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MONOCHLORAMINE DECAY IN MODEL AND DISTRIBUTION SYSTEM WATERS

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Abstract—Chloramines have long been used to provide a disinfecting residual in distribution systems where it is difficult to maintain a free chlorine residual or where disinfection by-product (DBP) formation is of concern. While chloramines are generally considered less reactive than free chlorine, they are inherently unstable even in the absence of reactive substances. These reactions, often referred to as “auto-decomposition”, always occur and hence define the maximum stability of monochloramine in water. The effect of additional reactive material must be measured relative to this basic loss process. A thorough understanding of the auto-decomposition reactions is fundamental to the development of mechanisms that account for reactions with additional substances and to the ultimate formation of DBPs. A kinetic model describing auto-decomposition was recently developed. This model is based on studies of isolated individual reactions and on observations of the reactive ammonia-chlorine system as a whole. The work presented here validates and extends this model for use in waters typical of those encountered in distribution systems and under realistic chloramination conditions. The effect of carbonate and temperature on auto-decomposition is discussed. The influence of bromide and nitrite at representative monochloramine concentrations is also examined, and additional reactions to account for their influence on monochloramine decay are presented to demonstrate the ability of the model to incorporate inorganic demand pathways that occur parallel to auto-decomposition. © 2001 Elsevier Science Ltd. All rights reserved

Key words—bromide, carbonate, disinfection, monochloramine, nitrite

INTRODUCTION

Chloramine disinfectants are produced by substitution reactions between free chlorine and ammonia in a process called chloramination. Strictly speaking, the chloramines include monochloramine (NH_2Cl), dichloramine (NHCl_2), and trichloramine (NCl_3). However, monochloramine is the predominant chloramine species under the conditions typically found in drinking water treatment. Monochloramine has the same oxidizing capacity as free chlorine on a chlorine atom basis, but it is a weaker disinfectant (Wolfe *et al.*, 1984). It is often used when free chlorine residuals are difficult to maintain or when they lead to excessive disinfection by-product (DBP) formation.

Chloramines are nonetheless inherently unstable at neutral pH values, even without the presence of reactive inorganic or organic substances, and auto-decompose by a complex set of reactions that ultimately result in the oxidation of ammonia and the reduction of active chlorine (Jafvert and Valentine, 1992). The rate of these reactions depends on the solution pH as well as on the ratio of chlorine to ammonia nitrogen (Cl/N ratio). In general, the larger the Cl/N ratio the faster the oxidation of ammonia.

To meet disinfection requirements and to minimize DBP formation it is desirable that the chloramine residual be as stable as possible. Unfortunately, in spite of the long history of chloramine use, the fate of chloramines in distribution systems and the characteristics and processes that influence their stability are largely unknown. A model to predict chloramine decay in the water phase has been proposed (Jafvert and Valentine, 1992; Ozekin *et al.*, 1996). The model takes into account the complex series of reactions that ammonia and chlorine undergo in aqueous solution, and it can predict chloramine auto-decomposition for a wide range of reaction conditions. However, the validity of the model was not tested under realistic chloramination conditions. Specifically, the model and rate coefficients were determined

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using very high monochloramine concentrations in phosphate-buffered water. Furthermore, all previous work was conducted at 25°C and the rate coefficients are therefore probably not applicable to waters with either lower or higher temperatures.

The present study was undertaken to evaluate the appropriateness of this model under more realistic water quality and chloramination conditions. Studies were conducted in carbonate-buffered waters. Carbonate provides not only buffering capacity but is also hypothesized to catalyze monochloramine decomposition (Valentine and Jafvert, 1988). An additional objective was to determine and incorporate temperature dependencies of important reactions. Finally, the general utility and validity of the model was demonstrated by extending it to include reactions involving bromide and nitrite, two inorganic species that can exert or catalyze a monochloramine demand in distribution system waters.

MONOCHLORAMINE AUTO-DECOMPOSITION MODEL FORMULATION

The monochloramine auto-decomposition model developed by Valentine and co-workers (Jafvert and Valentine, 1992; Ozekin *et al.*, 1996) is shown in Table 1. This model only accounts for the auto-decomposition of monochloramine. As such, it is the starting point for the development of more comprehensive reaction models that incorporate additional loss pathways. The model includes four principle reaction schemes: (1) substitution/hydrolysis reactions involving HOCl and ammonia or the chlorinated ammonia derivatives (reactions 1.1–1.4); (2) disproportionation reactions of the chloramine species (reactions 1.5–1.6); (3) redox reactions that occur in the absence of measurable levels of free chlorine (reactions 1.7–1.10); and (4) equilibrium reactions involving the protonation/deprotonation of chlorine, ammonia, and the carbonate species (reactions 1.11–1.14).

As shown in Table 1, chloramine loss by auto-decomposition is a relatively complex process. How-

ever, the overall rate of chloramine loss for neutral pH values and above is primarily limited by the rate of formation of dichloramine (Jafvert and Valentine, 1992). Dichloramine formation occurs through both monochloramine hydrolysis (reactions 1.2 and 1.3) and by a general acid catalyzed monochloramine disproportionation reaction (reaction 1.5). The relative importance of these pathways on the formation of dichloramine is dependent on factors like pH, ionic strength, temperature, and alkalinity. Once dichloramine forms it decomposes via a series of rapid redox reactions. The products of these reactions are primarily ammonia, chloride, and nitrogen gas, however, nitrate also forms under some conditions (Vikesland *et al.*, 1998).

General acid-catalyzed monochloramine disproportionation (reaction 1.5) is of interest since it suggests that a variety of proton-donating species (e.g., general acid catalysts) can act to accelerate monochloramine decay:



where $k_d = \sum k_i[\text{HA}_i]$ and k_i is the specific rate coefficient for the i th proton-donating species HA_i (this includes hydrogen ion). Previous studies have shown that acetic acid (Granstrom, 1954) as well as sulfate and phosphate (Valentine and Jafvert, 1988) acts in this capacity. Using a linear free-energy relationship (LFER), Valentine and Jafvert (1988) concluded that carbonate species also have the potential to act as catalysts. For carbonate-buffered waters, the general acid-catalyzed rate coefficient k_d is hypothesized to have the following form:

$$k_d = k_{\text{H}^+}[\text{H}^+] + k_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3] + k_{\text{HCO}_3}[\text{HCO}_3^-] \quad (1)$$

where k_{H^+} ($= 4 \times 10^4 \text{ M}^{-2} \text{ h}^{-1}$) is the hydrogen-ion-specific rate coefficient (Granstrom, 1954), and $k_{\text{H}_2\text{CO}_3}$ and k_{HCO_3} are the rate coefficients for catalysis by carbonic acid and bicarbonate ion, respectively. Using their LFER, Valentine and Jafvert (1988) estimated $k_{\text{H}_2\text{CO}_3}$ and k_{HCO_3} to be 2.7×10^3 and

