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UNIVERSITY OF CALIFORNIA
RIVERSIDE

Environmental Persistence, Fate and Transport of Monochloramine in Surface Waters
Receiving Treated Wastewater

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Environmental Sciences

by

Miguel Angel Garcia

September, 2018

Dissertation Committee:

Dr. Michael Anderson, Chairperson

Dr. Jay Gan

Dr. Sharon Walker

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2018

The Dissertation of Miguel Angel Garcia is approved:

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University of California, Riverside

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ABSTRACT OF THE DISSERTATION

Environmental Persistence, Fate and Transport of Monochloramine in Surface Waters
Receiving Treated Wastewater

by

Miguel Angel Garcia

Doctor of Philosophy, Graduate Program in Environmental Sciences
University of California, Riverside, September 2018
Dr. Michael Anderson, Chairperson

Monochloramine is typically used in water distribution systems as a secondary disinfectant but it also forms in wastewater treatment systems by the reaction of ammonia and chlorine. As a result of this, monochloramine is expected to be found in rivers and lakes that receive treated wastewater effluent. Once there, as an oxidant and disinfectant, monochloramine can disrupt algal and bacterial communities. Monochloramine has also been linked to the formation of chlorinated byproducts that may be harmful to aquatic ecosystems. While many efforts have been made to understand the stability of monochloramine in water distribution systems, few studies have been dedicated to understanding the fate and transport of monochloramine in surface waters. A deeper knowledge of the environmental fate and transport of monochloramine is needed to understand monochloramine's persistence in surface waters and to predict its potential impacts to aquatic environments. This study assessed loss mechanisms that affect the stability of monochloramine and developed a comprehensive model describing its persistence, fate and transport in surface waters.

The partitioning of monochloramine between the aqueous and gas phase has not been extensively studied. To better understand monochloramine's potential for volatilization, the dimensionless Henry's law constant of monochloramine was determined using an equilibrium headspace technique. The resulting values ranged from 8×10^{-3} to 4×10^{-2} over a temperature range of 11-32 °C, indicating a semi-volatile compound, and were found to be consistent with quantitative structure activity relationship predictions. The Henry's constant values for monochloramine suggests that volatilization could be a relevant loss process in open systems such as in rivers and lakes.

The stability of monochloramine in the presence of DOC from different surface waters was assessed implementing the specific UV absorption at 280nm normalized to DOC concentration ($SUVA_{280}$) as a proxy of the reactivity of DOC towards monochloramine. Results confirmed that monochloramine reacts with DOC in surface waters via two pathways: a direct oxidation of DOC by monochloramine resulting in NH_4^+ , Cl^- and oxidized carbon species followed by chlorination of dissolved organic matter by the hypochlorous acid formed during monochloramine auto-decomposition resulting in the formation of chlorinated organic compounds. Chlorination was found to be more predominant in samples with lower $SUVA_{280}$, while oxidation was found to be more extensive in samples with higher $SUVA_{280}$.

In a separate experiment, the concentration of monochloramine solution in contact with bottom sediment was found to decrease rapidly ($t_{1/2}$ values of 0.1-13 days), with rate constants increasing exponentially with the total oxidant demand of the sediments. Considering that the reaction between monochloramine and sediments will be limited by

the transport across the benthic boundary layer, the effect of rapid mixing on the rate of reaction was considered. Monochloramine concentration was found to decrease at a greater rate in a rapidly mixed sample than in a sample with minimum periodic mixing, with reaction rate constants of $1.46 \times 10^{-1} \text{ hr}^{-1}$ and $1.00 \times 10^{-1} \text{ hr}^{-1}$ respectively. This indicates that a correction factor for transport should be included with the rate constant expression originally presented. Monochloramine was also found to decrease more rapidly than dissolved oxygen, suggesting that monochloramine is a more reactive oxidant than oxygen.

The results determined in this study for the Henry's constant of monochloramine and its reaction with DOC from surface waters and with bottom sediments were combined with rate constants for the auto-decomposition of monochloramine and related reactions (Jafvert and Valentine, 1992; Vikesland et al., 2001) to develop a model for the fate and transport of monochloramine in surface waters. The model was found to be in good agreement with field data collected from the Santa Ana River, near Riverside, CA and the New River, near Calexico, CA, during the spring of 2016 in Southern California with relative root-mean-square error values between predicted and observed concentrations below 0.05. Monochloramine was rapidly lost in the New River, decreasing from $72 \mu\text{g/L}$ at the Mexican border to $<1.0 \mu\text{g/L}$ 5.63 km downstream (corresponding to a travel time of 1.5 hrs). Monochloramine was more persistent in the Santa Ana River, decreasing from $16 \mu\text{g/L}$ at the discharge of the Riverside Water Quality Control Plant to $15 \mu\text{g/L}$ 4.8 km downstream (travel time of 2.5 hrs).

Results showed that auto-decomposition accounted for approximately 10% monochloramine lost in both rivers. Volatilization was found to be more important in the Santa Ana River than in the New River, accounting for 30% and 5% monochloramine loss respectively. Monochloramine losses due to reactions with DOC accounted for 15% in the Santa Ana River and 42% in the New River. Monochloramine interactions with sediments were also an important loss process, accounting for 45% loss in the Santa Ana River and 43% of monochloramine loss in the New River. The model demonstrates that monochloramine will be more persistent in the Santa Ana River than in the New suggesting that the effect of chlorinated organic compounds would be more of a concern in the Santa Ana River than the New River and the longer persistence of monochloramine may result in greater downstream impacts to bacterial and algal communities.

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Chapter 1 Introduction

1.1 Background

Monochloramine (NH_2Cl) is a compound formed from the reaction of ammonia with chlorine, with oxidative properties and relatively high stability in water at room temperature. Monochloramine is often used as a secondary disinfectant in drinking water treatment as a replacement to chlorine. Although less effective as a disinfectant, monochloramine is more stable and allows for better maintenance of adequate chlorine residuals and has a lower potential of forming undesirable disinfection byproducts than chlorine. Other applications for monochloramine also include its use in cooling water towers to control biological growth and in swimming pool disinfection (Chien et al., 2012; Hery et al., 1995). In addition to this, monochloramine can form during the chlorination of wastewater with poor nitrogen removal. As a result of this, monochloramine is expected to be present in surface waters receiving treated wastewater.

In the case of drinking water treatment, it is important to have a comprehensive understanding of the stability of monochloramine in order to ensure proper disinfection, to prevent the formation of undesirable disinfection byproducts, and to protect the health of consumers. Although monochloramine has been found to be safer than chlorine while providing adequate disinfection, there is still the potential for the formation of significant concentrations of undesirable disinfection byproducts at relatively high monochloramine concentrations (Bougeard et al., 2010; Hong et al., 2013; Hua et al., 2008). Furthermore, monochloramine has been found to cause acute hemolytic anemia in hemodialysis patients

when tap water containing monochloramine was used for dialysis (Kjellstrand, C. M., 1974; Eaton, J.W., 1973; Tipple, M.A., 1988).

It is also important to understand the environmental fate and transport of monochloramine in order to protect the integrity of surface waters that come into contact with chlorinated wastewater. Recent literature has questioned the safety of monochloramine discharge into surface waters, suggesting that monochloramine will generate significant concentrations of potentially harmful byproducts such as chloroacetic acids and chloroform in surface waters (Chuang et al., 2015; Lu et al., 2009). Monochloramine has also been linked to formation of the suspected carcinogenic compound *N*-nitrosodimethylamine (NDMA) in water distribution systems and in surface waters (Aydin et al., 2012; Junghoon et al., 2002). These studies suggest that there is potential for the formation of undesirable byproducts in surface waters regularly receiving treated wastewater and that these compounds have the potential to negatively impact aquatic environments. More importantly, monochloramine can also be a problem in lakes and rivers where, as an oxidant, it can disrupt natural ecosystems by affecting bacterial and phytoplankton communities; monochloramine present at concentrations greater than 0.1 mg L⁻¹ has been found to significantly inhibit the growth of algae (Adachi et al., 2004). Although the US currently lacks regulations for the discharge of monochloramine into surface waters, Canada has responded to these potential issues by setting discharge standards at 20 ppb (Health Canada, 1996).

1.2 Problem Statement

Because of the concerns that monochloramine and its byproducts present to aquatic environments, there has been an increasing interest in understanding the persistence of monochloramine in water distribution systems and its fate and transport in surface waters. To date, there have been several models developed to predict the persistence of monochloramine and its stability in water distribution systems (Jafvert and Valentine, 1992; Vikesland et al., 2001). However, very few efforts have been dedicated to study what happens to monochloramine after it is discharged into rivers and lakes. This general trend has led to development of models that are more representative of closed systems that omit properties of monochloramine that could play a more important role in surface waters. While previous studies provide the bases for understanding the persistence of monochloramine in controlled conditions such as in water distribution systems, they may not necessarily accurately represent what happens in natural waters. While these studies fail to provide a complete description of the mechanisms that affect the stability of monochloramine in natural open systems, they provide a fundamental starting point to develop a more comprehensive environmental fate model.

1.3 Research Objectives

The main goal of this project was to assess potential loss mechanisms for monochloramine in surface waters receiving treated wastewater and to use the obtained results to develop a comprehensive model for the environmental persistence, fate and transport of monochloramine.

Objective 1: To estimate the volatility of monochloramine by determining its non-dimensional Henry's constant and assess its potential for volatilization from surface waters.

Hypothesis 1: Considering that typically chlorine substituted compounds tend to have higher volatility than the non-chlorinated counterpart, it is expected that monochloramine, being a chlorinated ammonia derivative, will be more volatile than ammonia.

Objective 2: To investigate the reactivity of monochloramine towards natural organic matter in surface waters by conducting kinetic experiments and determining the parameters that affect reactions between monochloramine and natural organic matter.

Hypothesis 2: Being an oxidative compound, monochloramine will readily react with the reduced organic matter in surface waters. Higher organic matter concentration will result in faster monochloramine consumption and greater byproduct formation.

Objective 3: To use previous literature describing the formation and auto-decomposition of monochloramine along with the results obtained in this project describing the volatility of monochloramine and its reactions with natural organic matter to develop a comprehensive model capable of accurately describing the environmental persistence, fate and transport of monochloramine in surface waters receiving treated wastewater.

Hypothesis 3: Considering that monochloramine has been found to be comparatively stable in water at room temperature, neutral pH, and free of organic matter or other reduce substances, it is expected that the environmental persistence, fate and transport of monochloramine in surface waters will be predominantly driven by volatilization and reactions with dissolved and sedimentary organic matter.

