches of samples so that correlations of BrO_3^- and CT during ozonation of raw waters can also be plotted in

Fig. 5 as a comparison. The solid line and upper right hand corner R^2 include all the samples with different ozone doses and different chemical additions. The dashed line and lower right hand corner R^2 include only the samples with different ozone doses.

For the correlations that include all the samples (solid lines), the linear correlation coefficients of TOBr and CT were in the range of 0.464–0.824, and the linear correlation coefficients of BrO_3^- and CT were in the

range of 0.018–0.274. Visual inspection also indicates that there is a reasonable correlation between TOBr and CT , but the data points of BrO_3^- and CT are quite scattered. It demonstrates that for each raw water, the correlation between TOBr and CT is less affected by the change of chemical composition of the water (i.e., addition of $\cdot OH$ scavengers/enhancers or HOBr scavenger), and TOBr seems to be a better indicator of CT than BrO_3^- .

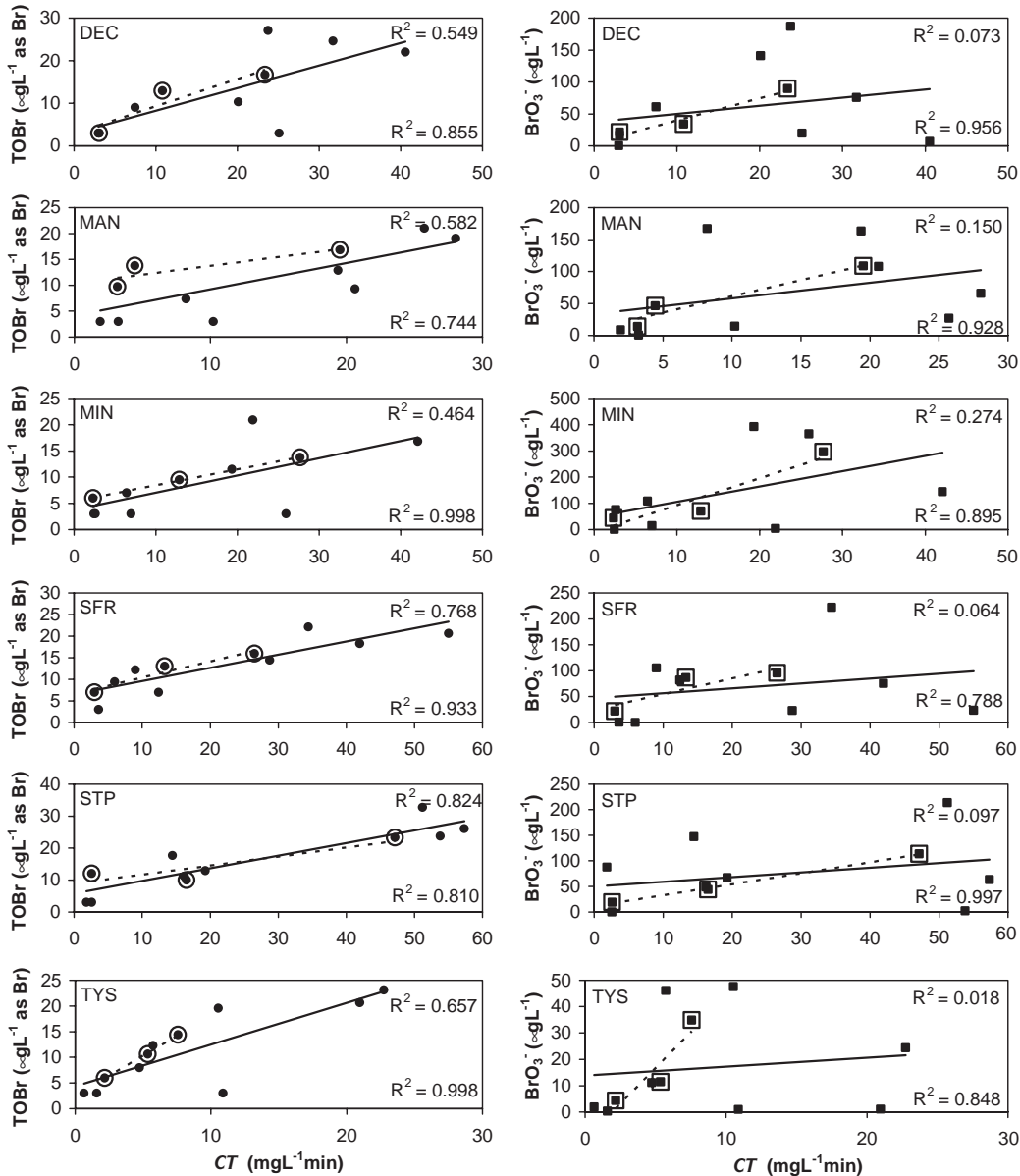
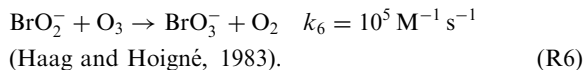
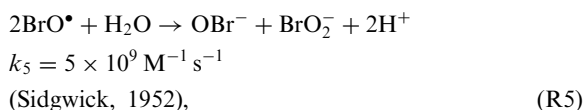
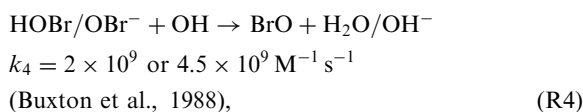
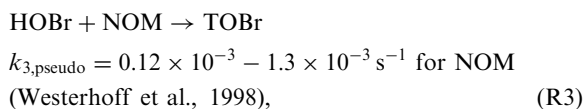
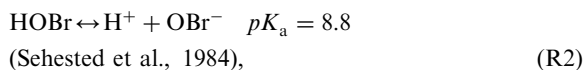
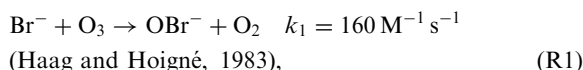


