

## Monochloramine and total haloamine decay after a short prechlorination time in the presence of bromide

A. Alsulaili, G. E. Speitel Jr. and L. E. Katz

### ABSTRACT

The Chlorine-Ammonia Process was developed recently as a preoxidation process to minimize the formation of bromate during ozonation of the waters containing a significant bromide concentration. Chlorine is added first followed by ammonia 5–10 minutes later, with the goal of sequestering bromide in monobromamine during the subsequent ozonation step. The goal of this research was to improve the Chlorine-Ammonia Process by introducing a very short prechlorination step (i.e. 30 seconds before addition of ammonia) to minimize overall disinfection by-product formation. Also, in this strategy, formation of a powerful halogenating agent, HOBr, is minimized and bromochloramine (NHClBr) is used predominantly instead of monobromamine to sequester bromide during ozonation. To support this improved approach to bromide sequestration, this study examined the formation and decay of bromochloramine as a function of operating conditions, such as pH and Cl<sub>2</sub>:N ratio, and refined a chemical kinetic model to predict haloamine concentrations over time.

**Key words** | bromide, bromochloramine, monochloramine, prechlorination

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### BACKGROUND

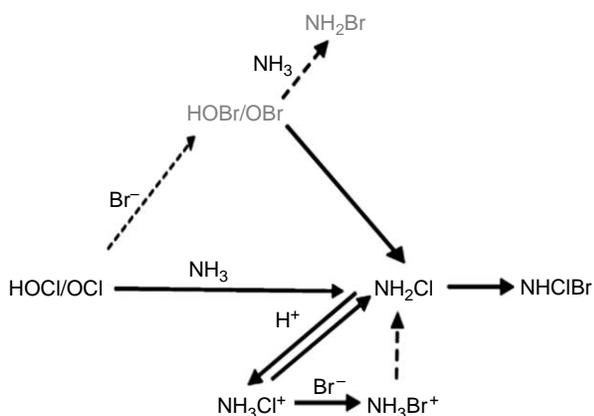
Chlorine has traditionally been used as a disinfectant for drinking water to inactivate pathogenic microorganisms. However, the reaction of chlorine with organic material in the water forms carcinogenic and mutagenic disinfection by-products (DBPs). Alternative disinfectants have been used to limit DBP formation while still providing adequate disinfection. The popularity of ozone and chloramines as disinfectants for drinking water has increased over the past 20 years because of their effectiveness as disinfectants and the reduction in halogenated DBP formation associated with their use. Unfortunately, ozonation of waters containing bromide can produce undesirable concentrations of bromate which is regulated in the U.S. at a Maximum Contaminant Level (MCL) of 10 µg/L. Different strategies have been used to control bromate formation during ozonation. The Chlorine-Ammonia Process involves the stepwise addition of chlorine and ammonia prior to ozonation to sequester bromide in bromamine species, thereby leading

to a significant reduction in bromate formation during ozonation. One concern with the Chlorine-Ammonia Process is the possibility of significant formation of other halogenated DBPs during the chlorination period.

### RESEARCH OBJECTIVES

The goal of this research was to improve the Chlorine-Ammonia Process to minimize overall DBP formation, including bromate. This goal will be achieved by introducing a very short prechlorination step (i.e. 30 seconds before addition of ammonia) such that the same level of bromate control can be achieved using a shorter free chlorination time. (Figure 1). Also, in this strategy formation of a powerful halogenating agent, HOBr, is minimized and bromochloramine (NHClBr) is used predominantly instead of monobromamine to sequester bromide during ozonation.

doi: 10.2166/ws.2010.171



**Figure 1** | Operative reaction pathway following a 30 second prechlorination control strategy (Dashed lines and gray lettering indicate minor pathways and species, respectively).

To support this improved approach to bromide sequestration, this study examined the formation and decay of bromochloramine as a function of operating conditions, such as pH and Cl<sub>2</sub>/N ratio, and refined a chemical kinetic model to predict haloamine concentrations over time.

## EXPERIMENTAL SECTION

### Materials

Aldrich 4% minimum available chlorine, a reagent grade sodium hypochlorite, was used as the source of HOCl and OCl<sup>-</sup>. Solid KBr was used as the source of the bromide ion. NH<sub>4</sub>Cl was used as the source of ammonia. Ammonia dosing solutions were prepared to provide 3.33 g/L as N. Millipore ultra pure water was used in preparing all the solutions. The pH was adjusted by addition of NaOH or HCl, and sodium carbonate was used to buffer the solutions. An ORION<sup>®</sup> 920A pH meter was used with an ORION Combination H/ATC probe to measure pH, and an Agilent 8453 UV spectrophotometer was used for all spectrophotometric measurements.

