Chapter 13

Reactivity of Bromine-Substituted Haloamines in Forming Haloacetic Acids

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When drinking water is chloraminated in the presence of bromide, bromine-substituted haloacetic acids typically form. Monochloramine is the dominant haloamine species under drinking water treatment conditions. In the presence of bromide, bromine-substituted haloamines, such as mono- and dibromamine, as well as bromochloramine may also form. These bromine-substituted haloamines are typically present in much lower concentrations than monochloramine, but are significantly more reactive in forming haloacetic acids (HAAs). The reactivity of the bromine-substituted haloamine species was studied in two different surface water supplies. HAA formation from each of the bromine-substituted species (NH_2Br, $NHBr_2$, and $NHBrCl$) was 4 to 12 times that from monochloramine (NH_2Cl).

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Background

Chloramines are widely used as a secondary disinfectant in drinking water treatment to control trihalomethane and haloacetic acid (HAA) formation; however, significant dihaloacetic acid (DXAA) concentrations have been observed to form. When bromide is present in source water, bromine-substituted haloacetic acids typically form during chloramination. Limiting the formation of bromine-substituted HAAs is of particular interest because recent studies have shown that they may pose a greater health risk than their chlorine-substituted counterparts (*1, 2, 3*). Monochloramine is the dominant haloamine species under drinking water treatment conditions. In the presence of bromide, however, bromine-substituted haloamines, such as mono- and dibromamine, as well as bromochloramine may also form (*4, 5, 6*). Even though these species are present in significantly lower concentrations than monochloramine, they may be more reactive. This research proposes that the variability in DXAA formation and speciation observed in natural waters is associated with the reactivities and relative concentrations of the different haloamine species that may be present. The objective of this research was to characterize the reactivity of bromine-substituted haloamine species in forming HAAs. Disinfection chemistry research in drinking water treatment has focused almost exclusively on disinfectant decay, and the reactivity of the predominant disinfectant present (*i.e.*, chlorine or monochloramine). Increased knowledge of the reactivity of bromine-substituted haloamines is necessary to understanding HAA formation in waters that contain bromide.

Materials and Methods

Haloamine Reactivity Experiments

The reactivity of haloamine species was studied under controlled conditions in two surface waters of differing characteristics. The individual haloamines were isolated to the extent possible and reacted with natural waters to characterize their reactivity in HAA formation. Experiments were conducted in batch reactors, and both the HAA and haloamine concentrations were measured over time.

Bromamine Reactivity

To characterize the reactivity of the bromamines in forming HAAs, natural waters were dosed with preformed bromamine stock solutions (*7*). Simultaneously, the concentrations of the individual bromamine species in the

stock solutions were measured spectrophotometrically. The pH of the water matched that of the dosing solution to ensure that the bromamine speciation did not change upon dosing. The individual haloamine species were also measured spectrophotometrically (7) in carbonate-buffered ultra pure water (UPW) at the same experimental conditions and haloamine doses as the bromamine reactivity experiments. The dose was selected to provide a target bromamine residual concentration between 0.5 and 1 mg/L as Cl_2 at 24 hours. Samples were incubated in amber glass bottles and capped headspace free with teflon-lined septa. Samples to analyze for the nine haloacetic acids (HAA_9) were collected at 5 minutes and again at 0.5, 1, 4, 24, 48, and 72 hours. Total combined oxidant concentrations were measured alongside the HAA samples to determine total oxidant demand. Control experiments were also run with chloramines instead of bromamines to determine relative differences in reactivity. These experiments were conducted at the same pH, buffer concentration, and initial haloamine concentration as the bromamine reactivity experiments, but were dosed with preformed chloramines (8) instead of bromamines.

Bromochloramine Reactivity

Bromochloramine formation is known to be highly dependent on pH (5). Consequently, solutions at pH 9 did not promote significant bromochloramine formation. Therefore, Lake Austin (LA) source water was dosed with preformed bromochloramine (7) stock solutions at pH 6.3 and 7.2. Experiments were performed at pH 7.2 to provide consistency with the bromamine reactivity experiments. The pH of the dosing solution matched that of the water. Samples were incubated in amber glass bottles and capped headspace free with teflon-lined septa. Samples were taken at 5 min and again at 0.5, 1, 4, and 24 hours for HAA_9 analysis. Total combined oxidant and monochloramine concentrations were measured immediately after dosing and alongside the HAA samples to determine total oxidant demand. In addition, haloamine speciation was monitored with membrane introduction mass spectrometry (MIMS) (7). Because the bromochloramine stock solutions contained significant concentrations of monochloramine, several control experiments were run with monochloramine to determine relative differences in reactivity. These experiments were conducted at the same pH, buffer concentration, and initial chloramine dose as the bromochloramine reactivity experiments.