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Chapter 2: The Henry's Constant of Monochloramine

2.1 Introduction

The Henry's constant for a chemical defines its equilibrium partitioning between the aqueous phase and gas phase, and thus is an important property governing the distribution and transfer between phases of volatile and semi-volatile chemicals. Although the volatility of monochloramine may not be of great importance in closed water distribution systems, it may become an important parameter in surface waters, cooling towers, indoor swimming pools, and other settings where strong mixing conditions and warm temperatures may promote the transfer of monochloramine into the air. An understanding of the tendency of monochloramine to transfer into the gas phase will allow for the development of models capable of predicting the stability of monochloramine in open waters. Based on our review, a single study has quantified a mole fraction-based dimensionless Henry's constant (K_H^m) of monochloramine at a value of 4.5×10^{-1} at 20°C , defined as the ratio between the mole fraction of monochloramine in the gas phase (X_{air}) and the mole fraction of monochloramine in the aqueous phase (X_{aq}) ($K_H^m = X_{\text{air}}/X_{\text{aq}}$) (Holzwarth et al., 1984). This is similar to their reported K_H^m value of 7.5×10^{-1} for ammonia.

The dimensionless Henry's constants presented here are calculated as the ratio of the concentrations (in mg/L) of monochloramine in the gas phase (C_{air}) and aqueous phase (C_{aq}) ($K_H = C_{\text{air}}/C_{\text{aq}}$). It was therefore necessary to recalculate this previously reported constant in terms of monochloramine concentration rather than in terms of mole fraction ratio in order to compare this value with other values presented here. K_H^m can be

recalculated in terms of K_H by expressing the mole fractions of monochloramine in the gas phase and the aqueous phase in terms of mg/L instead of mole fractions. X_{air} and X_{aq} can be expressed in units of mg/L by being multiplied by the molecular weight of monochloramine and divided by the total volume of the gas phase and the total volume of the aqueous phase respectively. Because the term representing the molecular weight of monochloramine will be canceled out when calculating the ratio $X_{\text{air}}/X_{\text{aq}}$, one then just needs to multiply K_H^m by the ratio between the total volume of the aqueous phase and the total volume of the gas phase ($V_{\text{air}}/V_{\text{aq}}$) to represent K_H^m in the same terms as K_H . The previously reported value of 4.5×10^{-1} was obtained by measuring the mole fractions of monochloramine in the gas phase and in the aqueous phase in a chamber where the ratio between the total volume of the aqueous phase and the total volume of the gas phase was maintained at 2.34×10^{-4} (Holzwarth et al, 1984). Multiplying the previously reported value by this gas/liquid volume ratio results in a K_H value of 1.0×10^{-4} expressed in the same terms as all the values reported here.

This concentration-based value derived from the reported mole fraction-based value for monochloramine is comparable to reported dimensionless Henry's constants of ammonia ($5.0 \times 10^{-4} - 9.0 \times 10^{-4}$) (Hales and Daves, 1979, Hashimoto et al., 1972 and Montes et al., 2009), and similar to the concentration-based value (1.7×10^{-4}) calculated from the mole fraction-based Henry's constant for ammonia of 7.5×10^{-1} (Holzwarth et al., 1984). This suggests that substitution of a hydrogen atom for a chlorine atom in ammonia to form monochloramine does not have a significant effect on the Henry's constant. This differs from what is often seen, where chlorine substitution increases the Henry's constants of

compounds (Hine and Mookerjee, 1975). It has been noted that Henry's constants can be estimated based on known structural contributions, assuming that each subunit has a precise effect on a compound's air-water partitioning (Hine and Mookerjee, 1975). For example, in the case of ammonia, each individual N-H bond will have a contribution of -1.10 to the overall $\log K_H$ (Hine and Mookerjee, 1975). Adding each individual N-H contribution results in an overall $\log K_H$ for ammonia of -3.30, representing a K_H of 5×10^{-4} , which is comparable to reported values (Montes et al., 2009).

Henry's constant of monochloramine was estimated based on this concept, considering that monochloramine is derived from ammonia where a hydrogen atom has been replaced by a chlorine atom. As noted, the contribution of the N-H bond to the overall K_H of monochloramine is known (Hine and Mookerjee, 1975) while the effect of substituting with a chlorine atom can be inferred from comparing the Henry's constant of other chlorinated and unchlorinated amines, such as methylamine and methylchloramine. Methylamine has a dimensionless Henry's constant value of 4.5×10^{-4} at 25°C (Christie and Crisp, 1967). Methylchloramine has a dimensionless Henry's constant value of 1.8×10^{-2} as estimated by vapor pressure and solubility values obtained from the Estimation Programs Interface software developed by the US Environmental Protection Agency. The corresponding $\log K_H$ of methylamine is -3.35 and that of methylchloramine is -1.74. The difference in $\log K_H$ among these two compounds can be attributed to the substitution of a hydrogen atom for a chlorine atom on N, where the addition of the chlorine atom increases the $\log K_H$ by 0.50.

With this, one can predict the Henry's constant of monochloramine by taking the Henry's constant value for ammonia, subtracting the contribution of an N-H bond (-1.10) and adding the contribution of an N-Cl bond (0.50). Making use of this concept, the predicted $\log K_H$ value for monochloramine is -1.69 at 25°C, corresponding a dimensionless Henry's constant of 2.0×10^{-2} . This value is in agreement with the notion that chlorinated compounds typically have higher Henry's constants than their unchlorinated counterparts and it is substantially greater than the previously reported value. Given this discrepancy, we reevaluated the Henry's constant of monochloramine in laboratory studies.

2.2 Materials and Methods

2.2.1 Reagents and preparation of standard monochloramine solution

A 100 mg/L monochloramine stock solution was prepared fresh before analysis by combining NaOCl (8.25% solution) and ammonium chloride. The chlorine to ammonia molar ratio was maintained at Cl:N = 1:3 to shift equilibrium in favor of monochloramine formation, reducing free chlorine in solution. A phosphate buffer was used to maintain the monochloramine stock solution at pH 7 to favor monochloramine formation over di and tri-chloramine formation. The monochloramine concentration of the stock solution was determined by the DPD Colorimetric Method 4500-Cl (Rice et al., 2012). This stock solution was then used to develop a calibration curve. The concentration of monochloramine in subsequent analysis was determined using the calibration curve developed for the stock solution implementing Hach method 10171 and referring back to the standard curve (Lee et al., 2007). Limit of detection of the method was determined to be $0.010 \text{ mg L}^{-1} \pm 0.007$.

2.2.2 Assessment of monochloramine's volatility and determination of its non-dimensional Henry's law constant

An initial assessment of monochloramine's ability to volatilize to the atmosphere was assessed by monitoring monochloramine concentrations over time in solutions in sealed vials with zero headspace and in solutions open to the atmosphere with and without aeration. All of the glassware used for this experiment was soaked in chlorine-free water for 48hrs and air dried. In this preliminary experiment, two 1 L monochloramine solutions with initial concentrations of 1.49 mg L^{-1} buffered at pH 7 were placed in open Erlenmeyer flasks (surface area-to-volume ratio of 0.03 cm^{-1}), with air introduced at the bottom of one of the flasks at an air flow rate of 10 mL s^{-1} . These solutions were maintained at a constant temperature of $23.0^\circ\text{C} \pm 1.3^\circ\text{C}$. At the same time, measurements were also obtained for a monochloramine solution in sealed vials with zero headspace that accounted for loss due to hydrolysis. Monochloramine concentrations were measured in these solutions every day for 5 days to determine rates of loss due to volatilization in these three different scenarios. Calculation adjustments were made for the change in volume over time due to water evaporation.

The non-dimensional Henry's constants or air-water partitioning coefficients for monochloramine were determined at various temperatures (approximately 11, 16, 21, 27, and 32°C) using an equilibrium headspace technique. Known volumes (V_L) of a monochloramine solution at concentrations of 0.8, 1.80 and 2.8 mg L^{-1} were placed in vials of known total volume ($V_T=160 \text{ mL}$). The vials were sealed immediately after adding the monochloramine solution with a Teflon-lined rubber stopper and an aluminum crimp seal. Vials were prepared with varying V_L (67, 51 and 27 mL), corresponding to head space

volumes of 93, 109, and 133 mL, respectively. A control was maintained with zero headspace (C_0) at each temperature studied to account for loss of monochloramine due to hydrolysis occurring during the equilibration period (Fig. 2.1). The resulting hydrolysis loss rates at different temperatures are in accordance with predictions made by others (Vikesland et al., 2001). To reach equilibrium, samples were shaken at constant temperature in the dark at 130 rpm overnight (approximately 22hrs). After this, monochloramine concentrations remaining in solution were measured by the detection method described above and compared to that of the control. The difference in concentration between the samples with varying headspace (C_{aq}) and that of the control was attributed to monochloramine transfer into the gas phase (C_{air}). This procedure was performed in two sets of triplicate measurements to assess the effect of temperature on the Henry's constant of monochloramine.

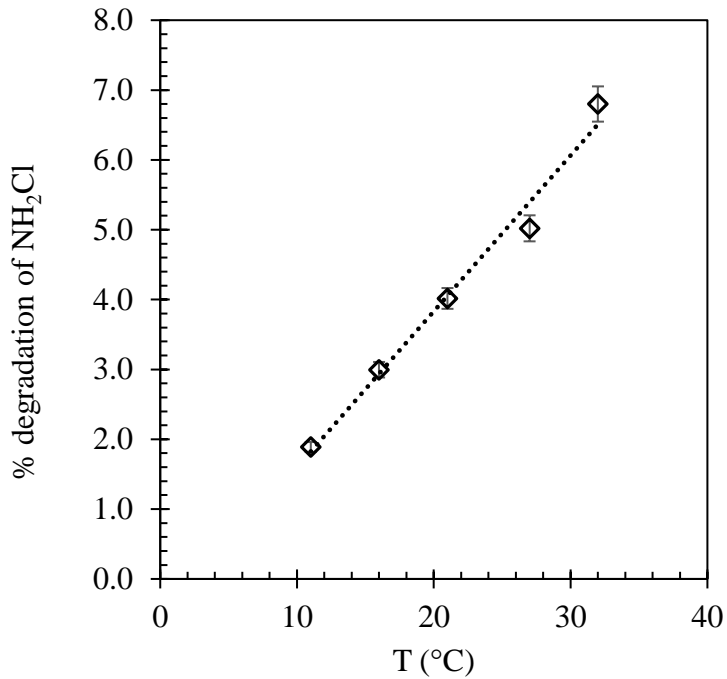


Figure 2.1. Percent degradation of monochloramine due to hydrolysis during the equilibration period (approximately 22hrs) at each temperature studied.

2.2.3 Calculation of dimensionless Henry's law constants

The dimensionless Henry's constants (K_H) for monochloramine at different temperatures were determined by calculating the ratio of monochloramine concentration in the air phase and in the aqueous phase at equilibrium where,

$$K_H = C_{\text{air}}/C_{\text{aq}} \quad (2.1)$$

Monochloramine concentration in the aqueous phase (C_{aq}) was measured directly while the concentration in the air phase (C_{air}) was determined by subtracting the monochloramine concentration in each sample (C_{aq}) from the concentration in the control sample (C_0), and accounting for the volume of the gas phase.