Table 1. Monochloramine decay model developed by Jafvert and Valentine (1992) and modified by Ozekin *et al.* (1996)

Reaction	Rate coefficient/equilibrium constant (25°C)	References
1.1 HOCl + NH ₃ → NH ₂ Cl + H ₂ O	$k_{1.1} = 1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$	Morris and Isaac (1981)
1.2 NH ₂ Cl + H ₂ O → HOCl + NH ₃	$k_{1.2} = 7.6 \times 10^{-2} \text{ h}^{-1}$	Morris and Isaac (1981)
1.3 HOCl + NH ₂ Cl → NHCl ₂ + H ₂ O	$k_{1.3} = 1.0 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$	Margerum <i>et al.</i> (1978)
1.4 NHCl ₂ + H ₂ O → HOCl + NH ₂ Cl	$k_{1.4} = 2.3 \times 10^{-3} \text{ h}^{-1}$	Margerum <i>et al.</i> (1978)
1.5 NH ₂ Cl + NH ₂ Cl → NHCl ₂ + NH ₃	k_d^a	This work
1.6 NHCl ₂ + NH ₃ → NH ₂ Cl + NH ₂ Cl	$k_{1.6} = 2.2 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$	Hand and Margerum (1983)
1.7 NHCl ₂ + H ₂ O → I	$k_{1.7} = 4.0 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$	Jafvert and Valentine (1987)
1.8 I + NHCl ₂ → HOCl + products	$k_{1.8} = 1.0 \times 10^8 \text{ M}^{-1} \text{ h}^{-1}$	Leao (1981)
1.9 I + NH ₂ Cl → products	$k_{1.9} = 3.0 \times 10^7 \text{ M}^{-1} \text{ h}^{-1}$	Leao (1981)
1.10 NH ₂ Cl + NHCl ₂ → products	$k_{1.10} = 55.0 \text{ M}^{-1} \text{ h}^{-1}$	Leao (1981)
1.11 HOCl → H + OCl ⁻	$pK_a = 7.5$	Snoeyink and Jenkins (1980)
1.12 NH ₄ ⁺ → NH ₃ + H ⁺	$pK_a = 9.3$	Snoeyink and Jenkins (1980)
1.13 H ₂ CO ₃ → HCO ₃ ⁻ + H ⁺	$pK_a = 6.3$	Snoeyink and Jenkins (1980)
1.14 HCO ₃ ⁻ → CO ₃ ²⁻ + H ⁺	$pK_a = 10.3$	Snoeyink and Jenkins (1980)

^a $k_d = k_{\text{H}^+}[\text{H}^+] + k_{\text{H}_2\text{CO}_3}[\text{H}_2\text{CO}_3] + k_{\text{HCO}_3}[\text{HCO}_3^-]$ where $k_{\text{H}_2\text{CO}_3} = 4 \times 10^4 \text{ M}^{-2} \text{ h}^{-1}$, $k_{\text{HCO}_3} = 800 \text{ M}^{-2} \text{ h}^{-1}$, $k_{\text{H}^+} = 2.5 \times 10^7 \text{ M}^{-2} \text{ h}^{-1}$ and I is the unidentified monochloramine auto-decomposition intermediate.

$7.2 \text{ M}^{-2} \text{ h}^{-1}$ respectively. However, no experimental studies were conducted to verify their findings. Therefore, prior to this study it was not known whether changes in carbonate would actually affect monochloramine decay and if the estimated rate coefficients would apply.

The monochloramine decomposition model shown in Table 1 was developed for a temperature of 25°C . However, in actual water distribution systems, depending on source and season, water temperatures can range from 5 to 35°C . Potentially pertinent reaction rates increase several fold over this range. Fortunately, while many equilibria and individual reactions may be influenced, only key rate limiting reactions and equilibria need be considered in a reaction-modeling effort. As discussed earlier, the overall rate of chloramine loss is primarily limited by the rate of dichloramine formation, and therefore only the temperature dependencies of reactions leading to its formation need be considered.

Previous studies have characterized the temperature dependence of key rate-limiting reactions: the formation of monochloramine (reaction 1.1), monochloramine hydrolysis (reaction 1.2), and the reaction between NH_2Cl and HOCl (reaction 1.3). Temperature dependencies obtained from the literature for these reactions are tabulated in Table 2. Monochloramine disproportionation (reaction 1.5) is also a potentially rate-limiting reaction. The temperature dependence of the hydrogen-ion-catalyzed rate coefficient (k_{H^+}) was previously determined to be $k_{\text{H}^+} = 3.78 \times 10^{10} \exp(-2169/T) \text{ M}^{-2} \text{ h}^{-1}$ by Granstrom (1954). Temperature dependencies for the carbonate-dependent terms were determined as part of this project and are tabulated in Table 2. The species whose equilibria are affected by temperature are: HOCl/OCl^- , $\text{H}_2\text{CO}_3/\text{HCO}_3^-$, $\text{HCO}_3^-/\text{CO}_3^{2-}$, and $\text{NH}_4^+/\text{NH}_3$. The temperature dependencies of these equilibria were obtained from the literature and may also be found in Table 2.

INCORPORATION OF REACTIONS OF NITRITE AND BROMIDE

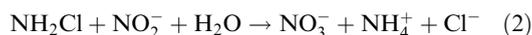
Previous work has established that many common drinking water contaminants can enhance mono-

chloramine decomposition. Two species of particular concern are nitrite (Valentine, 1985; Hao *et al.*, 1994; Margerum *et al.*, 1994) and bromide (Galal-Gorchev and Morris, 1965; Trofe *et al.*, 1980; Bousher *et al.*, 1989). Both of these species readily react with monochloramine and can thus cause monochloramine loss. Nitrite exerts a true "demand", while bromide actually acts in a catalytic manner to enhance the auto-decomposition of monochloramine.

Nitrite is not typically found in raw waters but it can form and build up to significant concentrations in finished waters due to incomplete bacterial nitrification of ammonia (Lieu *et al.*, 1993). In fact, nitrite concentrations as high as 2 mg NL^{-1} have been measured in distribution system waters (Arber *et al.*, 1985). Bromide, on the other hand, is found in most raw waters used to produce drinking water at concentrations that range from a few micrograms per liter up to several milligrams per liter (Siddiqui and Amy, 1993). In a comprehensive study, Amy and co-workers (1994) found that the average bromide concentration in raw waters treated in the United States was $100 \mu\text{g L}^{-1}$ with a range of $0\text{--}2.3 \text{ mg L}^{-1}$. Since mechanisms for the reactions of these species with monochloramine are known, it should be possible to account for their effects by incorporating the appropriate reactions in the overall model.