Analytical Methods

A TOC analyzer (Sievers Model 800 Series) equipped with an autosampler was used to measure the TOC and DOC (7). Bromide analyses were performed

by ion chromatography with conductivity detection in accordance with EPA Method 300.1 (9), and the ultra-violet light absorbance was measured at 253.7 nm in accordance with Standard Method 5910 (10). Alkalinity was measured following Standard Method 2320 (10). HAA samples were measured in accordance with USEPA Method 552.2 (9) on a gas chromatograph with a micro electron capture detector and were extracted immediately to avoid complications that may arise due to sample preservation (7).

Total chloramine residual concentrations were measured by spectro-photometry as total chlorine using Hach DPD Total Chlorine Reagent Powder Pillows with Hach DPD Method 8021 adapted from Standard Method 4500-Cl. Monochloramine was measured by spectrometry at 655 nm using Hach Monochlor F Reagent Powder Pillows according to Hach Method 10171. Total combined oxidant residual was measured by spectrophotometry as total chlorine using Hach DPD Total Chlorine Reagent Powder Pillows with Hach DPD Method. The concentrations of the individual bromamine species were measured by spectrometry in a 10-cm pathlength quartz cell (6).

The Membrane Introduction Mass Spectrometry (MIMS) procedure, developed by Shang and Blatchley (11), was used with modifications (7) to detect the presence of chloro- and bromo-substituted haloamines, in particular bromochloramine. Gazda et al. (12) formed NHBrCl by reacting NH_2Cl with Br^- at a 12:1 Br^-:NH_2Cl molar ratio and a pH of 6.5. These researchers monitored the reaction in real-time using MIMS and concluded that bromochloramine was the predominant reaction product. These reaction conditions resulted in rapid formation and decay of bromochloramine. Therefore, a lower Br^-:NH_2Cl molar ratio of 5:1 was used to slow the kinetics of bromochloramine decay. The resulting spectra of this reaction mixture (Figure 1) indicated that bromochloramine and monochloramine were the predominant species present. Ions with m/z values of 51 ($NH_2{}^{35}Cl^{+}$) and 53 ($NH_2{}^{37}Cl^{+}$) represent monochloramine, and those with values of 129 ($NH^{79}Br^{35}Cl^{+}$), 131 ($NH^{79}Br^{37}Cl^{+}$ and $NH^{81}Br^{35}Cl^{+}$) and 133 ($NH^{81}Br^{37}Cl^{+}$) represent bromochloramine. In addition, ion fragments of bromochloramine observed at 79 ($^{79}Br^{+}$), 81 ($^{81}Br^{+}$), 93 ($NH^{79}Br^{+}$), and 95 ($NH^{81}Br^{+}$) were similar to those of Gazda et al. (12). They also observed ions at m/z 97, but did not report observing ions clustered around m/z 160 (Br_2).

Halaomine Reactivity

The reactivity of different haloamine species was studied in Lake Austin (LA) and Metedeconk River (MR) source water. The water quality characteristics for each of these waters are shown in Table I. LA source water is a low specific ultraviolet absorbance (SUVA), high bromide, hard, high
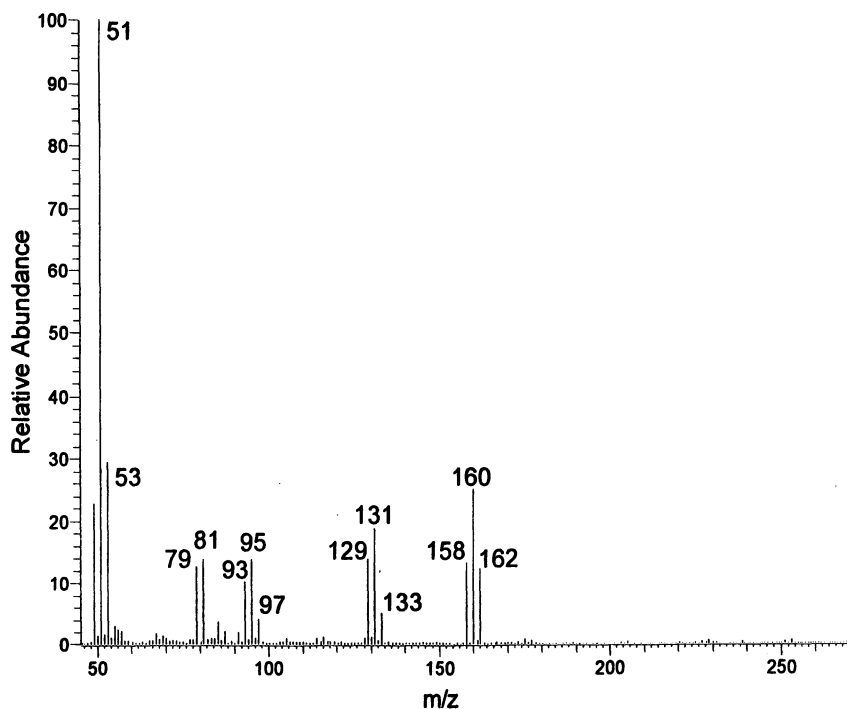
*Figure 1. Mass spectrum for 0.14 mM NH₂Cl + 0.7 mM Br⁻ (pH 6.3
and 5 mM Carbonate buffer) 10 minutes after Br⁻ addition*