Where,

$$C_{\text{air}} = ((C_0 - C_{\text{aq}}) * V_L) / (V_T - V_L)$$

C_{air} = Monochloramine concentration in the gas phase (mg/L)

C_0 = Monochloramine concentration in the control sample (mg/L)

C_{aq} = Monochloramine concentration in the aqueous phase (mg/L)

V_L = Known volume of monochloramine solution in vial (mL)

V_T = Total volume of vial (mL)

2.3 Results and Discussion

2.3.1 Monochloramine volatilization

Monochloramine concentrations decreased more rapidly in the solutions open to the atmosphere and actively aerated when compared with sealed samples with zero headspace (Fig. 2.2a). In this closed system, volatilization was suppressed by maintaining zero headspace and the only loss mechanism was attributed to hydrolysis. In this case, the hydrolysis loss rate was estimated at 0.04 day^{-1} , representative of a half-life of about 16 days. The concentration of monochloramine decreased more rapidly in the open quiescent system (Fig. 2.2), with a loss rate of 0.08 day^{-1} , corresponding to a half-life of 8.5 days. This loss rate was found to be about twice as fast as the hydrolysis-only loss rate, providing evidence for monochloramine's potential for volatilization. Finally, monochloramine concentration decreased most rapidly in the aerated sample (Fig. 2.2), where aeration at 10 mL/sec yielded a loss rate of 0.35 day^{-1} , about four times faster than the sample not being aerated and about eight times faster than the control in the sealed vials with no headspace. This 10 mL sec^{-1} aeration is representative of the turbulence of rapid flowing rivers. With

a volatilization loss rate of 0.35 day^{-1} , monochloramine is expected to have a half-life of about $2.0 \text{ days} \pm 0.0$, suggesting that volatilization may be a relevant loss mechanism for monochloramine in strongly-mixed surface waters. This volatilization loss approaches the rate of loss of monochloramine due to reactions with natural organic matter from river sources with low organic matter concentrations ($0\text{-}15 \text{ mg-C L}^{-1}$) (Duirk et al., 2005), but will likely be a less significant loss mechanism in waters with significantly higher organic matter concentrations.

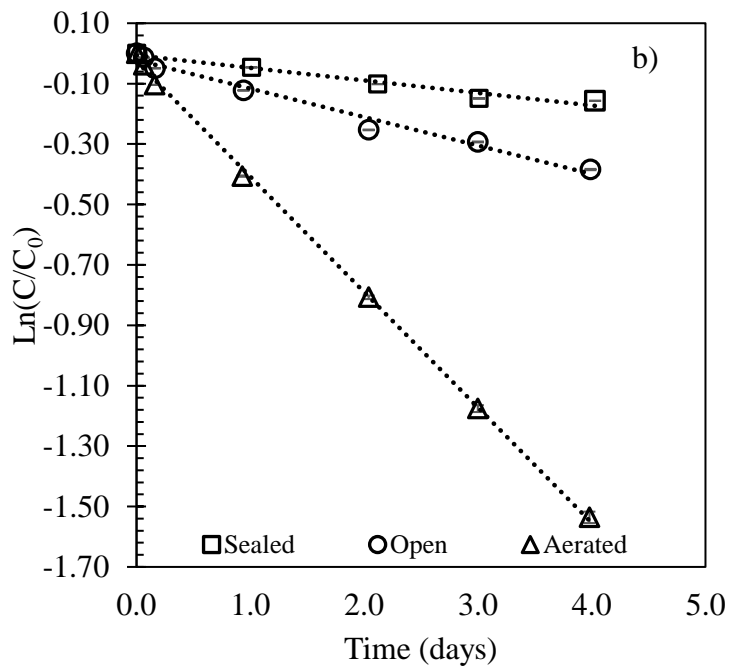
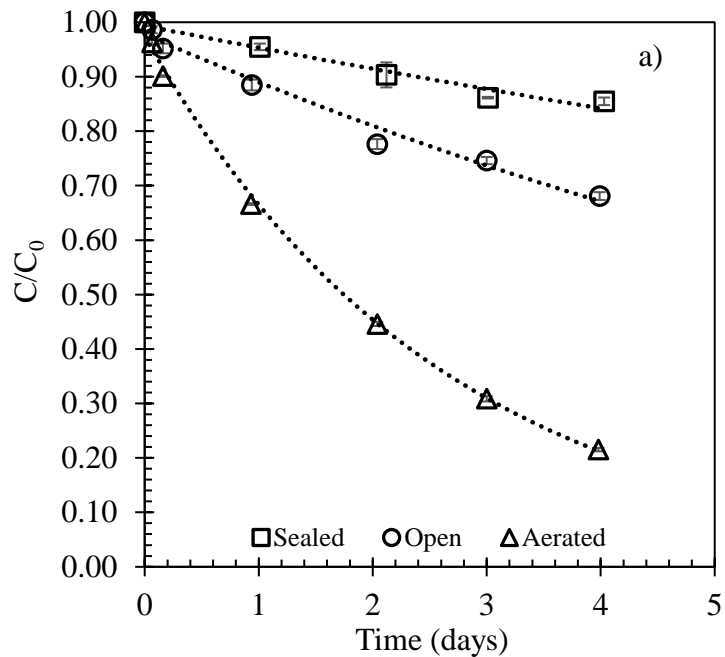


Figure 2.2. Monochloramine loss due to volatilization and hydrolysis a) Relative monochloramine concentration (C/C_0) with respect to time. b) Natural logarithm of monochloramine relative concentration with respect to time. $[\text{NH}_2\text{Cl}]_0 = 1.49 \text{ mg L}^{-1}$, $T = 25^\circ\text{C}$. Error bars represent standard deviations for mean values from triplicate measurements.

2.3.2 Henry's law constant of monochloramine

The above results indicate that monochloramine can volatilize from water even under quiescent conditions with a low surface-to-volume ratio (Fig. 2.2). Equilibration in sealed vials with known volumes of headspace confirm that monochloramine will partition some mass to the gas phase; with correction for hydrolysis in control samples, we calculated non-dimensional Henry's constant values from 8×10^{-3} to 4.4×10^{-2} at temperatures from approximately 11 to 32 °C (Fig. 2.3). Henry's constants in non-dimensional and dimensional (mol/L-atm) are also presented in Table 2.1. The average non-dimensional Henry's constant values across this temperature range were reasonably described by Eq.2.2, where T represents temperature in °C ($r^2=0.97$).

$$K_H = 0.0037e^{0.0759T} \quad (2.2)$$

Using this regression equation, the dimensionless Henry's constant for monochloramine at 25°C is calculated at 2.5×10^{-2} which is in good agreement with the estimated value of 2.0×10^{-2} from our structure-activity relationship predictions. The experimental value is approximately 35 times larger than the reported values for ammonia, which range between 5×10^{-4} and 9×10^{-4} (Hales and Daves, 1979, Hashimoto et al., 1972 and Montes et al., 2009). At the same time, the obtained value is comparable to the Henry's constant of semi-volatile inorganic compounds such sulfur dioxide, which has a Henry's constant of 3.3×10^{-2} (Nazaroff and Alvarez-Cohen, 2001). As previously noted, the dimensionless Henry's constant for monochloramine has been reported once before (following correction from mole fraction units) as 5×10^{-4} at 20 °C (Holzwarth et al., 1984), which is considerably lower than the results of this study. Although the study by Holzwarth

et al (1984) also used an equilibrium headspace method as used in this project, they implemented a less reliable detection method for monochloramine than the one used in this project. Holzwarth et al. (1984) used an absorption spectrum method that uses the natural absorbance of monochloramine, which once was considered a reliable technique but has since been replaced by more reliable and sensitive colorimetric methods. The performance and limitations of absorption spectrum methods for the detection of monochloramine are unknown and scientists have opted to use more reliable derivatization methods that provide higher selectivity and lower limits of quantitation (Kinani et al., 2012). With this in mind, it is speculated that the previously reported value may be in error.

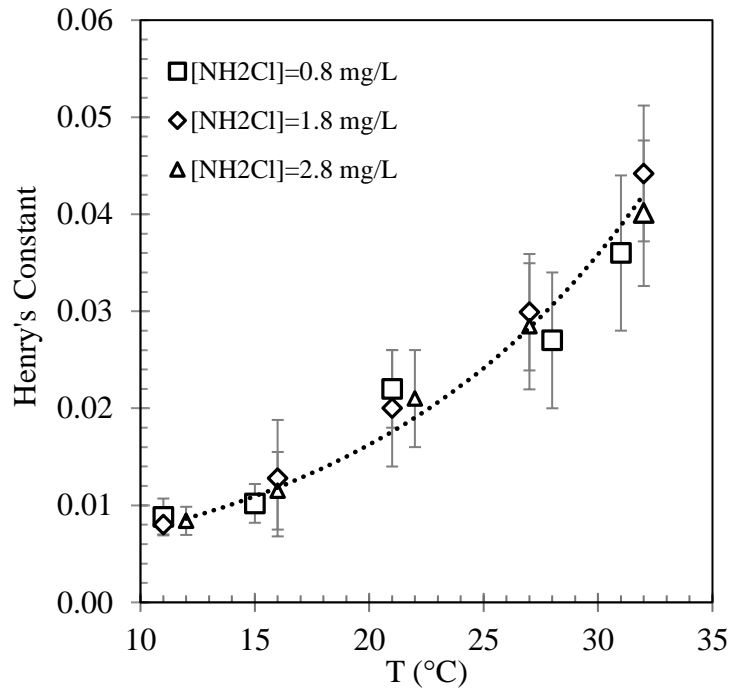


Figure 2.3. Temperature dependency of Henry's constant. Error bars represent standard deviations for mean values from triplicate measurements.

Table 2.1. Summary of Henry's law constants for monochloramine at different temperatures

T (K)	$K_H = C_{air}/C_{aq}$ (dimensionless)	$K'_H = C_{aq}/p_{gas}$ (mol L ⁻¹ atm ⁻¹)
284	8.0 E-03	3.4 E-04
289	1.3 E-02	5.4 E-04
294	2.0 E-02	8.3 E-04
300	3.0 E-02	1.2 E-03
305	4.4 E-02	1.8 E-03

3.3.3 Volatilization activation energy

By applying Van't Hoff's equation on the temperature dependency of monochloramine's Henry's constant, we were able to obtain values for the enthalpy of vaporization (ΔH_{vap}) and entropy of vaporization (ΔS_{vap}). The resulting values of 56.8 kJ mol⁻¹ and 129.1 J K⁻¹ mol⁻¹ respectively, are comparable to the enthalpy and entropy values of semi-volatile compounds such as naphthalene, with $\Delta H_{vap}=55.6$ kJ mol⁻¹ and $\Delta S_{vap}=156.1$ J K⁻¹ mol⁻¹ (Chikos and Acree, 2003). These resulting values for the enthalpy and entropy of vaporization for monochloramine suggest that, although monochloramine will be more stable in the aqueous phase than volatile compounds, it will partition some mass into the gas phase at ambient temperatures.