Nitrite reactions

In theory, monochloramine reacts with nitrite to produce nitrate according to the stoichiometric reaction:



This stoichiometry indicates that for every nitrite molecule that reacts with monochloramine that one molecule of nitrate and one molecule of ammonia are produced. This reaction therefore not only leads to the direct abiotic formation of nitrate, but simultaneously produces ammonia, which can subsequently undergo biologically mediated nitrification. This net stoichiometry can be attributed to a direct reaction between NH_2Cl and NO_2^- and/or to a reaction between NO_2^- and the HOCl produced by monochloramine hydrolysis. Under typical water

Table 2. Temperature dependency of reaction rate coefficients and equilibrium constants. *T* in K

Reaction	Rate coefficient/equilibrium constant	References
$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_{1.1} = 2.37 \times 10^{12} \exp(-1510/T) \text{ M}^{-1} \text{ h}^{-1}$	Morris and Isaac (1981)
$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$	$k_{1.2} = 6.7 \times 10^{11} \exp(-8800/T) \text{ h}^{-1}$	Morris and Isaac (1981)
$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_{1.3} = 1.08 \times 10^9 \exp(-2010/T) \text{ M}^{-1} \text{ h}^{-1}$	Margerum <i>et al.</i> (1978)
$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$	$k_{1.5} = k_{\text{H}^+}^{\text{H}^+} [\text{H}^+] + k_{\text{HCO}_3^-} [\text{HCO}_3^-] + k_{\text{H}_2\text{CO}_3} [\text{H}_2\text{CO}_3]$ $k_{\text{H}^+} = 3.78 \times 10^{10} \exp(-2169/T) \text{ M}^{-2} \text{ h}^{-1}$ $k_{\text{HCO}_3^-} = 1.5 \times 10^{35} \exp(-22144/T) \text{ M}^{-2} \text{ h}^{-1}$ $k_{\text{H}_2\text{CO}_3} = 2.95 \times 10^{10} \exp(-4026/T) \text{ M}^{-2} \text{ h}^{-1}$	Granstrom (1954) This work This work
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$\text{p}K_{\text{a}} = 1.48 \times 10^{-4} (T) - 9.39 \times 10^{-2} (T) + 21.2$	Snoeyink and Jenkins (1980)
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	$\text{p}K_{\text{a}} = 1.19 \times 10^{-4} (T) - 7.99 \times 10^{-2} (T) + 23.6$	Snoeyink and Jenkins (1980)
$\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$	$\text{p}K_{\text{a}} = 1.03 \times 10^{-4} (T) - 9.21 \times 10^{-2} (T) + 27.6$	Bates and Pinching (1950)
$\text{HOCl} \rightleftharpoons \text{OCl}^- + \text{H}^+$	$\text{p}K_{\text{a}} = 1.18 \times 10^{-4} (T) - 7.86 \times 10^{-2} (T) + 20.5$	Morris (1966)

Table 3. Nitrite-monochloramine reactions and rate coefficients (Margerum *et al.*, 1994)

Reactions	Rate coefficients	References
3.1 $H^+ + NH_2Cl + NO_2^- \xrightleftharpoons[k_{-1}]{k_1} NH_3 + NO_2Cl$	$k_1' = 4.90 \times 10^{10} M^{-1} hr^{-1}$ $k_{-1}'/k_4 = 5.5 \times 10^5 M^{-1}$	Margerum <i>et al.</i> (1994)
3.2 $HOCl + NO_2^- \xrightleftharpoons[k_{-2}]{k_2} NO_2Cl + OH^-$	$k_1 = \text{unknown}$	
3.3 $NO_2Cl + NO_2^- \xrightleftharpoons[k_{-3}]{k_3} N_2O_4 + Cl^-$	$k_2/k_4 = 217 M^{-1}$	Johnson and Margerum (1991)
3.4 $N_2O_4 + OH^- \xrightarrow{k_3} NO_3^- + NO_2^- + H^+$	$k_3 = \text{fast}$	
3.5 $NO_2Cl \xrightleftharpoons[k_{-4}]{k_4} NO_2^+ + Cl^-$	$k_4 = \text{unknown}$	
3.6 $NO_2^+ + OH^- \xrightarrow{k_5} NO_3^- + H^+$	$k_5 = \text{fast}$	

Table 4. Bromide-monochloramine reactions and rate coefficients. (Galal-Gorchev and Morris, 1965; Bousher *et al.*, 1989)

Reactions	Rate coefficients	References
4.1 $NH_2Cl + H^+ \xrightleftharpoons{K} NH_3Cl^+$	$K = 28 M^{-1}$	Gray <i>et al.</i> (1978)
4.2 $NH_3Cl^+ + Br^- \xrightarrow{k_{Br}} NH_2Br + Cl^- + H^+$	$k_{Br} = 1.8 \times 10^8 M^{-1} h^{-1}$	Trofe <i>et al.</i> (1980)
4.3 $NH_2Cl + NH_3Br^+ \xrightarrow{\text{fast}} NHBrCl + NH_4^+$		
4.4 $HOCl + Br^- \xrightarrow{k_{HOCl}} HOBr + Cl^-$	$k_{HOCl} = 5.1 \times 10^5 M^{-1} h^{-1}$	Bousher <i>et al.</i> (1986)
4.5 $HOBr + NH_2Cl \xrightarrow{\text{fast}} NHBrCl + H_2O$		
4.6 $NHBrCl + NH_2Cl \xrightarrow{\text{fast}} N_2 + Br^- + 2Cl^- + 3H^+$		

treatment conditions, it has been shown (Valentine, 1985; Margerum *et al.*, 1994) that the direct reaction between molecular monochloramine and nitrite dominates. Margerum *et al.* (1994) proposed a reaction mechanism involving the formation of the reactive intermediate, nitril chloride (NO_2Cl) (Table 3). Once formed, NO_2Cl decomposes by two parallel pathways: a reaction with NO_2^- to form N_2O_4 (reaction 3.3) and dissociation to give NO_2^+ and Cl^- (reaction 3.5). These intermediates then undergo a series of further reactions that ultimately lead to the production of nitrate.

Consistent with this mechanism and kinetic studies, Margerum and co-workers (1994) proposed the following rate expression to describe monochloramine loss due to reactions with nitrite alone:

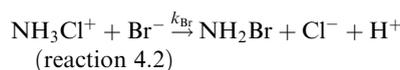
$$-\frac{d[NH_2Cl]}{dt} = \frac{k_1'[H^+][NH_2Cl][NO_2^-](1 + k_{-1}'/k_4[NO_2^-])}{k_{-1}'/k_4[NH_3] + (1 + k_2/k_4[NO_2^-])} \quad (3)$$

where $k_1' = 4.90 \times 10^{10} M^{-2} h^{-1}$. Absolute values of k_{-1}' , k_2 and k_4 , are not known, however, the ratios k_{-1}'/k_4 and k_2/k_4 were determined by Margerum *et al.* (1994) to be $5.50 \times 10^5 M^{-1}$ and $217 M^{-1}$ respectively. To account for monochloramine loss due to reactions with nitrite, the expression given by Eq. (3) was included as a monochloramine loss pathway in the comprehensive model.