Table I. Typical source water quality characteristics

Parameter	LA Source	MRr Source
pH	8.1	6.7
TOC (mg/L)	3.55	3.25
DOC (mg/L)	3.45	3.01
Alkalinity (mg CaCO₃/L)	150	14
SUVA (L/mg-m)	2.11	4.87
Bromide (μg/L)	168	27

alkalinity source water, while MR source water is characterized as a moderately high SUVA, low bromide source water.

Bromamine Reactivity

LA and MR waters were dosed with preformed bromamine stock solutions that contained predominantly mono- or dibromamine based on the pH and Br_2:N ratio selected. Bromamine chemistry is similar to that of the chloramines (6), and as with the chloramine system, bromamine reactions are also catalyzed by both phosphate and carbonate buffers (6). In light of this, only low (less than 0.5 mM) phosphate buffer concentrations were used when necessary to minimize their influence on the reactions of interest. Bromamine doses were selected to provide a target residual concentration between 0.5 and 1 mg/L as Cl_2 at 24 hours. However, both bromamine residual and HAA_9 concentrations were measured at 48 and 72 hours to confirm the reaction conditions were NOM-limited.

Lake Austin source water

The initial conditions of the bromamine reactivity experiments performed in LA water are shown in Table II. They were selected to determine the influence of small concentrations of phosphate buffer, pH, and Br_2:N ratio on HAA formation. The pH and Br_2:N ratio directly influenced which bromamine species dominated, allowing their reactivities to be compared. This comparison was made by the HAA yield, which is the ratio of HAA to DOC concentration.

Table II. Summary of bromamine reactivity experiments in LA water

pH	Br_2:N molar ratio	Phosphate Buffer (mM)	Dose (mg Cl_2/L)	Dose (NH_2Br; $NHBr_2$) (mM)
9	0.05	0	2.1	0.024; 0.003
9	0.05	0.18	2.0	0.022; 0.003
7.2	0.05	0.31	3.0	0.005; 0.019
7.2	0.667	0.33	1.9	0; 0.013

After 24 hours of incubation, each of the four experimental conditions resulted in similar HAA yield, while dibromoacetic acid (DBAA) was the predominant HAA formed (Figure 2). In addition, the results show that bromamines are significantly more reactive than chloramines. After 24 hours of contact in Lake Austin source water (Figure 3), the bromamine species formed

approximately four times the HAA$_9$ yield as the chloramines, indicating that the bromamine species are reactive enough to play a significant role in HAA formation in waters that contain bromide. Because each experiment was dosed with approximately 2 mg/L as Cl$_2$ of total bromamine, the reactivity of mono- and dibromamine could be compared. Each of these conditions resulted in similar HAA yields.

Metedeconk River source water

As with LA water, MR water was dosed with different bromamine solutions formulated to produce predominantly mono- or dibromamine (Table III). However, the bromamine decay rate in MR was significantly greater than that of LA water; therefore, higher initial doses were necessary to provide the target oxidant residual at 24 hours. In addition to the higher initial doses, waters were also spiked with additional bromamines at 48 hours to ensure that the HAA formation was NOM limited. The initial and 48-hour spike dose concentrations were selected to provide a total oxidant residual between 0.5 and 1 mg Cl$_2$/L at 24 and 72 hours, respectively.