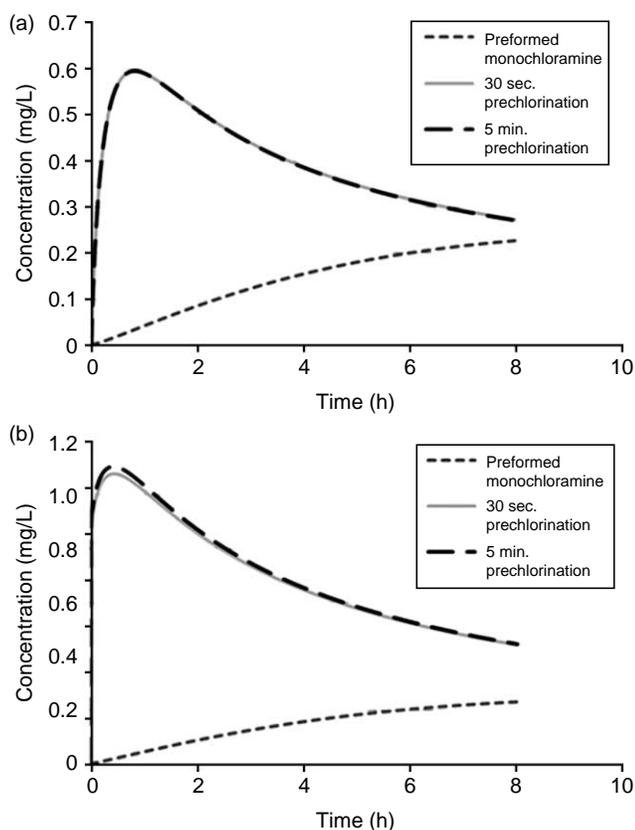
For the total chlorine dosing solution and standard curve, the exact concentration of the chlorine dosing solution was measured prior to dosing using Standard Method 4500-Cl B (APHA 1998) and by spectrophotometry. The pH of each sample was increased to 11 with NaOH, and the absorbance at a wavelength of 292 nm was used to

determine the concentration of OCl<sup>-</sup> assuming a molar absorptivity of 362 M<sup>-1</sup> cm<sup>-1</sup> (Furman & Margerum 1988).

For the monochloramine standard curve, preformed monochloramine was created by mixing aqueous ammonium chloride (NH<sub>4</sub>Cl) and sodium hypochlorite (NaOCl) solutions. These solutions were formulated so that approximately equal volumes of the two, when combined, produced the desired Cl<sub>2</sub>/N ratio (3/1 mass ratio). Both solutions were adjusted to pH 9 with HCl and/or NaOH. Prior to creating preformed chloramines, the concentration of the chlorine solution was measured as described above. The volume of ammonium solution added was adjusted to ensure the correct Cl<sub>2</sub>/N ratio. The chlorine solution was added slowly to the ammonium solution with constant mixing in an ice bath at 1°C. After 15 minutes of mixing, the concentration of the monochloramine solution was measured using Standard Method 4500-Cl B and by spectrophotometry using a molar absorptivity of 461 M<sup>-1</sup> cm<sup>-1</sup> at λ<sub>max</sub> of 243 nm for NH<sub>2</sub>Cl (Kumar & Margerum 1987) prior to dosing the samples. Two measurements were made. If these measurements differed by more than 0.1 mg/L a second pair was made. If the second pair of measurements differed by more than 0.1 mg/L the solution was discarded and remixed. An average of the two appropriate measurements was used in the calculations. All solutions were mixed with Millipore ultra pure water. This procedure was used successfully in previous chloramination research (Symons 1998).

### Methods

The first step in developing a method for modeling monochloramine and total chlorine concentrations is to study the effect of chloramine addition mode on bromamine speciation. Figure 2 shows model results from the Unified Haloamine Model developed by Pope (2006) for 5 minutes of prechlorination time, 30 seconds of prechlorination time and preformed monochloramine. The results indicate that the two prechlorination times yield almost identical bromochloramine and total bromamine concentration profiles. Therefore, all experiments were run using a 30-second prechlorination time such that the same level of bromate and DBP formation control was achieved using a minimum free chlorination exposure time.



**Figure 2** | Model prediction of (a) Bromochloramine, (b) Bromamine + Bromochloramine formation and decay in organic free water ( $\text{TOTCl}_2 = 2 \text{ mg/L}$ ,  $\text{Cl}_2/\text{N} = 3/1$ ,  $\text{TOTCO}_3 = 4 \text{ mM}$ ,  $\text{Br}^- = 1 \text{ mg/L}$ ,  $T = 22^\circ\text{C}$ , and  $\text{pH} = 7$ ).