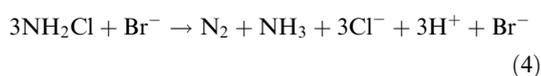
Bromide reactions

Trofe *et al.* (1980), Valentine and Selleck (1983), and Bousher *et al.* (1989) showed that bromide is oxidized in the presence of monochloramine according to the mechanism given in Table 4. Two rate-

limiting reactions are important. One is a reaction between bromide and the free chlorine produced by monochloramine hydrolysis. The other is the oxidation of bromide by the monochlorammonium ion (NH_3Cl^+) produced by the ionization of monochloramine. The reactions of these species lead to the production of monobromamine (NH_2Br) and hypobromous acid ($HOBr$).



Under chloramination conditions, bromide oxidation by monochlorammonium ion usually dominates. Once formed, $HOBr$ and monobromamine undergo further rapid reactions to produce mixed chlorobromamines, primarily $NHBrCl$ (Valentine, 1986). The chlorobromamines undergo their own set of auto-decomposition reactions leading to the ultimate regeneration of bromide (Galal-Gorchev and Morris, 1965; Bousher *et al.*, 1989). Because reactions of the bromamines and mixed chlorobromamines are generally much faster than those of the chloramines, these compounds do not accumulate to any appreciable extent (Valentine, 1986). In this case, bromide should primarily act to catalyze the overall rate of chloramine decay according to the net reaction (which assumes nitrogen gas is the main oxidized nitrogen containing product):



Assuming that bromide is constant and all bromamines are low in concentration and at

pseudo-steady state, the following differential equation was derived and was included in the monochloramine decay model:

$$-\frac{d[\text{NH}_2\text{Cl}]}{dt} = 3k_{\text{Br}}K[\text{NH}_2\text{Cl}][\text{Br}^-][\text{H}^+] + 2k_{\text{HOCl}}[\text{HOCl}][\text{Br}^-] \quad (5)$$

The second term accounts for the oxidation of bromide by HOCl produced from monochloramine hydrolysis. The factor of two is derived from the consideration of the overall stoichiometry of this specific loss pathway.

Reaction modeling and parameter estimation

The reaction model encompassing all of the reactions in Tables 1–4 was solved using the computer subroutine DDRIV2 developed by the National Institute of Standards and Technology (NIST) and Los Alamos National Laboratory (LANL). DDRIV2 uses Gear's method to solve the set of simultaneous differential equations derived from the reactions in Tables 1–4 to obtain molar concentrations of NH_3/NH_4 , HOCl/OCl^- , NH_2Cl , NHCl_2 , NO_2^- , Br^- and H^+ . The model considers ionic strength effects for all equilibria using the extended Debye–Huckel relationship to calculate activity coefficients. The pH may either be fixed or allowed to vary according to the presumed reaction stoichiometry using appropriate buffer intensity relationships.

Revised values for the carbonate species rate coefficients (k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$) were determined using data obtained from experiments that utilized a wide range of carbonate concentrations (Valentine *et al.*, 1998). The monochloramine decay data from these experiments were used in conjunction with the reaction model and the values for k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$ were systematically varied. New values for k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$ were then obtained using a weighted non-linear least-squares subroutine to minimize residuals. The revised values for k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$ were 800 and $40,000 \text{ M}^{-2} \text{ h}^{-1}$ respectively. These values are significantly higher than those initially estimated by Valentine and Jafvert (1988). However, because their estimates were based upon an extrapolation of a LFER it is not surprising that the values do not coincide. Our values are based on direct measurements made from experiments in which the carbonate concentration was varied and are within the errors

associated with the use of the LFER. These new values are included in Table 1.

The temperature dependence of the k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$ rate coefficients was evaluated using the Arrhenius relationship:

$$k = Ae^{-E_a/RT} \quad (6)$$

where A is the frequency factor, E_a is the activation energy, R the ideal gas constant, and T the temperature. Activation energies for k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$ were calculated by coupling the main monochloramine decomposition model to a non-linear regression subroutine which was fed experimental data. The program then calculated activation energies for the carbonate species (E_{a,HCO_3} and $E_{a,\text{H}_2\text{CO}_3}$) using the values for k_{HCO_3} and $k_{\text{H}_2\text{CO}_3}$ at 25°C and experimental data obtained at other temperatures. The calculated activation energies were: $E_{a,\text{HCO}_3} = 180 \text{ kJ/mol}$ and $E_{a,\text{H}_2\text{CO}_3} = 30 \text{ kJ mol}^{-1}$. The Arrhenius relationships obtained for each coefficient are tabulated in Table 2. These relationships as well as the temperature relationships obtained from the literature were incorporated into the comprehensive model.

EXPERIMENTAL

Experiments were conducted using carbonate-buffered laboratory water as well as several waters collected from actual distribution systems. The laboratory prepared solutions were made using deionized water obtained from a Barnstead ULTRO pure water system. All chemicals used in these experiments were analytical laboratory grade. The pH of all solutions was measured with a Fisher model 420m after appropriate calibration. All glassware was cleaned by soaking it in a concentrated chlorine bath ($\sim 5000 \text{ mg L}^{-1} \text{ Cl}_2$) for a period of at least 24 h. After the glassware was cleaned, it was thoroughly rinsed with deionized water, and then allowed to dry.

Distribution system waters were collected from five cities that treat widely different types of source water. These waters were collected at the end of each plant's treatment scheme just before secondary disinfectant addition. When the waters arrived at the University of Iowa, any chlorine residual added during primary treatment had completely decayed and there was no need to dechlorinate the waters. The five cities were: Iowa City, IA; Cedar Rapids, IA; Belle Glade, FL; Minneapolis, MN; and State Project Water from Metropolitan Water Works in the Los Angeles area. Water quality characteristics for these five waters are tabulated in Table 5.

Monochloramine stock solutions were prepared by the addition of free chlorine to a well-stirred solution of ammonium chloride. Bicarbonate was used to buffer the

Table 5. Distribution system water characteristics

Water	pH	TOC (mg L^{-1})	UV (cm^{-1})	Alkalinity (mM HCO_3)
Iowa City, IA	8.8	1.2	0.031	1.76
Cedar Rapids, IA	8.9	1.45	0.03	1.3
Belle Glade, FL	10.7	12.2	0.266	0.78
Minneapolis, MN	7.9	3.4	0.034	0.48
Joseph Jensen, CA	7.55	1.8	0.058	1.88

system, and the pH of the solution was adjusted to 8.5 or greater by the addition of NaOH. After a designated amount of free chlorine was added to the solution, it was mixed for 30 min before using it in an experiment. The concentration of monochloramine in the stock was measured using the DPD-FAS titrimetric method (APHA *et al.*, 1992). Ionic strength (μ) was controlled using sodium perchlorate and was varied between 0.005 and 0.1 M.