Similar to LA water, after 24 hours the bromamines formed predominantly DBAA in MR water (Figure 4). MR water was also more reactive than LA water, which was not unexpected since it had a greater SUVA than LA (Table II). Twenty-four hours after dosing, the bromamine species formed greater than 6 times the HAA$_9$ yield as the chloramines (Figure 5). Also, upon spiking the MR waters with additional bromamines, very little additional HAAs formed, indicating that these experiments were most likely NOM limited.

Table III. Summary of bromamine reactivity experiments in MR water

pH	Br$_2$:N molar ratio	Phosphate Buffer (mM)	Dose (mg Cl$_2$/L)	Dose (NH$_2$Br; NHBr$_2$) (mM)
9	0.05	0	4.8	0.057; 0.005
9	0.05	0.40	5.0	0.056; 0.007
7.2	0.05	0.83	9.2	0.022; 0.054
7.2	0.667	1.43	9.0	0; 0.063

Both the chloramines and bromamines formed predominantly DXAAs, and both resulted in an initial rapid period of HAA formation, followed by a slower period. Chloraminated source waters incubated at pH 7.2 exhibited greater DXAA formation than that at pH 9. During the initial 30 minutes of reaction time, similar concentrations of DXAA formed regardless of pH; however, after
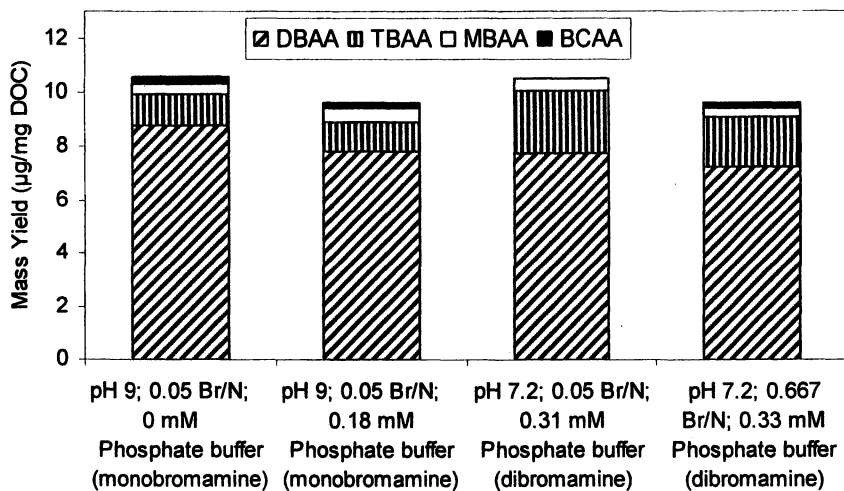
Figure 2. HAA yield and speciation in Lake Austin source water after 24 hours incubation (parentheses indicate dominant bromamine present)
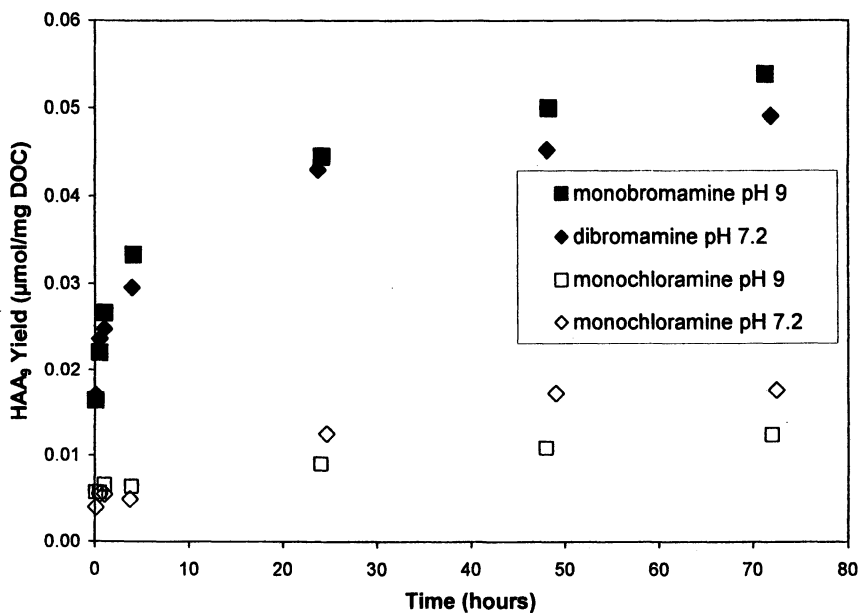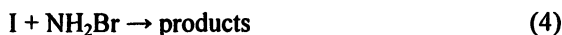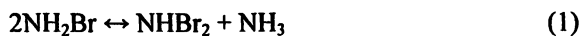