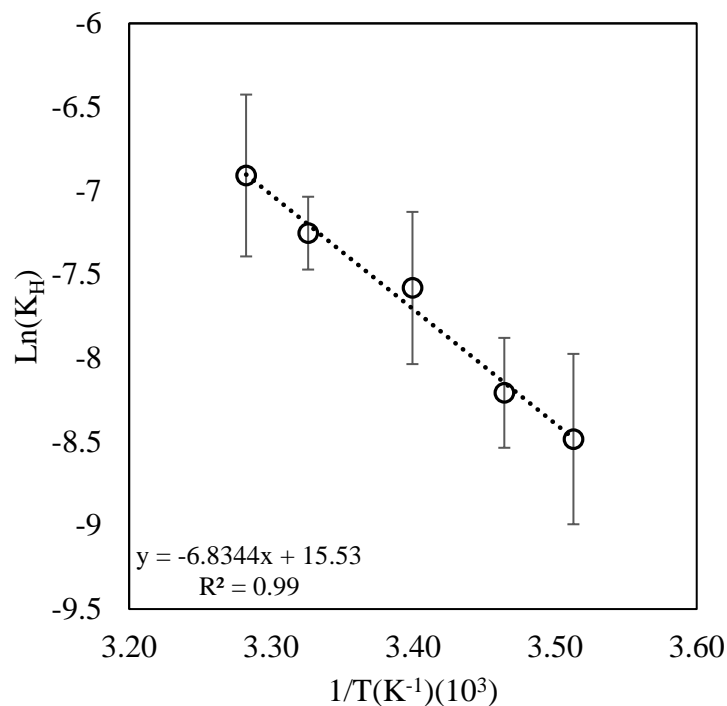


Figure 2.4. Monochloramine's Henry's constant with respect to temperature. The corresponding enthalpy and entropy of vaporization are $\Delta H_{\text{vap}}=56.8\pm 2.8 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{vap}}=129.1\pm 6.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

2.4 Conclusions

It is expected that the high mixing conditions of many rivers and other surface waters will promote the loss of volatile and semi-volatile compounds into the atmosphere (Cadena et al., 1984). We were interested in assessing the aqueous phase-gas phase partitioning of monochloramine to quantify its Henry's constant and understand its tendency to be lost to the atmosphere in open environmental systems. The experimentally obtained Henry's constant for monochloramine was found to be in better agreement with a value estimated from structure-activity relationships than the previously reported value. At the same time, the results obtained suggest that monochloramine is more volatile than ammonia, expected as a result of replacing an N-H bond in ammonia for a N-Cl bond. Ammonia is considered to be a semi-volatile compound with an average dimensionless

Henry's constant of 7.0×10^{-4} at room temperature (Montes et al., 2009) and an enthalpy of vaporization of 23.3 kJ mol^{-1} (Cotton and Wilkinson, 1962). Studies on the rate of loss of ammonia from water to the atmosphere in flooded fields and streams have identified volatilization as a dominant loss mechanism (De-Xi et al., 2007; Weiler et al., 1979). Monochloramine, with a Henry's constant of 1.7×10^{-2} at 20°C , is more volatile than ammonia, and the loss of monochloramine to the atmosphere may become a relevant loss pathway that deserves attention when considering the fate and transport of monochloramine in water.

2.5 References

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Chapter 3: Monochloramine interactions with organic matter from surface waters.

3.1 Introduction

Over the past years, there have been a number of studies assessing the stability of monochloramine in drinking water treatment and in water distribution systems with relation to organic matter (Duirk et al. 2002, 2005, 2006). Some studies have identified the potential formation of disinfection byproducts in relation to monochloramine reactions with specific dissolved organic carbon (DOC) fractions (Hua et al. 2015). Hua et al. (2005) also reported a strong correlation between specific UV absorbance and the formation of monochloramine byproducts, attributing higher byproduct formation to higher aromaticity. In another instance, a model was developed to describe the reaction between monochloramine and DOC as occurring in two distinctive steps; a rapid and direct reaction between monochloramine and DOC and a slower reaction occurring between DOC and the hypochlorous acid produced by monochloramine auto-decomposition (Duirk et al. 2005). Although studies like these provide the bases for understanding the persistence of monochloramine in controlled environments, they may not necessarily accurately represent what happens in natural waters.

These studies have focused primarily on the auto-decomposition of monochloramine and its stability in the presence of low DOC concentrations. In the case of surface waters, an understanding of monochloramine auto-decomposition is still relevant but surface waters will contain DOC at higher concentrations and potentially different reactivities than the water found in treatment plants and in distribution systems.

Furthermore, none of these studies have addressed the loss of monochloramine in surface waters in contact with sediments potentially rich in organic matter. It therefore becomes important to assess the stability of monochloramine under environmentally relevant conditions to accurately predict its persistence in surface waters both in the water phase as well as in contact with sediment. The goal of this study was to assess the loss of monochloramine in the presence of natural DOC and in contact with sediment from different surface water sources. A model was then developed to predict the loss of monochloramine from natural surface waters in the presence of organic matter.

3.2 Materials and Methods

A monochloramine stock solution was prepared as described in Chapter 2. Water samples were collected during the spring of 2016 from the Santa Ana River, New River, Lake Elsinore and Lake Perris in Southern California. Santa Ana River water was collected a mile downstream of the discharge from the Riverside Water Quality Control Plant in the city of Riverside where water is treated to tertiary standards. New River water was collected in the city of Calexico where the river is mostly composed of untreated wastewater or chlorinated primary-treated wastewater from the city of Mexicali, Mexico. Water from the shores of Lake Perris, a mesotrophic lake, was collected at a depth of 50cm. Finally, water was collected from Lake Elsinore, a eutrophic lake, in close proximity to the incoming treated wastewater discharge. Lake Elsinore has received up to 8 mgd annually of tertiary treated wastewater from Elsinore Valley Municipal Water District as a supplemental supply of water during periods of low water level (EVMWD, 2018). All samples were transported in ice and filtered immediately upon arrival to the laboratory with

a Surfactant-Free Cellulose Acetate 0.45 μ m filter. On the same day pH, conductivity and ammonia levels were measured. Total carbon and dissolved organic carbon were measured with the aid of a Shimadzu Total Carbon Analyzer 5000a. The UV absorbance of the water samples was measured at 280nm with the aid of a Varian Cary 50 UV-Vis spectrophotometer. The specific UV absorbance (SUVA) was calculated by dividing the absorbance at 280 nm by the dissolved organic carbon concentration. Samples were then spiked with monochloramine to a concentration of 2.00mg/L. A control was prepared by spiking monochloramine to DDI water buffered to a pH of 7.35 with the aid of a phosphate buffer (5.2mM). Each of the samples were then subdivided into several 40mL sealed vials with zero headspace for individual analysis and incubated in the dark at constant temperature. Monochloramine concentrations were measured in the samples over several days by the method described in Chapter 2. A control sample prepared by adding monochloramine to DDI water was maintained. The decrease in monochloramine concentration in the DDI water sample was attributed to monochloramine auto-decomposition. The effect of monochloramine auto-decomposition was subtracted from the observed degradation of monochloramine in the surface water samples to obtain reaction rate constants representative of monochloramine reactions with DOC.

Table 3.1. Water characteristics

Surface water	[NH ₂ Cl] μ gL ⁻¹	SUVA ₂₈₀ (m ⁻¹ L mg-C ⁻¹)	pH	Conductivity (mScm ⁻¹)	[NH ₄ ⁺] (mg L ⁻¹)
Santa Ana River	16	2.7	7.46	0.95	0.14
New River	72	7.5	7.21	5.67	3.00
Lake Perris	<10	4.3	7.32	1.12	0.17
Lake Elsinore	83	6.5	7.48	3.08	0.20

Sediment samples were collected from the Santa Ana River, Lake Perris and Lake Elsinore, as well as additional two sites from a lake not included in the above measurements (Canyon Lake) to expand range of sediment properties in this assessment. Sediments samples were placed in individual plastic beakers with an area of 104cm^2 and a volume of 1557cm^3 . Enough sediment was added to fill 623cm^3 of the beaker. Then, 830ml of a 2.00mgL^{-1} monochloramine solution was added to the top of the sediments leaving 1cm of open space at the surface. The monochloramine solution was carefully added to the top of the sediment without any mixing. The samples were then covered with parafilm and stored in the dark at a constant temperature of $22^\circ\text{C} \pm 1.2$. A control was prepared with Ottawa sand with minimum organic matter content. Overlying water was gently stirred every 4 hours. Monochloramine concentration in the water above the sediment was measured throughout 7 days with MonochlorF as described in Chapter 2.

Since reaction with bottom sediments implicitly involves transport from the water column to the sediments through the benthic boundary layer, a separate experiment evaluated the loss of monochloramine under well-mixed conditions, as might be expected in a rapidly flowing river or stream. To approximate well-mixed mixing conditions, reaction chamber was constructed from a plastic beaker with an area of 104cm^2 and a volume of 1557cm^3 , with a sealed plastic lid, to prevent air entering the container, which a YSI PRO-DO dissolved oxygen probe with small paddle mixer and a sampling port were fitted. 360g of sediment and 830mL of monochloramine solution (2.00mgL^{-1}) were added to the chamber. The sample was continuously mixed and samples were withdrawn several times each day for two days and analyzed for monochloramine as described above.

Dissolved oxygen concentration in the overlying water was also measured over time using the YSI PRO-DO optical probe.

The total oxidant demand of the sediment samples was estimated by adding a 100 mM hypochlorous acid solution to a known amount of sediment and mixing vigorously for several days. The concentrations of hypochlorous acid in these sediment mixtures were measured daily over several days until the concentrations did not change for three days in a row or more. At this point, it was assumed that all the reduced species within the sediment had been completely oxidized by the hypochlorous acid. The difference between the initial and final concentration of hypochlorous acid indicated the amount of oxidant needed to oxidize all the reduced species in the sediment. Others have successfully use this technique to determine the total oxidative potential of dissolved organic carbon in surface water samples (Duirk et. al. 2002, 2005, and 2006). This amount of oxidant was then normalized by the amount of sediment in the mixture for a calculation of the sediment's total oxidant demand described as $[\text{OCl}^-]$ mM g⁻¹ sediment. The concentration of hypochlorous acid in solution was determined using the commercially available reagent DPD Free Chlorine reagent by allowing 3 min contact time between the sample and the reagent and then measuring absorbance at 530nm with a Varian Cary 50 UV-Vis spectrophotometer.

In order to determine the efficacy of the developed model, the stability of monochloramine in the presence of dissolved organic carbon was assessed in an additional water sample not previously included in the model data. A water sample was collected at the discharge point from the Rapid Infiltration and Extraction (RIX) Facility in the city of Colton, CA. The RIX facility receives secondary treated water from adjacent cities and

employs natural bio-filtration before discharging into the Santa Ana River. The water sample collected was filtered with a Surfactant-Free Cellulose Acetate 0.45 μ m filter before measuring its physicochemical properties. The pH of the sample was measured at 7.2, ammonia concentration was 0.48 mg/L, dissolved organic carbon was 19.79 mg-C/L and the Specific UV absorption at 280 nm (SUVA₂₈₀) was calculated at 4.2 Lm⁻¹mg-C⁻¹. Sample was then spiked with monochloramine to a concentration of 2.00mg/L and then placed in individual 45mL vials with zero headspace for individual subsequent analysis. Samples were constantly shaken and maintained at a constant temperature of 30°C. Decrease in monochloramine concentration over time in this water sample was assessed daily using MonochlorF with the method described in Chapter 2.