In general, monochloramine decay experiments were run by spiking aliquots of chloramine stock into a batch of the source water of interest. The exact volume of the aliquot was based on a targeted initial chloramine concentration and sample volume. The source waters were either produced in the laboratory or were obtained from actual water distribution systems. Once produced, the solutions were poured into 128 mL amber bottles that were subsequently sealed and stored in the dark in an incubator set at 4, 10, 25, or 35°C until they were analyzed. One experiment that used water obtained from the Minneapolis, MN treatment plant was monochloraminated at the plant and was used as received. All experiments were run in duplicate, the average error between replicate monochloramine measurements was ≤ 0.00141 mM.

RESULTS AND DISCUSSION

Monochloramine auto-decomposition in laboratory waters

The monochloramine auto-decomposition model readily predicts monochloramine loss over an initial concentration range of 0.01–0.106 mM (0.71–7.53 mg L⁻¹ as Cl₂) (Fig. 1). This range is similar to that used in drinking water treatment. The ability of the model to account for monochloramine decay at these low concentrations and for the higher concentration range under which it was developed (Jafvert and Valentine, 1992) indicates that the important reactive mechanisms responsible for monochloramine loss are all included in the model. Changes in the initial monochloramine concentration could have affected the rate limiting reactions responsible for monochloramine loss, and this would have been evidenced by the inability of the model to predict monochloramine loss for different initial concentra-

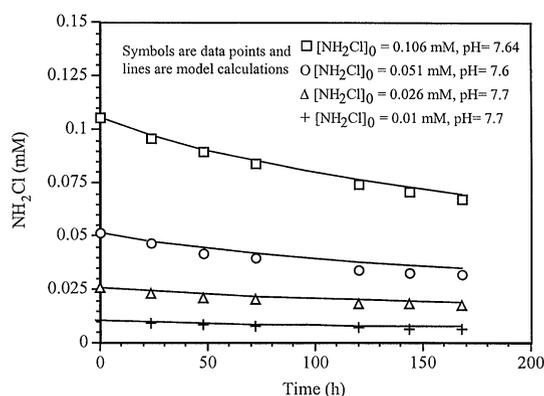


Fig. 1. Monochloramine decomposition as a function of initial concentration. $\text{Cl}/\text{N} = 0.7 \text{ mol mol}^{-1}$, $C_{\text{T,CO}_3}$ (Total carbonate concentration) = 4 mM, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

tions. In addition, monochloramine auto-decomposition is not a function of ionic strength, a fact that is consistent with model predictions (Fig. 2). The lack of an ionic strength effect on the decay rates reflects the relative insensitivity of the equilibria and key species concentrations to changes in ionic strength. This observation is important since it indicates that the experimental and model results obtained using our baseline ionic strength of 0.1 M should be essentially identical to those obtained under more typical drinking water ionic strengths.

When the solution pH is decreased from 8.3 to 6.6, the rate of monochloramine loss increases (Fig. 3). This accelerated loss occurs due to the enhanced rate at which dichloramine forms at lower pH values. Once formed, dichloramine rapidly decomposes thereby leading to oxidant loss. The correspondence between the model calculations and the measured monochloramine concentrations was quite good for all of the tested reaction conditions. This level of agreement suggests that the model is robust enough to account for the wide range of pH values observed in distribution system waters.

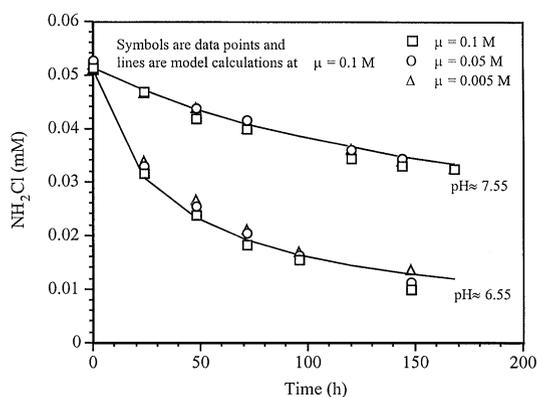


Fig. 2. Effect of ionic strength (μ) on monochloramine decomposition. $\text{Cl}/\text{N} = 0.7 \text{ mol mol}^{-1}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $T = 25^\circ\text{C}$.

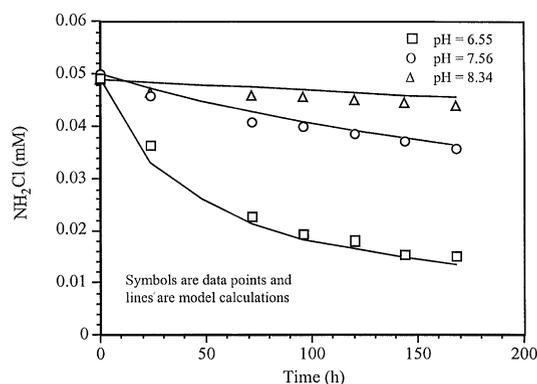


Fig. 3. Monochloramine decay as a function of solution pH. $[\text{NH}_2\text{Cl}]_0 = 0.05 \text{ mM}$, $\text{Cl}/\text{N} = 0.6 \text{ (mol mol)}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

The Cl/N molar ratio is an important variable in chloramination practice since it affects the free ammonia concentration initially introduced into the distribution system. For a fixed monochloramine concentration, the amount of free ammonia present increases as the Cl/N molar ratio decreases. The presence of free ammonia is of potential concern in distribution systems where biologically mediated ammonia nitrification occurs. Therefore, it might be supposed that using relatively high Cl/N ratios would tend to limit ammonia in the distribution system. This is not necessarily the case, however, since lower Cl/N ratios lead to a more stable disinfectant residual (Fig. 4). Based on these results, the net effect of Cl/N ratios on nitrification is not easily deduced. Increased ammonia would favor nitrification, by providing more bioavailable nitrogen, while increased stability of monochloramine would tend to favor bacterial inactivation. Therefore, the overall effect of changes in the Cl/N ratio on nitrification may need to be examined on a case by case basis. For all of the tested Cl/N ratios, the correspondence between the model calculations and the measured monochloramine concentrations was quite good. This agreement indicates that the model is capable of handling a wide variety of different Cl/N ratios.