Fig. 5. Correlation of TOBr, BrO_3^- versus CT during ozonation of the six waters. $DOC \cong 3.0 \text{ mg L}^{-1}$, $Br^- \cong 400 \mu\text{g L}^{-1}$, $pH = 7.5$ with phosphate buffer, temperature = 22°C , variables include different ozone doses and different chemical additions. The solid line and upper right hand corner R^2 include all the samples with different ozone doses and different chemical additions (\bullet or \blacksquare). The dashed line and lower right hand corner R^2 include only the samples with different ozone doses (\circ or \square).

For the correlations that include only the samples with different ozone doses (dashed lines), the linear correlation coefficients of TOBr and CT were in the range of 0.744–0.998, and the linear correlation coefficients of BrO_3^- and CT were in the range of 0.788–0.997. This indicates that under the circumstance where ozone dose was the only variable, both TOBr and BrO_3^- correlated well with CT for all the waters. With regard to the correlation of BrO_3^- and CT , it has been reported that for a given chemical composition and temperature of a water, there is a well-defined relationship between BrO_3^- and ozone exposure (von Gunten et al., 2001). In particular, TOBr fits CT better for waters MIN (R^2 0.998), SFR (R^2 0.933) and TYS (R^2 0.998), while BrO_3^- fits CT better for waters DEC (R^2 0.956), MAN (R^2 0.928) and STP (R^2 0.997). It suggests that TOBr can be used to estimate CT especially when the errors are relatively large in using BrO_3^- to estimate CT , and TOBr and BrO_3^- are most likely complementary to each other in the CT fitting. Note that for each trend line, either TOBr versus CT or BrO_3^- versus CT , there is generally a positive y -intercept, which could be attributed to an initial fast reaction. Several studies have shown that BrO_3^- formation as a function of ozone exposure is almost linear after an initial fast increase (von Gunten and Hoigné, 1994; von Gunten et al., 2001). To the authors' knowledge, the linear relationship between TOBr and CT was observed for the first time. Given the findings that TOBr versus CT and TOBr versus bromoform correlated well linearly, one would expect that bromoform and CT may correlate linearly. The results show that for the correlations that include only the samples with different ozone doses, the linear correlation coefficient of bromoform and CT for each water was: DEC, 0.945; MAN, 0.314; MIN, 0.999; SFR, 0.997; STP, 1.000; TYS, 0.870.

To better understand the relationships between TOBr or BrO_3^- formation and CT during ozonation, it is necessary to sort out the mechanisms behind the two linear functions (TOBr versus CT and BrO_3^- versus CT). BrO_3^- and TOBr formed in ozonation processes from the oxidation of bromide through a combination of ozone and $\cdot OH$ reactions. Their formation involves NOM and up to six oxidation states of bromine. Because both O_3 and $\cdot OH$ can act simultaneously or in sequence on NOM and various bromine oxidation levels, the whole reaction system is extremely complicated and highly non-linear. Kinetic modeling involving more than 50 coupled kinetic equations has been applied to predict BrO_3^- formation (Pinkernell and von Gunten, 2001; Westerhoff et al., 1998). Those coupled highly non-linear kinetic equations, however, cannot give any hint of the linear functions of TOBr or BrO_3^- versus CT . To obtain the linear relationships, some main pathways for TOBr and BrO_3^- formation during ozonation may be important.