3.3 Development of model

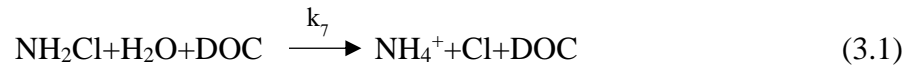
The model presented here includes the sub-model described by Jafvert and Valentine (1992), which includes all the reactions involved in monochloramine formation and auto-decomposition as shown in Table 3.2. The proposed model here describes the loss of monochloramine in the presence of DOC as occurring via two pathways, an initial oxidation of DOC by monochloramine (Eq. 3.1) followed by chlorination of DOC by the hypochlorous acid resulting from the auto-decomposition of monochloramine (Eq. 3.2). Considering that the monochloramine auto-decomposition forming hypochlorous acid is relatively slow, the chlorination step is found to be slower than the oxidation step in this scheme. In order to determine the reaction rate for the first and the second step of the reaction it was necessary to delineate when the first step of the reaction terminates and the second step commences. To accomplish this, it was assumed that the initial

monochloramine demand represented the DOC oxidation step while the remaining monochloramine would form hypochlorous acid, which would participate in the DOC chlorination step. Initial monochloramine demand was defined as the amount of monochloramine consumed within a contact time of 4 hrs.

The model presented here represents an overall second order reaction scheme, first order with respect to monochloramine/HOCl and first order with DOC. All of the resulting rate constants for the reactions of monochloramine with organic carbon were obtained by spiking different surface water samples with monochloramine and measuring its decrease in concentration over time. The resulting rate constants for reactions of hypochlorous acid and organic carbon were empirically derived from the observed degradation of monochloramine.

Table 3.2. Monochloramine decay model developed by Jafvert and Valentine (1992). T in K.

	Reaction	Rate/equilibrium constants	Temperature dependency
1	$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_1 = 1.5 \times 10^{10} \text{ M}^{-1}\text{h}^{-1}$	$k_1 = 2.37 \times 10^{12} e^{(-1540/T)} \text{ M}^{-1}\text{h}^{-1}$
2	$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$	$k_2 = 7.6 \times 10^{-2} \text{ h}^{-1}$	$k_2 = 6.7 \times 10^{11} e^{(-8800/T)} \text{ h}^{-1}$
3	$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_3 = 1.0 \times 10^6 \text{ M}^{-1}\text{h}^{-1}$	$k_3 = 1.08 \times 10^9 e^{(-2010/T)} \text{ M}^{-1}\text{h}^{-1}$
4	$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_2\text{Cl}$	$k_4 = 2.3 \times 10^{-3} \text{ h}^{-1}$	
5	$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$	k_5	
6	$\text{NHCl}_2 + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_2\text{Cl}$	$k_6 = 2.2 \times 10^8 \text{ M}^{-1}\text{h}^{-1}$	
7	$\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-$	$\text{pK}_a = 7.5$	$\text{pK}_a = 1.18 \times 10^{-4} T^2 - 7.86 \times 10^{-2} T + 20.5$
8	$\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$	$\text{pK}_a = 9.3$	$\text{pK}_a = 1.03 \times 10^{-4} T - 9.21 \times 10^{-2} T + 27.6$



3.4 Results and discussion.

3.4.1 Monochloramine reactions with dissolved organic carbon.

The loss of monochloramine in the different surface water samples was assessed over time at a constant pH of 7.0 and constant temperature of 30°C in sealed vials with no headspace (Fig. 3.1). Under these conditions, monochloramine loss was assumed to be the result of monochloramine auto-decomposition and reactions with DOC (Table 3.2, Eq. 3.1, 3.2). The monochloramine concentration in the control samples decreased slowly over time. These results are well described by auto-decomposition reactions and coincide with the rate expressions of Jafvert and Valentine (1992). Monochloramine concentration decreased more rapidly in surface water samples with DOC present (Fig. 3.1). For example, monochloramine loss was very rapid in New River water, with >90% loss within one day, while monochloramine was more persistent in Santa Ana River with <90% loss after one day (Fig. 3.1).

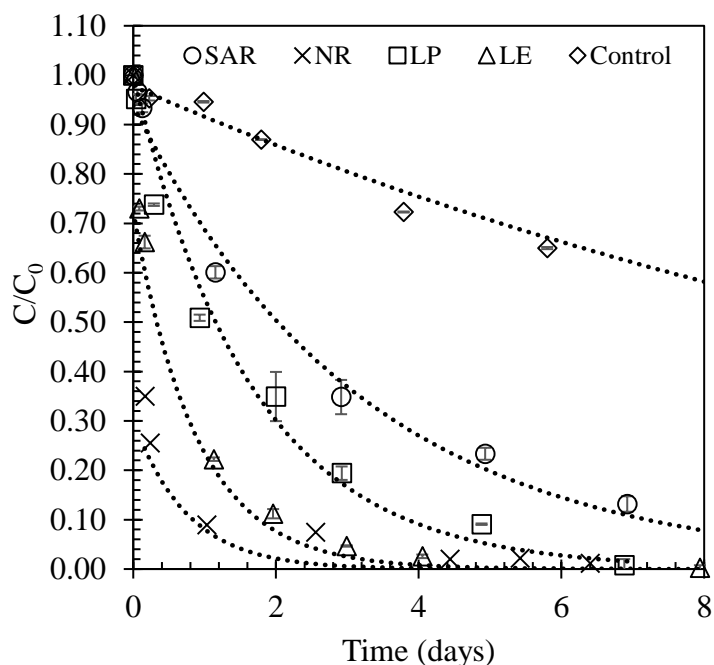


Figure 3.1. Monochloramine degradation in the presence of dissolved organic carbon from different surface waters as relative monochloramine concentration (C/C_0) with respect to time. Control (\diamond) Santa Ana River (SAR) (\circ), New River (NR) (\times), Lake Perris (LP) (\square), Lake Elsinore (LE) (\triangle). $[\text{NH}_2\text{Cl}] = 2.00\text{mg/L}$, $T = 30^\circ\text{C}$, $\text{pH} = 7.02$. Lines represent model predictions. Error bars from $n=3$.

The fitted rate constants and half-lives are shown in Table 3.3. The obtained reaction rate constants for monochloramine oxidation of DOC were found between 2.92×10^3 and $2.52 \times 10^4 \text{ M}^{-1}\text{hr}^{-1}$. Duirk et al. (2005) reported reaction rate constant for this reaction in samples with SUVA_{280} values of $1.6\text{--}3.2 \text{ m}^{-1}\text{L mg-C}^{-1}$ at range of $1.05 \times 10^4\text{--}3.45 \times 10^4 \text{ M}^{-1}\text{h}^{-1}$. While our values are broadly consistent with Duirk et al. (2005), they were generally somewhat lower. The discrepancy between the obtained values and the previously reported values may be explained by the different approach in the determination of reactive DOC concentration. The work here writes the rate expression in terms of the total DOC concentration while Duirk et al. (2005) used free chlorine to estimate a reactive

site fraction within the DOC structure. In this case, Duirk et. al. (2005) predicts that only a portion of the total DOC will be reactive towards monochloramine and thus estimates lower initial reactive DOC concentrations.

Rate constants for the chlorination of DOC were calculated between 2.18×10^3 and $1.05 \times 10^4 \text{ M}^{-1}\text{hr}^{-1}$. Reported rate constants for these reactions vary greatly in the literature, with values ranging from 3.60×10^2 - $3.6 \times 10^{12} \text{ M}^{-1}\text{hr}^{-1}$ (Deborde and Von Gunten, 2008). Duirk et al. (2005) reported rate constant values for this reaction between 5.72×10^5 and $6.12 \times 10^5 \text{ M}^{-1}\text{hr}^{-1}$. Once again, discrepancy between the obtained values and the previously reported values is likely, at least in part, due to the different approach in determination of reactive DOC concentration, as described above.

The direct reaction of monochloramine with DOC (Eq. 3.1, k_7) represented only a small fraction of the monochloramine loss in some samples, such as the Santa Ana River, while it represented most of the monochloramine loss in others, such as in the New River. The predominance of monochloramine loss driven by this reaction was most significant in the New River sample followed by Lake Elsinore, Lake Perris, and Santa Ana River samples, in that order. Monochloramine loss by this process in the New River water was about 65%, while in Lake Elsinore and Lake Perris samples it was 25% and 9%, respectively, and in the Santa Ana River samples was only 8%. Although reaction rate constants across the samples varied with DOC concentrations, there is no clear correlation between DOC concentration and monochloramine reactivity towards it. Moreover, rate constants were found to vary by nearly an order of magnitude for the direct reaction of monochloramine with DOC (k_7) and by nearly five times for the reaction of HOCl with

DOC (k_8). This suggests that monochloramine reactivity in this experiment not only depends on DOC concentration but is also highly sensitive to its chemical properties, as discussed later on this section.

Table 3.3. Rate constants and their corresponding half-lives with 95% confidence intervals. T = 30 °C

Surface Water	[DOC] (mgL ⁻¹)	SUVA ₂₈₀ (Lm ⁻¹ mg-C ⁻¹)	k_7 (M ⁻¹ hr ⁻¹)	$t_{1/2}$ (hr)	k_8 (M ⁻¹ hr ⁻¹)	$t_{1/2}$ (hr)
Santa Ana River	33.1	2.7	$2.92 \times 10^3 \pm 3.18 \times 10^2$	31.2 ± 3.4	$2.18 \times 10^3 \pm 6.05 \times 10^1$	43.2 ± 1.2
New River	45.1	7.5	$2.52 \times 10^4 \pm 1.05 \times 10^3$	2.4 ± 0.1	$1.05 \times 10^4 \pm 1.17 \times 10^3$	7.2 ± 0.8
Lake Perris	19.7	4.3	$1.20 \times 10^4 \pm 2.25 \times 10^3$	14.4 ± 2.7	$7.28 \times 10^3 \pm 8.43 \times 10^2$	21.6 ± 2.5
Lake Elsinore	36.6	6.5	$1.31 \times 10^4 \pm 2.23 \times 10^3$	7.2 ± 1.2	$4.15 \times 10^3 \pm 5.18 \times 10^2$	19.2 ± 2.4

The degradation of monochloramine in the presence of DOC was previously observed by Duirk et al. (2005) and was attributed to a direct reaction of monochloramine with a specific DOC fraction (Eq.1) along with a reaction between the hypochlorite ion formed from monochloramine auto-decomposition and a different DOC fraction (Eq 3.2 and reactions 1,2 from Table 3.2). This conclusion was attained due to the fact that, under constant pH and DOC concentrations, the rate constant for the reaction of hypochlorite ion with DOC increased with decreasing monochloramine concentrations instead of decreasing (Duirk et al. 2005). If monochloramine would be reacting with DOC during the chlorination of DOC, then the reaction rate would be expected to increase with increasing monochloramine concentration. Instead, Duirk et al. (2005) observed the opposite, suggesting that monochloramine could not be the reactive species during this reaction. Duirk et al. (2005) concluded that the intermediate hypochlorite ion resulting from monochloramine auto-decomposition must be the species reacting with DOC during the chlorination reactions. The observed increase in the rate of the reaction during chlorination of DOC with decreasing monochloramine concentration can be explained by considering

that HOCl not only will react with DOC but will also react with any NH_3 in solution to reform monochloramine. Monochloramine solutions for these experiments are always prepared with excess ammonia to increase monochloramine stability so the higher the monochloramine concentration the higher the NH_3 residual. Therefore, higher monochloramine concentrations will favor monochloramine reformation leaving less HOCl available to react with DOC.