Effect of carbonate As discussed earlier, previous studies have shown that general acid catalysts like phosphate, sulfate, and acetic acid can accelerate monochloramine decay by catalyzing monochloramine disproportionation. The carbonate species, in addition to their pH buffering capabilities, also have this potential. When the carbonate concentration was increased for a given pH, it was found that monochloramine decay accelerates (Fig. 5). For example, the half-life of 0.05 mM monochloramine at pH 6.6 is approximately 40 h in 4 mM bicarbonate but only 25 h in

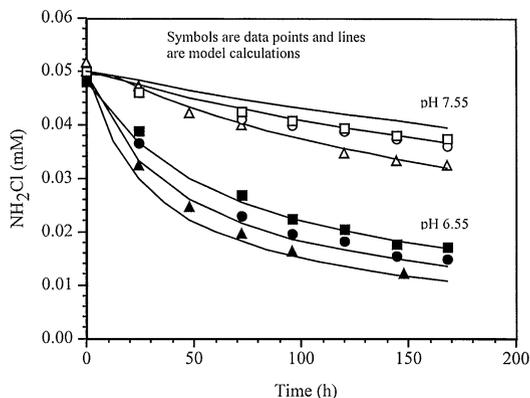


Fig. 4. Monochloramine decay as a function of Cl/N ratio. Cl/N = 0.5 (\square , \blacksquare), Cl/N = 0.6 (\circ , \bullet), and Cl/N = 0.7 (\triangle , \blacktriangle). Open symbols are for pH \approx 6.5 and filled symbols are for pH \approx 7.5. $[\text{NH}_2\text{Cl}]_0 = 0.05 \text{ mM}$, $C_{\text{T,CO}_3} = 4 \text{ mM}$, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

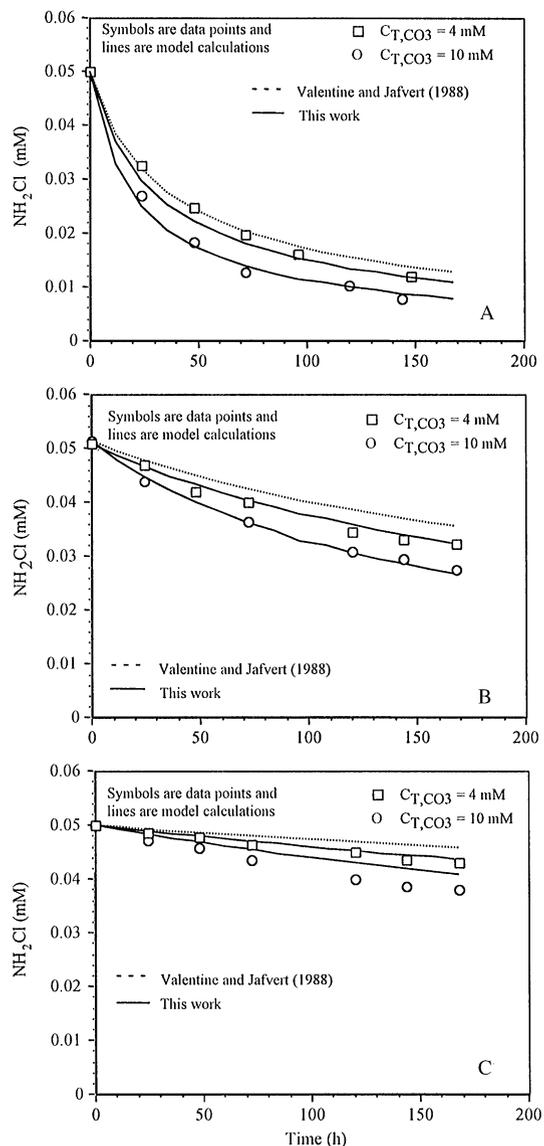


Fig. 5. Effect of total carbonate concentration on monochloramine decay at (A) pH \approx 6.6, (B) pH \approx 7.6, and (C) pH \approx 8.3. Cl/N = 0.7 mol mol $^{-1}$, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

10 mM bicarbonate. This acceleration implies that bicarbonate acts as a general acid catalyst to accelerate monochloramine loss.

The model significantly underpredicts the monochloramine decay rate when Valentine and Jafvert's (1988) estimated rate coefficients for $k_{\text{HCO}_3^-}$ and $k_{\text{H}_2\text{CO}_3}$ are used in the monochloramine decay model (Fig. 5). Model predictions made using the rate coefficients determined in this study are also shown in Fig. 5. For all the experiments, the predicted values obtained using the experimentally determined rate coefficients and the measured experimental values are quite close. These revised constants should be considered more appropriate since they are based upon measurements and not prediction.

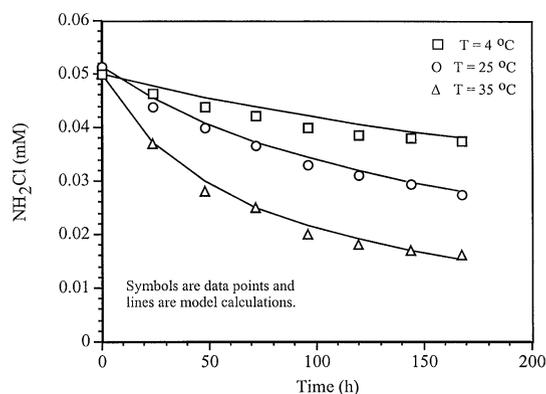


Fig. 6. Effect of temperature on monochloramine decomposition. $\text{Cl}/\text{N} = 0.7 \text{ mol mol}^{-1}$, $\text{pH} = 7.5$, $C_{\text{T},\text{CO}_3} = 10 \text{ mM}$, $\mu = 0.1 \text{ M}$.

Effect of temperature To model the effect of changes in temperature it was necessary, as previously discussed, to account for the effects of temperature on the kinetics of (1) monochloramine formation, (2) dichloramine formation via reaction of HOCl with NH_2Cl , and (3) monochloramine disproportionation. In addition, the temperature dependence of the equilibria governing the speciation of H_2CO_3 , HCO_3^- , NH_4^+ , and HOCl was also considered. By including these temperature dependencies, the model is able to account for monochloramine decay as a function of temperature (Fig. 6). Using these temperature dependencies it is now possible to account for monochloramine auto-decomposition over the wide range of temperatures observed in distribution systems.

Temperature has a very large effect on monochloramine stability over the range of 4–35°C (Fig. 6). In addition, it was found that monochloramine is more stable at lower temperatures as expected. The half-life of monochloramine at $\text{pH} 7.5$ is about 75 h at 35°C but exceeds 300 h at 4°C.

Influence of nitrite and bromide on monochloramine loss

Effect of nitrite Experiments to examine the effect of nitrite on monochloramine decay were conducted for a monochloramine concentration of 0.05 mM (3.55 mg/L as Cl_2) and a nitrite concentration of 0.036 mM (0.5 mg N/L) $^{-1}$. These concentrations are typical of those that might be found within distribution systems (Hao *et al.*, 1994).