By introducing the R_c value (ratio of the concentrations of OH radicals and ozone, $R_c = [\cdot OH/O_3] = 10^{-9}$ – 10^{-7}), von Gunten (2003) successfully determined the main pathways for BrO_3^- (and TOBr) formation during the second phase of an ozonation process, which are summarized as shown in Fig. 6. Here is a list of the major reactions:



According to reaction (R3), the rate of TOBr formation can be expressed as Eq. (1):

$$d[TOBr]/dt = k_3[NOM][HOBr]. \quad (1)$$

The NOM and Br^- doses used were

$$C_{NOM,0} \cong 3 \text{ mg L}^{-1} \text{ as } C = 2.5 \times 10^{-4} \text{ M as } C = 1.25 \times 10^{-4} \text{ M as } 2C,$$

$$C_{Br^-,0} \cong 400 \text{ } \mu\text{g L}^{-1} \text{ as } Br = 5 \times 10^{-6} \text{ M as } Br.$$

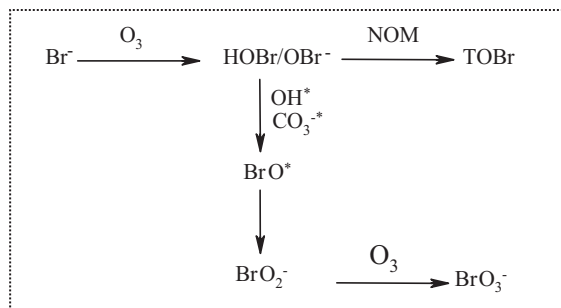


Fig. 6. The main pathways for TOBr and BrO_3^- formation during the secondary phase of an ozonation process.

Assuming two carbons in NOM can provide a reaction site for a bromine atom to incorporate in, $C_{\text{NOM},0}$ is about 25 times greater than $C_{\text{Br}^-,0}$. Also, since $[\text{HOBr}]$ is a small part of $C_{\text{Br}^-,0}$, $C_{\text{NOM},0}$ should be much larger than $[\text{HOBr}]$, the consumption of NOM due to the reaction with HOBr can be neglected.

It is known that during ozonation, O_3 (and its degradation product $\cdot\text{OH}$) can compete with HOBr on NOM, but this does not mean to reduce the natural organic precursors for TOBr. On the one hand, since both O_3 and HOBr can act as strong electrophiles, O_3 would destroy nucleophilic centers otherwise attacked by HOBr. On the other hand, since O_3 is particularly well suited for the production of methyl ketones from a wide variety of organic compounds, which is considered a major source of trihalomethanes and TOX, O_3 would enhance the formation of TOBr. Reckhow et al. (1986) studied the effect of ozonation on organic halide precursors and found that for the chlorination at pH 7.5 buffered with phosphate, NOM preozonated with an O_3 dose of 3 mg L^{-1} produced approximately the same amount of TOX as the unozonated NOM. Haag and Hoigné (1983) reported that bromoform levels produced from ozonation are similar with preozonated NOM and unozonated NOM. If O_3 oxidized away the organic precursors, one would expect less bromoform after preozonation, which is contrary to their observed results. Therefore, under specific reaction conditions (e.g., pH 7.5 buffered with phosphate), the reaction of O_3 with NOM does not affect the concentration of natural organic precursors for the formation of TOBr, i.e., $[\text{NOM}]$ is approximately a constant ($\cong C_{\text{NOM},0}$). Thus, Eq. (1) can be integrated as Eq. (2):

$$\int d[\text{TOBr}] = k_3 C_{\text{NOM},0} \int [\text{HOBr}] dt, \quad (2)$$

$$[\text{TOBr}] = [\text{TOBr}]_{\text{ini}} + k_3 C_{\text{NOM},0} \int [\text{HOBr}] dt, \quad (3)$$

where $[\text{TOBr}]_{\text{ini}}$ is the concentration of TOBr formed during the initial reaction phase.

Amy et al. (1995) observed an increase in TOBr with a concurrent increase in bromine exposure during ozonation. They explained that the increase in bromine exposure enhances the probability of interaction between bromine and NOM, thus leading to more TOBr production. Now that the concept of bromine exposure is the term, $\int [\text{HOBr}] dt$, their observation can be quantitatively explained by Eq. (3).

In consideration of reaction (R1), the oxidation of Br^- by O_3 to form OBr^- , and many other reactions that consume O_3 such as $\text{O}_3 + \text{OH}^-$, $\text{O}_3 + \text{NOM}$, $\text{O}_3 + \text{BrO}_2^-$, an assumption is made that bromine exposure is

proportional to ozone exposure:

$$\int [\text{HOBr}] dt = \alpha \int [\text{O}_3] dt, \quad (4)$$

where α is a constant coefficient. Substitute Eqs. (4) into (3):

$$[\text{TOBr}] = [\text{TOBr}]_{\text{ini}} + (\alpha k_3 C_{\text{NOM},0}) CT. \quad (5)$$