Sodium carbonate was added to Millipore ultra pure water to buffer the solution in a 2-L Erlenmeyer flask covered with foil. Bromide was added and continuously mixed for five minutes, then chlorine was added, and then ammonia was added 30 seconds later to get the target  $\text{Cl}_2/\text{N}$  ratio. This  $\text{Cl}_2/\text{N}$  ratio was based on the initial chlorine concentration; therefore, the actual  $\text{Cl}_2/\text{N}$  ratio at the start of the chloramination step was lower. The exact ammonia concentration added was used in the modeling, so no inaccuracies were introduced. This solution was then proportioned into 250-mL brown glass bottles that were capped with Teflon-lined septa with zero headspace, which were then incubated in the dark until the time of the analysis.

The total chlorine residual was measured using spectrophotometry to measure total chlorine at a wavelength of 530 nm using Hach DPD ( $\text{N,N}$ -diethyl-*p*-phenylenediamine). The Hach Total Chlorine Reagent Powder with the Hach

DPD test Method 8167 is adapted from Standard Method 4500-Cl. Standards of approximately 0, 0.5, 1.5, 2.5, and 3.5 mg/L as  $\text{Cl}_2$  were analyzed in triplicate prior to the samples to prepare the standard curve. The standards were created from the chlorine dosing solution, which was prepared with Aldrich 4% minimum available chlorine, reagent grade sodium hypochlorite. First, the exact concentration of the dosing solution was measured using Standard Method 4500-Cl B, and by spectrophotometry at a wavelength of 292 nm and molar absorptivity of  $362 \text{ M}^{-1} \text{ cm}^{-1}$  for  $\text{OCl}^-$ . Then, a primary dilution standard (PDS) was created by diluting the dosing solution to a concentration of 100 mg/L as  $\text{Cl}_2$  with ultra pure water. Finally, the standards were prepared by diluting the DPS to the desired concentration with ultra pure water.

The total chlorine measurement includes free chlorine ( $\text{HOCl}$  and  $\text{OCl}^-$ ), free bromine ( $\text{HOBr}$  and  $\text{OBr}^-$ ), chloramines (monochloramine and dichloramine), bromamines (monobromamine and dibromamine), and bromochloramine. Under typical drinking water treatment conditions (neutral pH and  $\text{Cl}_2/\text{N}$  ratios 3–5/1), virtually all chlorine and bromine are present as combined chlorine and bromine.

The monochloramine residual was also measured using spectrophotometry to measure monochloramine at a wavelength of 655 nm using Hach Monochlor F Reagent Powder Pillows with Hach Method 10171. Monochloramine standards of approximately 0, 0.5, 1, 2, and 3.5 mg/L as  $\text{Cl}_2$  were analyzed in triplicate prior to the samples to prepare the standard curve. This measurement only measures monochloramine (Shang & Blatchley 1999).

## Experimental matrix

Batch experiments were conducted over a range of pH, bromide concentrations,  $\text{Cl}_2/\text{N}$  ratios, and carbonate concentrations. Table 1 summarizes the experimental matrix.

## MODELING

A kinetic model was developed to predict haloamine concentrations over time, with a particular focus on understanding bromochloramine chemistry. The model is

**Table 1** | Experimental matrix

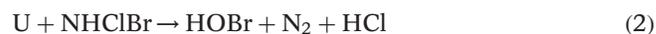
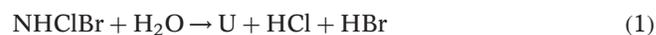
No.	pH	Cl <sub>2</sub> /N ratio	Bromide (µg/L)	Carbonate buffer (mM)
1	6.55	3/1	1,000	2
2	6.55	3/1	1,000	4
3	6.55	3/1	1,000	7
4	6.55	3/1	1,000	10
5	6.55	3/1	1,000	15
6	7.10	3/1	1,000	4
7	8.05	3/1	1,000	4
8	8.05	3/1	1,000	7
9	8.05	3/1	1,000	10
10	6.55	3/1	100	4
11	6.55	1/1	1,000	4
12	8.05	3/1	100	4

based on the Unified Haloamine Model developed by Pope (2006), and incorporates the monochloramine decay model developed by Vikesland *et al.* (2001), the bromamine decomposition model developed by Lei *et al.* (2004), the bromochloramine formation and decay reactions developed by Gadza & Margerum (1994) and Trofe *et al.* (1980), and various equilibrium expressions. Also, a new bromochloramine decay mechanism was introduced including bromochloramine auto-decomposition and bromochloramine reaction with monochloramine.