An experiment was conducted here under the same conditions as those described by Duirk et al. (2005) for the water samples used in this study. The same results were obtained (Fig. 3.2) and it was determined that monochloramine cannot indeed be the reactive species during DOC chlorination. It was therefore confirmed that monochloramine participates only in DOC oxidation and that the monochloramine loss observed in the second half of the reaction is driven by the consumption of the intermediate hypochlorite ion.

The fact that monochloramine only participates in DOC oxidation is of great significance as this reaction scheme will provide fundamental knowledge to predict the potential formation of specific byproducts. In the model developed by Duirk et al. (2005) for the reaction with DOC in treated drinking water it was observed that monochloramine only participates in DOC oxidation, that this reaction rate is faster than the reaction rate for DOC chlorination, and that only a very small portion of monochloramine is consumed during DOC oxidation. The results presented here show a similar trend for the surface water samples from the Santa Ana River and Lake Perris. However, the opposite trend was observed for waters from the New River and Lake Elsinore, where the majority of

monochloramine is consumed during DOC oxidation. This is a relevant finding as it suggests that the majority of monochloramine in the New River and Lake Elsinore will be consumed through oxidation of DOC, limiting the amount of monochloramine available to generate HOCl which in turn will limit the chlorination of DOC. This finding therefore suggests that there should be a higher degree of chlorination of DOC expected to occur in the Santa Ana River and Lake Perris than in the New River and Lake Elsinore.

Previous reports have shown that monochloramine will react with DOC only in a redox reaction with negligible transfer of chlorine, while reactions between DOC and hypochlorite ion will result in chlorination of organic structures rather than oxidation (Duirk et al. 2005). Although other studies have shown that very little monochloramine is reduced in the presence of DOC under typical drinking water treatment and water distribution system conditions, evidence is presented here to suggest that monochloramine reduction is much more significant than chlorination when it reacts with the DOC present in surface waters. This is of importance because given the different reaction schemes, it is reasonable to expect that chlorinated organic byproducts will be formed at different concentrations in natural waters compared to those found in water distribution systems. In the case of some of the surface waters analyzed here, with a higher amount of monochloramine being rapidly oxidized, only a small concentration of hypochlorite ion will be expected to be available to transfer a chlorine into organic matter. With this, it is predicted that the presence of chlorinated organic compounds will be relatively less predominant in natural waters and waters receiving minimally treated wastewater than what is observed in many water treatment scenarios.

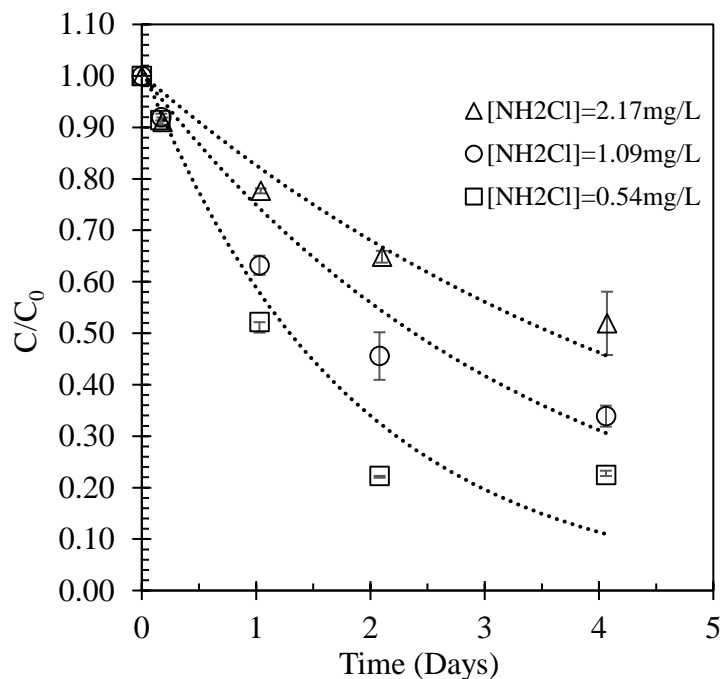


Figure 3.2. Monochloramine loss in water sample from the Santa Ana River as a function of initial monochloramine concentration (C/C_0). $T=30^\circ\text{C}$, $\text{pH } 7.02$. $[\text{DOC}]=35.0\text{mg/L}$. $\text{SUVA}_{280}=2.9\text{Lm}^{-1}\text{mg}\cdot\text{C}^{-1}$. Lines represent model predictions.

In order to better understand the reactivity of DOC towards monochloramine, it was necessary to explore some properties of natural organic matter. Aromaticity was estimated using the specific UV absorption at 280nm (SUVA_{280}) as a proxy (Hua et al. 2015). In the study presented here, the SUVA_{280} of the water samples were measured and plotted against the corresponding rate constants (Fig. 3.3). By doing so, it was possible to determine that the resulting rate constants have an approximately linear dependency on the initial aromaticity of the water samples as described by SUVA_{280} measurements. As others have described, it was determined that higher aromaticity will result in higher reactivity resulting in faster monochloramine losses (Hua et al. 2015).

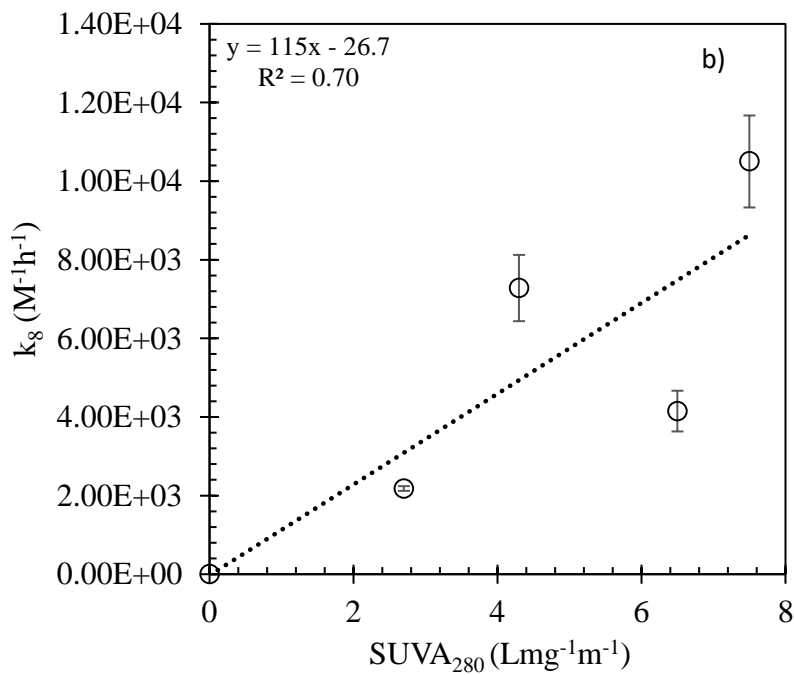
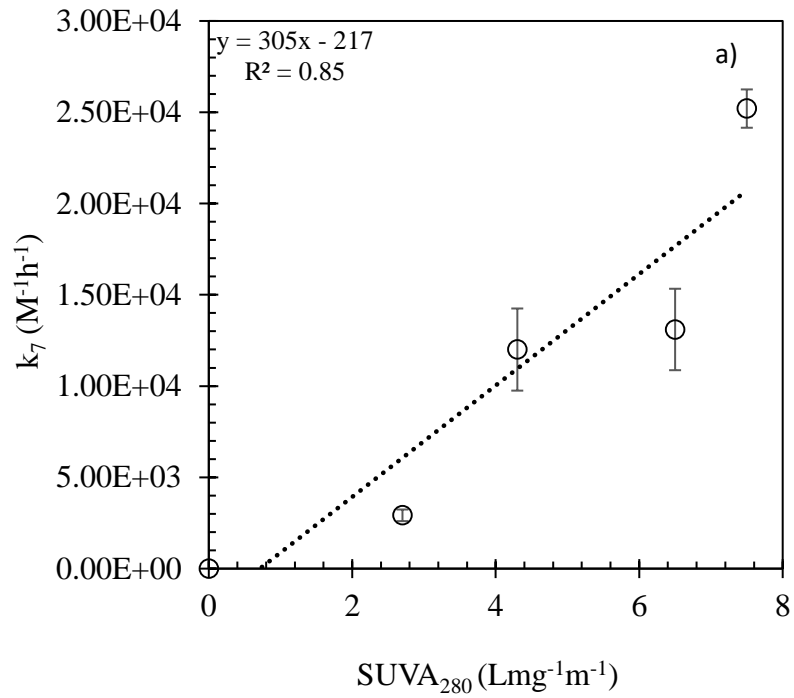


Figure 3.3. Resulting reaction rate constants from the loss of monochloramine in the presence of dissolved organic carbon with respect to initial $SUVA_{280}$ a) DOC oxidation b) DOC chlorination. Lines represent a linear fit. Error bars from $n=3$.

Changes in SUVA₂₈₀ were monitored over the course of all reactions (Fig. 3.4). Changes in SUVA₂₈₀ have been widely used to characterize organic matter properties and to predict the potential formation of chlorinated byproducts (Hua et al., 2015, Weishaar et al. 2003). It has been reported that free chlorine is capable of disrupting aromatic rings within organic matter structures, causing an overall decrease in SUVA₂₈₀ (Yang et al. 2008). In other cases where the chlorine concentration is not substantial, chlorine is incorporated into the organic molecules without disrupting the aromatic structures. In such cases, SUVA₂₈₀ is expected to increase in relation to chlorine substitution into organic matter (Li et al. 2000).