Figure 3. Haloamine reactivity in Lake Austin source water

approximately 30 minutes more rapid kinetics were observed in the water incubated at pH 7.2. The increased HAA formation at lower pH indicates that acid catalyzed chloramine reactions may be responsible. Therefore, monochloramine decay products such as NH_3Cl^+, $NHCl_2$, HOCl may be the cause of the more rapid HAA formation at low pH after the initial 30 minutes of reaction. Lei *et al.* (6) postulated that the reactions for bromamine decomposition are analogous to the chloramines. Hence, monobromamine disproportionates into dibromamine (reaction 1), and dibromamine hydrolysis (reaction 2) may result in an unidentified reaction intermediate (I), which can react with $NHBr_2$ or NH_2Br (reactions 3 and 4) to form HOBr and various other products. Therefore, NH_2Br, $NHBr_2$, or HOBr may be responsible for the observed HAA formation.

$$2NH_2Br \leftrightarrow NHBr_2 + NH_3 \qquad (1)$$

$$NHBr_2 + H_2O \rightarrow I \qquad (2)$$

$$I + NHBr_2 \rightarrow HOBr + products \qquad (3)$$

$$I + NH_2Br \rightarrow products \qquad (4)$$

Greater concentrations of HOBr may form under conditions that promote the formation and decay of $NHBr_2$. The increased tribromoacetic acid (TBAA) observed at pH 7.2 in comparison to pH 9, may be a result of either higher concentrations of $NHBr_2$ decomposition products, such as HOBr, or pH effects on NOM. At low pH, the carboxylic and phenolic functional groups of the NOM are more neutralized, decreasing the electrostatic repulsion between adjacent functional groups and causing the NOM molecule to coil (*13, 14*). This change in structure may influence the reactivity of the NOM. MR water, unlike LA, had greater HAA yields when dibromamine was the dominant bromamine species. This difference in reactivity may be a result of the NOM in MR simply being more reactive, or that dibromamine is more reactive than monobromamine. However, these data do indicate that bromamines are significantly more reactive than chloramines and, therefore, may be important contributors to HAA formation in waters that contain bromide.

Bromochloramine Reactivity

LA water was dosed with preformed bromochloramine stock solutions at pH 6.3 and 7.2. Because bromochloramine formation is highly dependent on pH (*5*), solutions at pH 9 did not promote significant bromochloramine formation. Experiments were performed at pH 7.2 to provide consistency with the
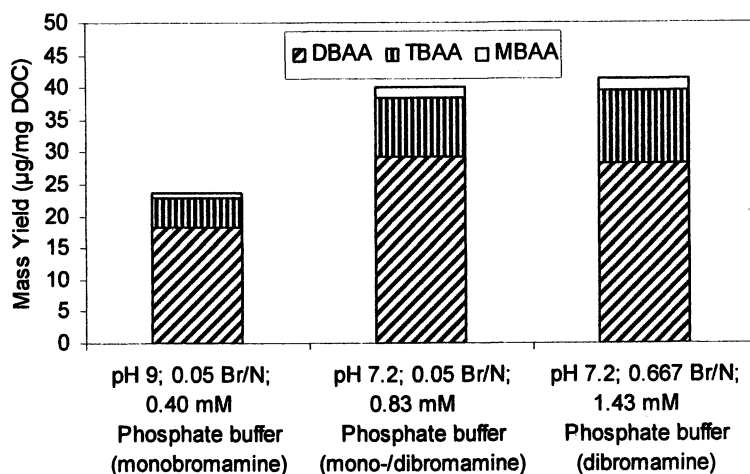
Figure 4. HAA yield and speciation in Metedeconk River source water after 24 hours incubation (parenthesis indicate dominant haloamine present)
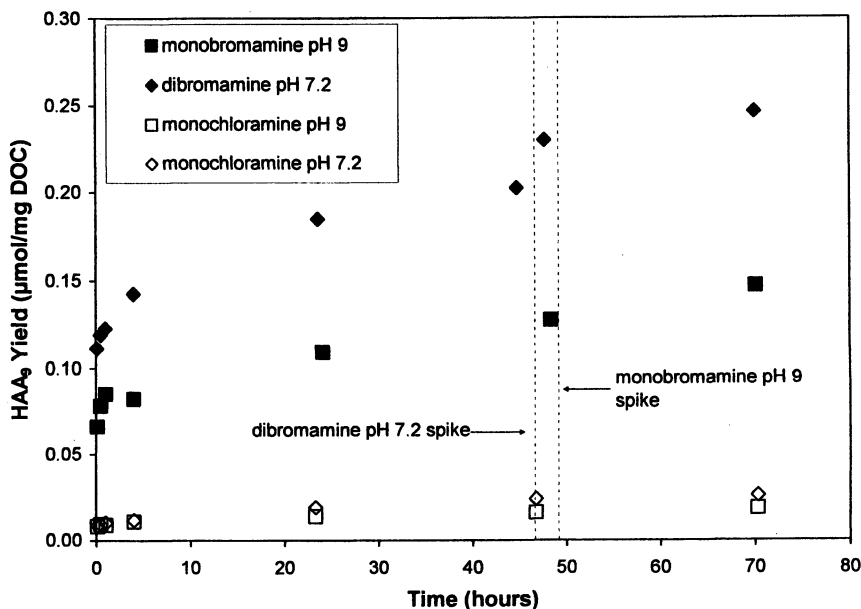
Figure 5. Haloamine reactivity in Metedeconk River source water (dashed line indicates time of additional bromamine spike)