The oxidation of bromide by hypochlorous acid plays a very important role in haloamine speciation, especially with a short prechlorination time (30 seconds) and a pH above neutral. Under these conditions, not all of the bromide will be oxidized to HOBr. We examined the kinetics of this reaction and found it to be an acid catalyzed reaction (Alsulaili 2009).

Information on bromochloramine decay is limited. Valentine (1986) proposed that NHBrCl decomposes to regenerate OBr<sup>-</sup> as a final product. However, using Valentine's reaction in our model failed to predict total chlorine and monochloramine decay, which suggests that this reaction does not adequately capture the decay. To model the decomposition of bromochloramine, the same reaction scheme responsible for dichloramine decay was assumed in which an unidentified intermediate (U) is

formed that can react with either monochloramine or bromochloramine.

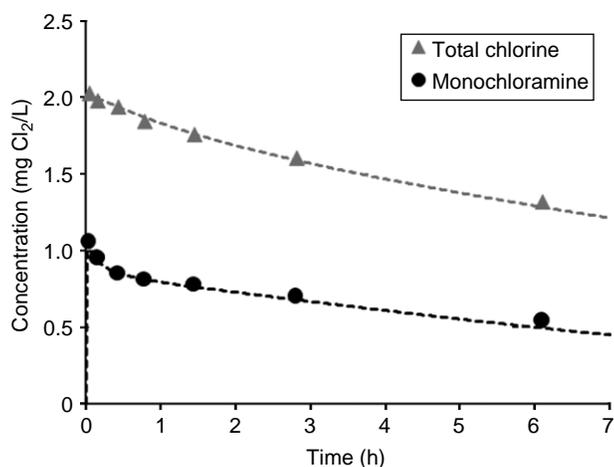


Reaction 1 is assumed to be the rate limiting reaction in this series. Because the intermediate species U was assumed to exist at a very low concentration, only the ratio of Reaction 2 to Reaction 3 is important. To simplify the modeling effort, the ratio of rate constants for Reaction 2 to Reaction 3 were fixed to the ratio used for dichloramine decay. The value of the rate constant for Reaction 2 and Reaction 3 was selected to be at least three orders of magnitude larger than the value of the rate constant of Reaction 1.

## RESULTS

The Unified Haloamine Kinetic Model of Pope (2006) that includes the new rate constant for the oxidation of bromide by hypochlorous acid failed to model the monochloramine and total chlorine decay over time, especially at high carbonate buffer concentration. One possible reason for the failure of the model is that one or more of the reactions is acid catalyzed. Since the model has been shown to predict total chlorine and monochloramine decay during preformed monochloramine addition schemes, it is likely that the reaction of monochloramine and HOBr to form bromochloramine and the decay of bromochloramine are the acid catalyzed reactions. To determine the acid catalysis rate expressions for these reactions a number of experiments were conducted with different carbonate buffer concentrations over a range of pH values and used in conjunction with Scientist<sup>®</sup> 3.0 software to estimate the effect of each acidic species on the rate constant. Both reactions of bromochloramine formation from the monochloramine reaction with HOBr and the decay of bromochloramine were fit simultaneously under each set of conditions selected to isolate a particular acid. Figure 3 shows an example of a model fit for one set of conditions.

The final expression of the rate constants of bromochloramine decay (Reaction 1) and bromochloramine



**Figure 3** | Monochloramine and total chlorine decay (pH = 6.55, TOTCO<sub>3</sub> = 2 mM, Br<sup>-</sup> = 1,000 µg/L, Cl<sub>2</sub>/N = 3/1, 30 seconds prechlorination time) (dash lines represent the Modified Unified Haloamine Model result).

formation from the reaction of monochloramine and HOBr can be written as a function of bicarbonate and carbonic acid concentration:

$$k = k_{\text{HCO}_3^-} [\text{HCO}_3^-] + k_{\text{H}_2\text{CO}_3} [\text{H}_2\text{CO}_3]$$

The revised model shows accurate predictions of monochloramine and total chlorine concentrations after 30 seconds of prechlorination at carbonate buffer concentrations below 7 mM and over a wide range of operating conditions (pH, Cl<sub>2</sub>/N ratio, and bromide concentration). The model also demonstrates the important role of bromochloramine relative to monobromamine as the main sequestering agent for bromide during subsequent ozonation. The reaction of monochloramine and hypobromous acid was found to be the dominant pathway of bromochloramine formation under the reaction conditions studied in this research.

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