In the case of the samples analyzed here, SUVA₂₈₀ increased markedly as monochloramine reacted with DOC in the Santa Ana River sample, although increases were much more modest for the Lake Elsinore and New River samples. This suggests that chlorine was incorporated into organic matter without disrupting the aromatic structures. It can be seen that the slope of SUVA₂₈₀ change was greater in the samples with smaller initial SUVA₂₈₀ compared to the samples with the highest initial SUVA₂₈₀. In this case, the Santa Ana River, with the smallest initial SUVA₂₈₀ presented the greatest increase over time. The Santa Ana River sample had an initial SUVA₂₈₀ of 2.7 Lmg⁻¹m⁻¹, 1.6 times smaller than that of Lake Perris and 2.4 times smaller than that of Lake Elsinore. Once all of the monochloramine had reacted with DOC, SUVA₂₈₀ in the Santa Ana River sample had increased 2.5 times while SUVA₂₈₀ in the Lake Perris and Lake Elsinore samples only increased 1.4 and 1.1 times respectively. Considering that increases in the SUVA₂₈₀ of organic matter have been linked to the incorporation of chlorine into organic structures

(Schwarzenbach et al. 1993), the results shown here indicate that there is a trend between the initial SUVA₂₈₀ of a sample and the expected degree of chlorination. These results suggest that there will be a greater degree of chlorination in samples with lower initial SUVA₂₈₀ compared to samples with higher initial SUVA₂₈₀. An explanation to this could be that samples with higher DOC will most likely have more complex organic structures that will create a hindering effect limiting monochloramine and free chlorine access to reactive sites. In addition to this, chlorination is expected to be less predominant in the New River and Lake Elsinore as a result of reduced HOCl availability since the majority of monochloramine is rapidly consumed during the first half of the reaction through oxidation of DOC.

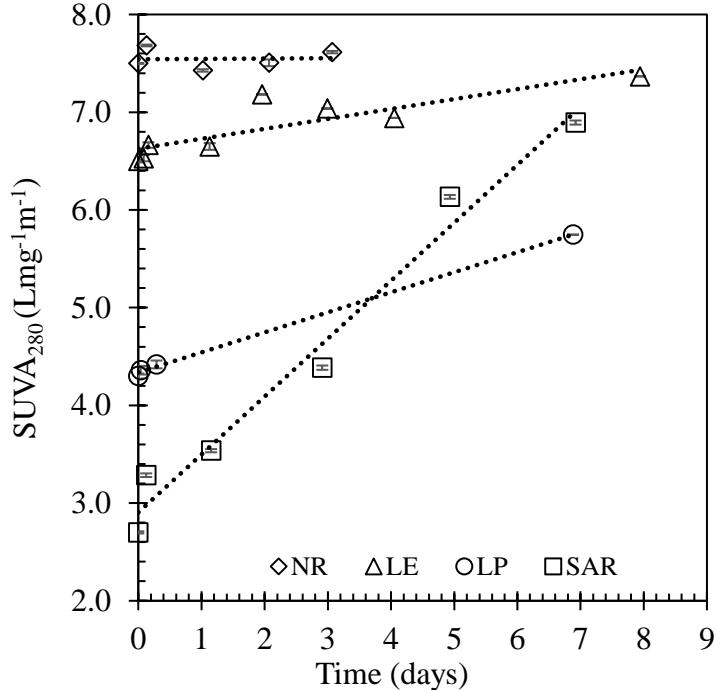


Figure 3.4. Change in SUVA₂₈₀ over time in different surface water samples spiked with monochloramine. New River (◇) Lake Elsinore (LE) (△), Lake Perris (LP) (○) and Santa Ana River (SAR) (□). T= 30 °C, [NH₂Cl]=2.00mg L⁻¹. Lines represent a linear fit. Error bars from n=3.

3.4.2 Model for the loss of monochloramine in the presence of dissolved organic carbon from surface waters.

The complete model presented here incorporates all the reactions involved in the formation and auto-decomposition of monochloramine in water as described by Jafvert and Valentine (1992) (Table 3.2.). It also incorporates the reactions shown in Eq.1 and 2. The rate constant for the reaction of monochloramine and DOC was estimated experimentally and labeled as k_7 (Table 3.4). The rate constant for the reaction of the hypochlorite ion and DOC (k_8) (Table 3.4) was estimated from the loss of monochloramine in the second half of the reaction. Both k_7 and k_8 can be described in terms of initial $SUVA_{280}$ ($Lmg^{-1}m^{-1}$) as shown in Table 3.4. This model was then fitted to the data obtained from the four different surface water samples. The parameters considered for the model were initial monochloramine concentration, initial ammonia concentration, initial $SUVA_{280}$ and temperature. The model was found to be in good agreement with the laboratory results (Fig. 3.1). The model data yielded relative root-mean-square error (rRMSE) values below 0.05 for all the surface waters analyzed.

Table 3.4. Rate constants for the reaction of monochloramine and hypochlorite ion with DOC. T in °K.

Reaction	Rate constant	Temperature dependency
$NH_2Cl + H_2O + DOC^{red} \rightarrow NH_4^+ + OCl + DOC$	$k_7 = 3.05 \times 10^2 \cdot SUVA_{280} - 2.17 \times 10^2 \text{ M}^{-1}\text{hr}^{-1}$	$1.0 \times 10^{-21} e^{(0.16/T)} \text{ M}^{-1}\text{hr}^{-1}$
$HOCl + DOC \rightarrow \text{Chlorinated compounds}$	$k_8 = 1.15 \times 10^2 \cdot SUVA_{280} - 2.67 \times 10^1 \text{ M}^{-1}\text{hr}^{-1}$	$5.0 \times 10^{-17} e^{(0.12/T)} \text{ M}^{-1}\text{hr}^{-1}$

To validate this sub-model, the stability of monochloramine was assessed in an additional water sample not previously included in the model data. The sample was collected at the discharge point from the Rapid Infiltration and Extraction (RIX) Facility in Colton, CA. All the physicochemical properties of the RIX sample were inputted into

the model to predict the persistence of monochloramine and were compared to laboratory data (Fig. 3.5). Based on $SUVA_{280}$, temperature and pH, monochloramine should have an initial reaction rate constant value of $4.35 \times 10^2 \pm 6.96 \times 10^1 \text{ M}^{-1} \text{ hr}^{-1}$ and a secondary reaction rate constant value of $2.64 \times 10^2 \pm 7.92 \times 10^1 \text{ M}^{-1} \text{ hr}^{-1}$. Using these values and other important physicochemical properties of the RIX water sample, the model presented here was found to accurately reproduce measured loss of monochloramine over time (Fig. 3.5) (rRMSE of 0.07).

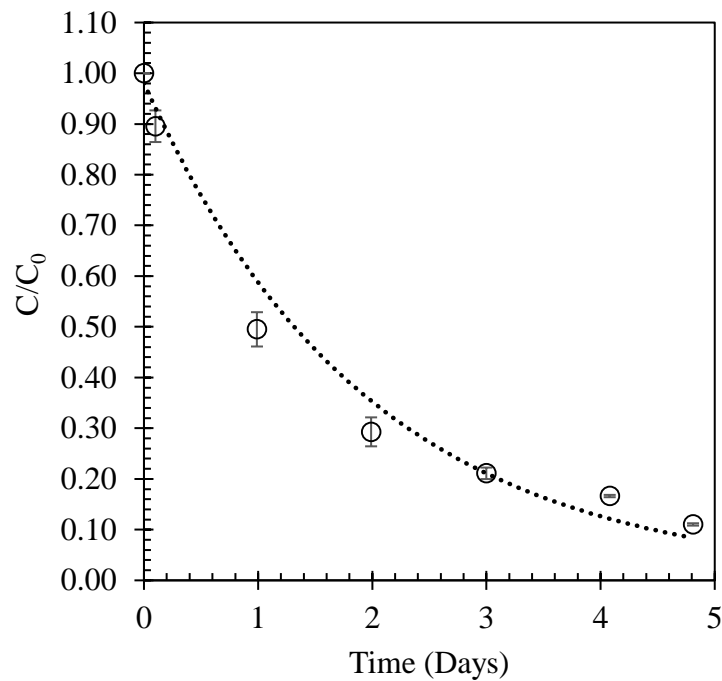


Figure 3.5. Monochloramine loss in water sample from the Rapid Infiltration and Extraction (RIX) Facility in Colton, CA as a function of initial monochloramine concentration (C/C_0). $T=30^\circ\text{C}$, pH 7.2. $[\text{DOC}]=19.79\text{mg/L}$. $SUVA_{280}=4.2 \text{ Lm}^{-1}\text{mg}^{-1}\text{C}^{-1}$. Dotted line represents model predictions. Error bars from $n=3$.

3.4.3 Monochloramine loss to sediment from surface waters: reactions with organic matter and other reduced species.

The loss of monochloramine in sediment from four different surface waters and Ottawa sand as control was monitored over time (Fig. 3.6). It was observed that monochloramine concentration decreased relatively quickly in all the samples compared to the control. In the case of Lake Elsinore and one of the sediment samples from Canyon Lake (CL₁), monochloramine was consumed almost entirely in a matter of a few hours, while it decreased at a slower pace in the other samples. In these experiments, the loss of monochloramine was attributed predominantly to the organic matter and other reduced species such as reduced iron, manganese and sulfide present in sediment. Although, in theory, all of these species could be isolated to determine their individual contribution to the loss of monochloramine in sediments, it was decided to group them together here and represent their collective reactivity towards monochloramine as the total oxidant demand of the sediment. The total oxidant demand was measured for each sediment sample and plotted against the monochloramine loss reaction rate constants (Fig. 3.7).

This total oxidant demand was found to have a strong correlation to the percent organic carbon in the sediments ($r^2 = 0.97$). The resulting rate constants were assumed to be pseudo-first order with respect to monochloramine since the concentration of reduced species in the sediments were found in large excess under the experimental conditions. At the same time, the oxidant demand of the sediments did not decrease significantly after completion of the reaction with monochloramine ($< 1.0 \times 10^{-3} \text{ mMg}^{-1}$).

It was observed that the rate constant has an exponential dependency on total oxidant demand with rate constants ranging from 0.05 for control to 48.38 d⁻¹ (Table 3.5). This

enable us to generate an expression for the rate constant of the reaction between monochloramine and the sediments as a function of initial oxidant demand (Eq. 3.3). These rate constants are of the same magnitude or in some cases greater than the resulting rate constants for the reaction of monochloramine with dissolved organic carbon. The results here suggest that monochloramine loss due to interaction with sediments has the potential to be a significant loss mechanism competing with monochloramine loss due to reactions with dissolved organic carbon in the water phase. This may be particularly significant in shallow river systems, where the close proximity of the sediment surface and rapid mixing conditions will permit constant contact between monochloramine and the sediments.