At a concentration of 0.5 mg N/L $^{-1}$, nitrite exerted a significant monochloramine demand (Fig. 7(A)). This result is consistent with the stoichiometry given by equation (2), which suggests that on a molar basis this nitrite concentration should decrease the monochloramine concentration by a maximum of 70%. Since the monochloramine concentration had decreased only by 50%, this total demand was not met

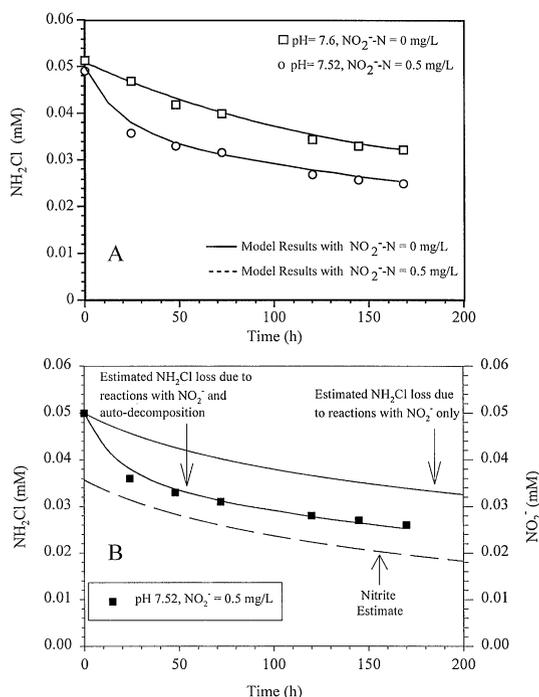


Fig. 7. Effect of 0.5 mg L^{-1} nitrite on monochloramine decomposition at $\text{pH} \approx 7.5$. (A) NH_2Cl loss in presence and absence of NO_2^- (B) Measured NH_2Cl loss, estimated NH_2Cl loss due to reactions only with NO_2^- , and estimated NH_2Cl loss due to auto-decomposition and NO_2^- oxidation. $\text{Cl}/\text{N} = 0.7 \text{ mol mol}^{-1}$, $C_{\text{T},\text{CO}_3} = 4 \text{ mM}$, $\mu = 0.1 \text{ M}$, $T = 25^\circ\text{C}$.

after 160 h, however this is not surprising based on the numerical solution of equation (4). Using a fourth-order Runge–Kutta subroutine (Stella Version 5) equation (4) was solved and used to predict both monochloramine loss due to reactions with nitrite and nitrite oxidation (Fig. 7(B)). Under the assumption that monochloramine loss only occurs via reactions with nitrite it is apparent that this nitrite concentration exerts a long-term demand that is not fully realized within 200 h. In addition, it can be seen that omitting auto-decomposition will lead to erroneous model predictions of monochloramine loss. When auto-decomposition is not taken into account, the predicted monochloramine loss rate is much slower than that observed experimentally.

Based on this limited set of data it appears that the mechanism of Margerum *et al.* (1994) for nitrite oxidation by monochloramine can be used in conjunction with the monochloramine auto-decomposition model to predict monochloramine loss under these conditions. Additional conclusions regarding the model's ability to predict nitrite oxidation or nitrate production are premature since the work here has identified only the rate-limiting reaction involving monochloramine. Current work continues in evaluating the model's ability to describe nitrite loss and nitrate formation.

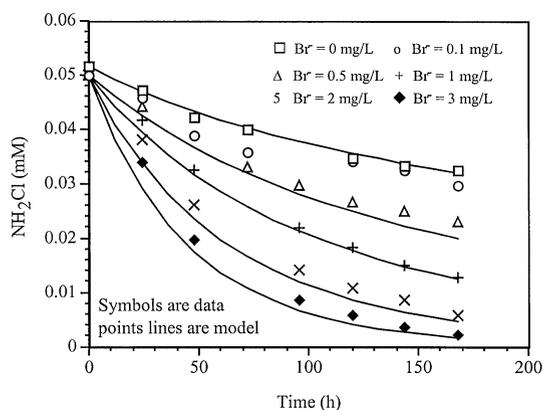


Fig. 8. Effect of 0–3 mg L⁻¹ bromide on monochloramine decomposition at pH ≈ 7.5. Cl/N = 0.7 mol/mol, C_{T,CO₃} = 4 mM, μ = 0.1 M, T = 25°C.

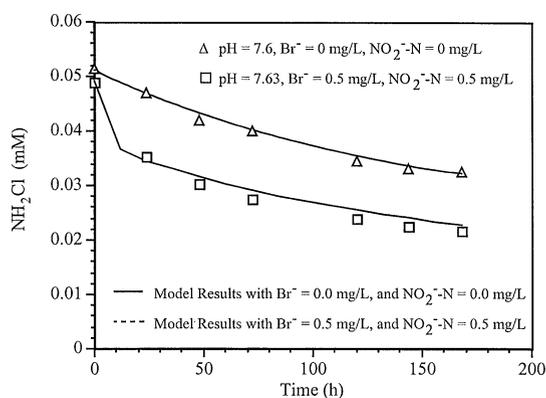


Fig. 9. Effect of 0.5 mg L bromide and 0.5 mg L⁻¹ nitrite on monochloramine decomposition at pH ≈ 7.6. Cl/N = 0.7 mol mol⁻¹, C_{T,CO₃} = 4 mM, μ = 0.1 M, T = 25°C.

Effect of bromide A readily discernable effect on monochloramine loss is evident at several tenths of a mg L⁻¹ of bromide (Fig. 8). However, at the low Br⁻ concentrations (<0.1 mg L⁻¹) often found in many distribution systems, reactions involving Br⁻ should not be considered a major monochloramine loss pathway. At a concentration of 0.1 mg L, the effect of bromide was minimal at both pH 6.5 and 7.5 and was only slightly significant at pH 8.3. Clearly, while bromide can exert a monochloramine demand at relatively high concentrations (and thus high bromide to monochloramine molar ratios), it should not have a significant effect at the lower concentrations often observed in many source waters.

The model results obtained by including the reaction scheme from Table 4 in the comprehensive model correspond quite well to the experimental data (Fig. 8). For a bromide concentration of 0.1 mg L⁻¹ the model predicts little if any bromide effect, as was experimentally observed. However, as the bromide concentration is increased and the effect of bromide becomes more prominent, the model does a good job at accounting for its effects.

Cumulative effect of bromide and nitrite

When two potentially reactive species are present in a given water it is impossible to say *a priori* what type of effect they may have on monochloramine decay. They may act competitively, where both react via parallel reaction pathways, or they could act synergistically if the reactions of one species influence the reactions of another species. To investigate the simultaneous reactions of bromide and nitrite, an experiment was conducted to examine monochloramine decay in the presence of 0.5 mg L⁻¹ bromide and 0.5 mg N L⁻¹ nitrite.

The two constituents together (Fig. 9) exert a monochloramine demand greater than that exerted by either alone (Figs 7 and 8). The combined

monochloramine decay model, encompassing auto-decomposition as well as reactions with nitrite and bromide, was able to predict monochloramine decomposition when both substances were present. This indicates that nitrite and bromide react independently via parallel pathways.