bromamine reactivity experiments. Again, like the bromamine reactivity experiments, carbonate or phosphate buffers were used to maintain the desired pH, but only small concentrations were used to minimize any undesired reactions that may occur. A summary of the bromochloramine reactivity experimental conditions is shown in Table IV.

Total combined oxidant and monochloramine concentrations were measured immediately after dosing and at various times thereafter. The bromochloramine concentration was approximated as the difference between these two measurements because MIMS analysis indicated that a majority of the bromine-substituted haloamine was bromochloramine (7). Greater concentrations of bromochloramine were observed in the dosing solution maintained at pH 6.3. However, the haloamine residual in this solution also decayed faster than the solution incubated at pH 7.2 (Figure 6). Therefore, incubation at pH 6.3 provided greater initial concentrations of bromochloramine, but at pH 7.2, the bromochloramine residual was maintained for a longer time.

Table IV. Summary of bromochloramine reactivity experiments in LA water

pH	Carbonate Buffer (mM)	Phosphate Buffer (mM)	Dose* (NH$_2$Cl; NHBrCl) (mg Cl$_2$/L)	Dose* (NH$_2$Cl; NHBrCl) (mM)
6.3	3.6	0	4.2; 2.9	0.058; 0.020
7.2	2.7	0.9	5.5; 1.8	0.078; 0.013

NOTE: *NH$_2$Cl measured by Hach method 10171; NHBrCl determined by difference between the total oxidant concentration measured by Hach DPD method 8021 and the NH$_2$Cl concentration