According to reaction (R6), the rate of BrO_3^- formation can be expressed as Eq. (6):

$$d[\text{BrO}_3^-]/dt = k_6 [\text{BrO}_2^-][\text{O}_3]. \quad (6)$$

Based on reactions (R5) and (R6), the rate of BrO_2^- formation can be expressed as Eq. (7):

$$d[\text{BrO}_2^-]/dt = k_5 [\text{BrO}^\bullet]^2 - k_6 [\text{BrO}_2^-][\text{O}_3]. \quad (7)$$

Since reaction (R6) is a very fast reaction, which prevents BrO_2^- from building up to measurable concentrations (Haag and Hoigné, 1983), it can be assumed that after the initial phase, the concentration of BrO_2^- quickly reaches a steady state:

$$d[\text{BrO}_2^-]/dt = 0 \text{ or } [\text{BrO}_2^-] = [\text{BrO}_2^-]_{\text{ss}}.$$

Then Eq. (6) can be integrated as

$$\int d[\text{BrO}_3^-] = (k_6 [\text{BrO}_2^-]_{\text{ss}}) \int [\text{O}_3] dt,$$

$$[\text{BrO}_3^-] = [\text{BrO}_3^-]_{\text{ini}} + (k_6 [\text{BrO}_2^-]_{\text{ss}}) CT, \quad (8)$$

where $[\text{BrO}_3^-]_{\text{ini}}$ is the concentration of BrO_3^- formed during the initial reaction phase. von Gunten (2003) attributes the rapid increase of BrO_3^- concentration during the initial phase to the rapid transformation of ozone into $\cdot\text{OH}$ radicals during the initial phase.

Eqs. (5) and (8) demonstrate that the concentrations of TOBr and BrO_3^- are linear functions of CT after some reasonable simplifications and assumptions are made. The slopes in the two equations are $\alpha k_3 C_{\text{NOM},0}$ and $k_6 [\text{BrO}_2^-]_{\text{ss}}$, respectively, which explain why the linear functions of TOBr or BrO_3^- versus CT are well defined as long as the chemical composition and temperature of a water are given. Eq. (8) also indicates that at a given temperature, whether BrO_3^- formation is a linear function of CT mainly depends on the steady state concentration of BrO_2^- . Since BrO_2^- is produced from the disproportionation reaction of BrO^\bullet , which is produced mainly via the oxidation of HOBr/OBr^- by $\cdot\text{OH}$, the addition of any OH radical scavengers/enhancers or HOBr scavengers would affect the steady state concentration of BrO_2^- , resulting in the scattered data of BrO_3^- versus CT . This explains why the linear function of BrO_3^- versus CT is more sensitive to the change of chemical composition of a water. Notably, the linear function of TOBr versus CT requires a high dose ratio of NOM/Br^- , and the bromide level ($\sim 400 \mu\text{g L}^{-1}$) used in this work is relatively higher than the typical values in

source waters, therefore, the linear relationship between TOBr and *CT* is expected to hold up for waters with normal levels of bromide as long as TOBr can be produced at appreciable levels during ozonation. Since all the six water sources tested are relatively low in SUVA values ($0.9\text{--}2.1\text{ L mg}^{-1}\text{ m}^{-1}$), further study is needed to examine whether the trends found in this research can be applicable for the high SUVA waters.

4. Conclusions

The results of this study can be summarized as follows:

- Increasing temperature generally increased the formation of bromoorganic DBPs, but at a relatively high temperature less bromoorganic DBPs were produced for two of the six waters with somewhat higher SUVA values. While the differing temperatures and differing water sources contributed to scatter in the data, there was a good linear relationship between bromoform and TOBr formed in the ozonated waters.
- The addition of hydrogen peroxide, ethanol, or ammonium dramatically decreased the formation of bromoorganic DBPs; *t*-butanol addition significantly increased the formation of bromoorganic DBPs; bicarbonate addition might increase or decrease bromoorganic DBP formation depending on the water sources. For all the waters treated with the chemical addition, the level of total organic bromine (TOBr) varied with the same pace as that of ozone exposure (*CT*), which suggests that TOBr formed during ozonation may be used to estimate the *CT*, a measure for the achieved degree of disinfection.
- The results demonstrate that for each water, the correlation between TOBr and *CT* was less affected by the change of chemical composition of the water in comparison to that between BrO_3^- and *CT*. For a given chemical composition and temperature of a water, there was a well-defined relationship between TOBr and *CT* just as that between BrO_3^- and *CT*. TOBr can be used to estimate *CT* especially when the errors are relatively large in using BrO_3^- to estimate *CT*, and TOBr and BrO_3^- are most likely complementary to each other in the *CT* fitting. For a given chemical composition and temperature, bromoform and *CT* correlated well linearly for five of the six waters. The possible mechanisms behind the linear functions of TOBr or BrO_3^- versus *CT* were sorted out. Since all the six water sources tested are relatively low in SUVA values, further study is needed to

examine whether the trends found in this research can be applicable for the high SUVA waters.

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