Chloramine decay in collected distribution system waters

Monochloramine decay in waters from five different treatment plants was studied to examine the applicability of the model in real waters: (1) University of Iowa Water Plant, Iowa, which receives its water from the Iowa River and mainly serves the University of Iowa. (2) Cedar Rapids, Iowa, which takes its water from relatively shallow wells near the Cedar River. (3) Belle Glade, Florida, which takes its water from Lake Okeechobee and has a high natural organic matter content. (4) Minneapolis, Minnesota, which softens Mississippi River water, and (5) Joseph Jensen Filtration Plant, California, which treats State Project Water. Table 5 shows some of the important water quality variables measured for each water source. Except where noted, these water samples were obtained from the water treatment train immediately ahead of chlorination and discharge to the distribution system.

Figure 10 shows monochloramine decay in the five collected waters along with model simulations. These model results were obtained without considering any natural organic matter (NOM), bromide, or nitrite effects and show a good agreement between the model and experimental data for Iowa City, Cedar Rapids, Joseph Jensen Treatment plant, and Minneapolis. However, a significantly higher decay rate was observed than predicted for the Belle Glade water source at pH 7.9. This may be attributed to the relatively high NOM and/or bromide concentrations in this water. Apparently these species were present

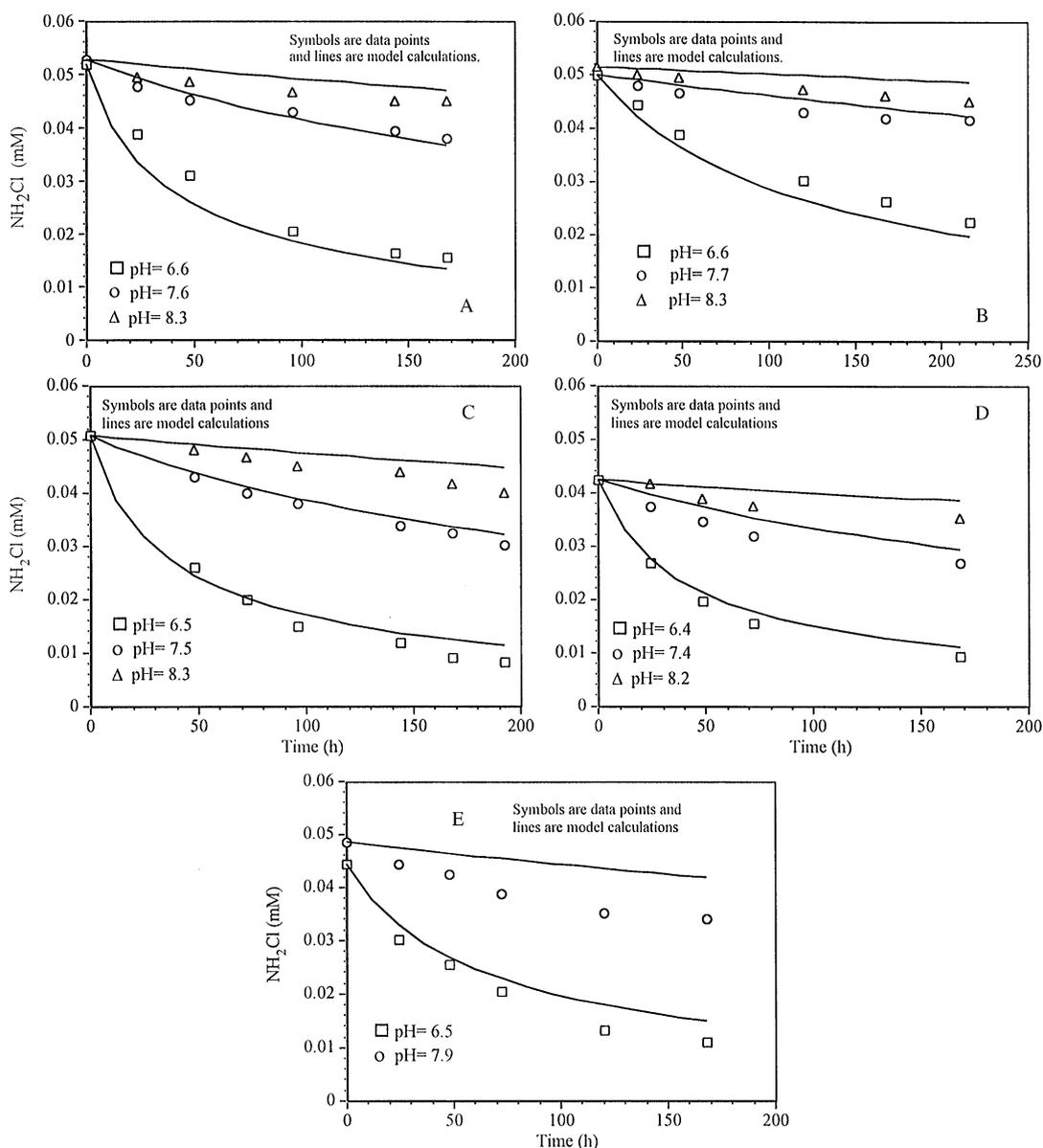


Fig. 10. Monochloramine decay in (A) Iowa City, (B) Cedar Rapids, (C) Joseph Jensen Treatment Plant, (D) Minneapolis, and (E) Belle Glade treated waters. $\text{Cl}/\text{N} = 0.7 \text{ mol mol}^{-1}$, $C_{\text{T},\text{CO}_3} = 1.76 \text{ mM}$, $T = 25^\circ\text{C}$.

at high enough concentrations that not considering the monochloramine demand of either led to significant errors. (No bromide measurements were made for this water; however, it is assumed that the bromide concentration is probably relatively high since this source water may be influenced by the ocean.) For the other waters, with NOM concentrations below 3.5 mg CL^{-1} , the model could adequately predict chloramine decay.

While the waters from the other four treatment plants were chloraminated upon receipt, the water from the Minneapolis treatment plant had already been treated with chloramine prior to our reception of it. To examine monochloramine decay in this water, its pH was adjusted in our lab and its

chloramine content was measured. The monochloramine in this water was then allowed to decay and the results were modeled. The good agreement between the predicted decay and the measured decay shows the ability of the comprehensive model to predict monochloramine decay in waters chloraminated under conditions other than those used in this laboratory.

CONCLUSIONS

The chloramine decomposition model was found to be very useful in describing chloramine decay under realistic water quality and chloramination

conditions in waters with low NOM concentrations. The revised model accounts for general acid catalysis by carbonate and allows for predictions over a range of water temperatures. The general utility of the auto-decomposition model was demonstrated by extending it to include fundamental reactions involving inorganic demand caused by bromide and nitrite.

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