The HAA yields with bromochloramine dosed at pH 6.3 and 7.2 (Figure 7) indicate that bromochloramine is reactive enough to play a significant role in HAA formation. A majority of the HAA formed was DBAA; however, significant quantities of TBAA and monobromoacetic acid (MBAA) were also observed. Only small amounts of bromochloracetic acid (BCAA) formed; therefore, most of the HAAs formed were bromine-substituted. Because the bromochloramine stock solutions contained significant concentrations of monochloramine, controls were run with monochloramine to determine relative differences in reactivity. These experiments were conducted at the same pH, buffer concentration, and chloramine dose as the bromochloramine reactivity experiments. Results indicated that bromochloramine was more reactive than monochloramine (Figure 8). After 24 hours, appreciably more HAA formed in the waters dosed with bromochloramine. In addition, since LA water contains
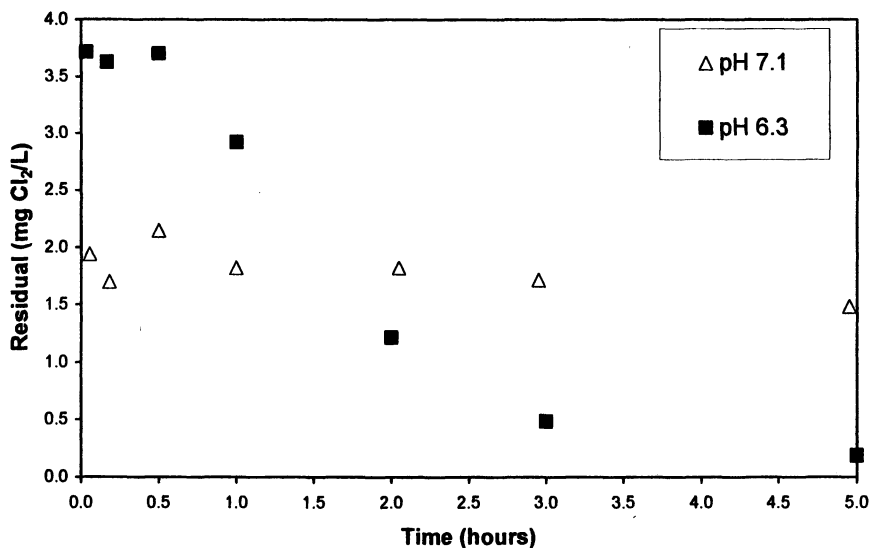
Figure 6. Bromochloramine decay kinetics in Ultrapure Water (UPW) at pH 6.3 (5:1 Br⁻/NH2Cl molar ratio; 3.6 mM total carbonate) and at pH 7.1 (5:1 Br⁻/NH2Cl molar ratio; 2.7 mM total carbonate; 0.9 mM total phosphate)
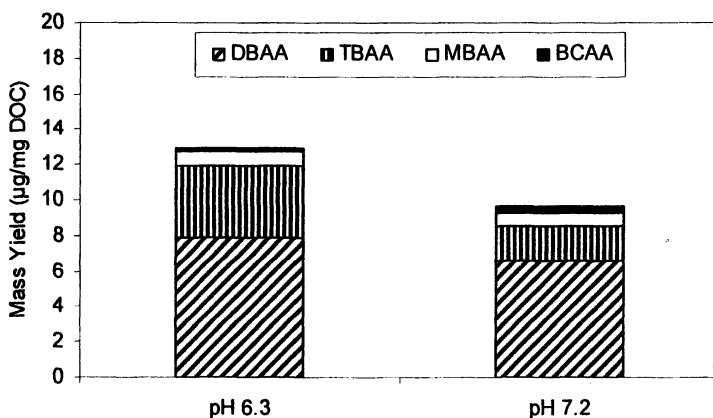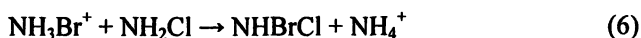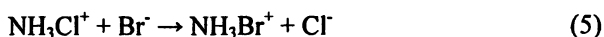

Figure 7. HAA yield and speciation in Lake Austin source water after 24 hours incubation (Predominant haloamines present - bromochloramine and monochloramine)

some bromide (168 µg/L), both bromine-and chlorine-substituted HAAs formed when the water was chloraminated. However, when the water was dosed with the bromochloramine solution, most of the HAAs were bromine-substituted. Therefore, the bromine-substituted halogen was more reactive than the chlorine-substituted halogen also present, out-competing it for available reactive NOM sites.

Bromochloramine or one of its decomposition products is responsible for the observed HAA formation. NHBrCl can form from reactions of monochloramine with bromide or HOBr. Trofe *et al.* (*5*) postulated the reaction mechanism:

$$NH_2Cl + H^+ \leftrightarrow NH_3Cl^+ \qquad (4)$$

$$NH_3Cl^+ + Br^- \rightarrow NH_3Br^+ + Cl^- \qquad (5)$$

$$NH_3Br^+ + NH_2Cl \rightarrow NHBrCl + NH_4^+ \qquad (6)$$

The equilibrium constant for Equation 4 for is 28 M^{-1} (*15*). Therefore, under drinking water treatment conditions, only very small amounts of monochloramonium ion will be present. However, NH_3Cl^+ will react with bromide to form NH_3Br^+ (Equation 5) which rapidly reacts with monochloramine to form bromochloramine (Equation 6). This reaction mechanism demonstrates that NHBrCl formation increases as pH decreases. In addition, monochloramine reacts with HOBr to form NHBrCl (*16*). Once formed, NHBrCl decomposes in base to regenerate OBr^- as a final product by equation 7 (*16, 17*).

$$2NHBrCl + OH^- \rightarrow N_2 + 3H^+ + 2\,Cl^- + Br^- + OBr^- \qquad (7)$$
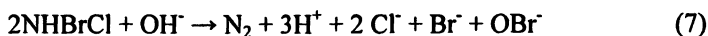
Therefore, in addition to NHBrCl, its decomposition products, such as HOBr, may be responsible for the HAAs formed in the presence of NOM.

Summary and Conclusions

The bromine-substituted haloamines monobromamine, dibromamine, and bromochloramine are significantly more reactive than monochloramine in forming HAAs. Therefore, even though they are present in much lower concentrations than monochloramine under drinking water treatment conditions, they are still reactive enough to play a role in HAA formation. MR source water was more reactive than LA, forming greater HAA yields in the presence of monobromamine, dibromamine, and monochloramine (Figure 9). These data illustrate the importance of source water characteristics on the relative reactivity
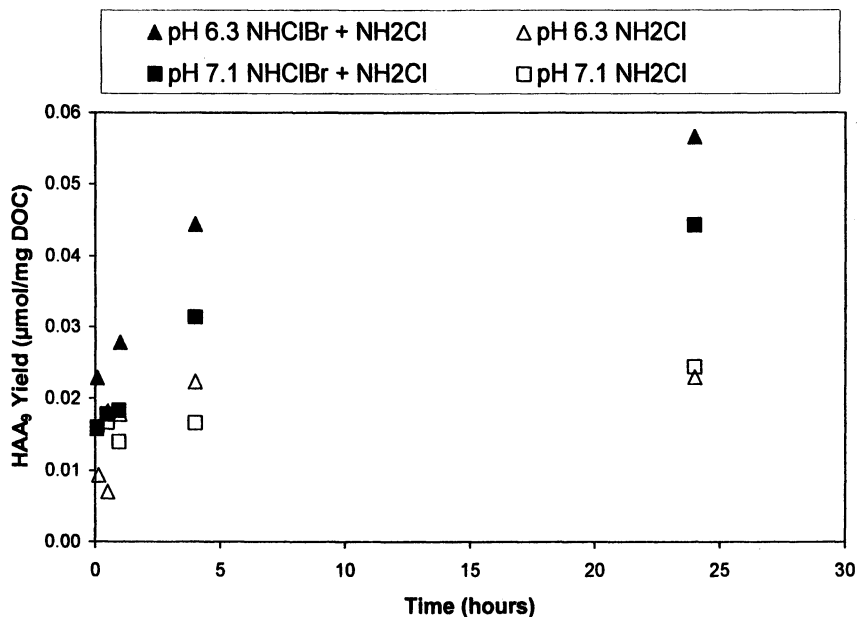
Figure 8. Bromochloramine reactivity in Lake Austin source water
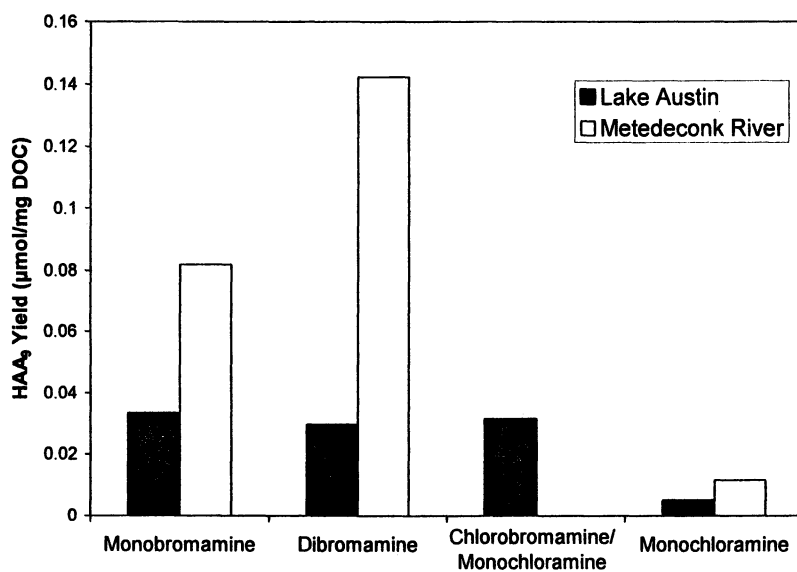

Figure 9. Different haloamine reactivities in Lake Austin and Metedeconk River source waters after 4 hour incubation at pH 7.2

of each species. The greater reactivity of MR water was expected based upon its higher SUVA (4.87) compared to Lake Austin (2.11). Therefore, the varying characteristics of NOM among source waters are significant factors in determining NOM's reactivity with the different bromine- and chlorine-substituted haloamines that may form in the presence of bromide during chloramination. The presence of bromine-substituted HAAs in chloraminated drinking water suggests that bromine-substituted haloamines are reactive enough to play a role in HAA formation even though they are present in much lower concentrations than monochloramine.

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