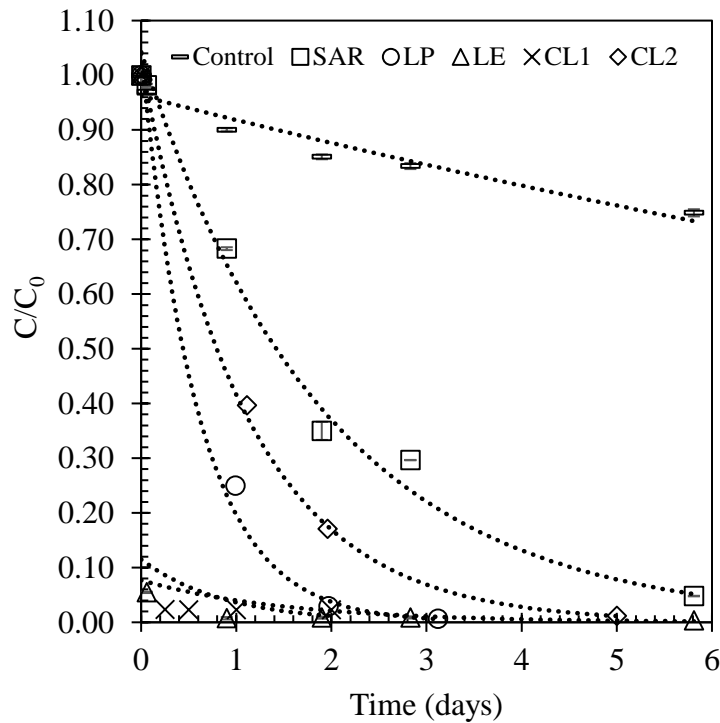


Figure 3.6. Monochloramine loss in Ottawa sand as control (-) and sediment from the Santa Ana River (SAR) (\square), Lake Perris (LP) (\circ), Lake Elsinore (LE) (\triangle) and Canyon Lake (CL1) (\times), (CL2) (\diamond). Lines represent an exponential fit. $[\text{NH}_2\text{Cl}] = 2.00\text{mg/L}$. Error bars from $n=3$.

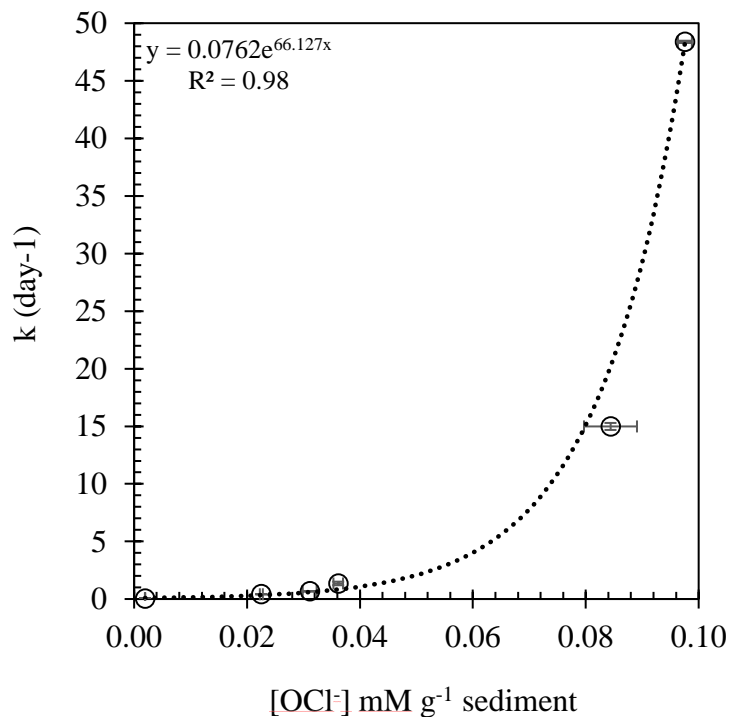


Figure 3.7. Reaction rate constant for the loss of monochloramine in sediment with relation to oxidant demand measured in mM of OCl per gram of sediment. Lines represent an exponential fit.

Table 3.5. Properties of different sediment samples and the resulting reaction rate constant for the loss of monochloramine in these sediments.

Sediment sample	% water	% OC	Oxidant Demand [OCl⁻] mM g⁻¹ sediment	k d⁻¹
Control (sand)	15.9	0.0	0.002	0.05 ± 0.00
Santa Ana River	8.1	0.1	0.023	0.41 ± 0.01
Lake Perris	13.4	5.9	0.036	1.35 ± 0.15
Canyon Lake #1	33.7	16.1	0.084	15.0 ± 0.30
Canyon Lake #2	19	4.5	0.031	0.67 ± 0.02
Lake Elsinore	78.1	20.8	0.098	48.4 ± 0.10



To validate this sub-model, the stability of monochloramine was assessed in an additional sediment sample not previously included in the model data. This additional sediment sample was collected from the Santa Ana River and was found to have had 20% water content, 9.8% organic carbon, and an oxidant demand of 0.054 mMg^{-1} . All the physicochemical properties of this sample were inputted into the sub-model to predict the persistence of monochloramine and were compared to laboratory data (Fig. 3.8). Based on the initial oxidant demand it is expected a reaction rate constant of 2.71h^{-1} . The experimental value for the rate constant was calculated at 2.40h^{-1} , which represents a relative root-mean-square error value of 0.03.

Although the proposed expression for the rate constant of the reaction between monochloramine and sediments shows good agreement with experimental data, it is necessary to consider if mixing will have an effect on the reaction rate constant. The rate constant expression for the loss of monochloramine in sediments as a function of oxidant demand (k_{sed}) presented here was obtained from laboratory experiments where monochloramine was exposed to sediments with minimum disturbance. It is expected that reactions between monochloramine and sediments will be limited by the transport across the benthic boundary layer, which will be affected by different mixing conditions. In order to determine if rapid, constant mixing would have any effect on the rate of the reaction between monochloramine and bottom sediments, a similar experiment as above was conducted comparing a sample with minimum mixing and a sample with rapid, constant mixing (Fig.8). The sediment sample used had 20% water content, 9.8% organic carbon, and an oxidant demand of 0.054 mMg^{-1} .

Monochloramine concentration was found to decrease at a greater rate in the rapidly mixed sample than in the sample with minimum periodic mixing. Monochloramine was also found to decrease more rapidly than dissolved oxygen, suggesting that monochloramine is a more reactive oxidant than oxygen. The observation of different rates of monochloramine loss under the two different rates of mixing provides evidence that mixing does have an effect on the rate of reaction of monochloramine with sediments. The reaction rate constant for the constantly mixed sample was calculated at $1.46 \times 10^{-1} \text{ hr}^{-1}$ while the reaction rate constant in the sample minimally mixed was $1.00 \times 10^{-1} \text{ hr}^{-1}$, this represents a difference of 40% between constant rapid mixing and minimal periodic mixing. This demonstrates that transport across the benthic boundary can limit the rate of reaction between monochloramine and sediments, and that a correction factor for transport should be included with the rate constant expression (Eq. 3) to account for mixing conditions. In this simple experiment, monochloramine reaction with bottom sediments due to enhanced mixing could be represented using a transport factor of 1.4 compared to a factor of 1 for the limited mixing condition. Loss of monochloramine from the overlying water occurred much more rapidly than dissolved oxygen, confirming it as a more reactive oxidant and highlighting the relatively slow rate of oxygen demand in this riverine sediment.

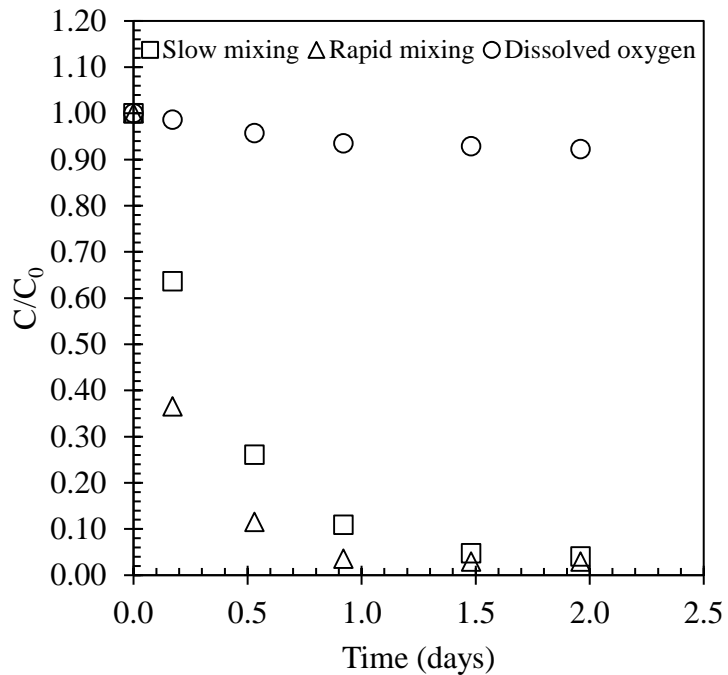


Figure 3.8. Effect of rapid mixing in the change in relative monochloramine concentration (C/C_0) in sediment. Oxidant demand = 0.054 mMg^{-1} , $T=25^\circ\text{C}$.

3.5 Conclusions

The majority of the studies conducted for the loss of monochloramine in the presence of DOC have been conducted in water distribution systems and other controlled systems that poorly represent how monochloramine will behave in natural systems. This study evaluated monochloramine reactions under more environmentally relevant conditions. It was found that SUVA_{280} serves as a reasonable proxy to estimate the expected reaction rate constants involved in the loss of monochloramine in the presence of DOC and to predict the degree of chlorination expected upon completion of the reaction. It was determined that monochloramine oxidation is more important in surface water samples than what has generally been observed in water distribution systems. At the same time, the relative amount of chlorination of organic matter may be less predominant in natural

systems with DOC that presents relatively high aromaticity. Finally, it was determined that monochloramine will readily react with bottom sediments rich in organic matter and other reduced substances, particularly in cases where monochloramine is likely to reach the sediment surface in a short period of time such as in shallow rivers. In the case of deep waters such as lakes, the loss of monochloramine due to interactions with the sediments will be of less significance because monochloramine concentration would be expected to decrease considerably due to reactions with dissolved organic carbon before being transported to the bottom of lakes.

3.6 References

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Chapter 4: Model for the fate and transport of monochloramine in surface waters.

4.1 Introduction

The stability of monochloramine in water distribution systems has been extensively studied and this has generated a series of models that predict the persistence of monochloramine in such systems. However, as noted, very few studies have been dedicated to the fate of monochloramine after it is discharged to rivers and lakes from wastewater treatment plants. The current models for the persistence of monochloramine are only applicable to systems such as water distribution systems, scenarios that may not necessarily incorporate all of the conditions and loss mechanisms that will affect the persistence of monochloramine in open surface water systems. Notwithstanding, they provide a fundamental starting point to develop a more comprehensive environmental fate model. More recently, the tendency of monochloramine to transfer from the aqueous phase into the gas phase has been investigated suggesting that volatilization losses can be a significant loss mechanism in rivers with high mixing conditions (Garcia and Anderson, 2018, Chapter 2). Moreover, some studies have indicated that monochloramine interactions with dissolved organic carbon and reduced species in sediments will be a significant pathway for the loss of monochloramine in surface waters (Chapter 3). The goal of this study was to expand on previous models for the formation and auto-decomposition of monochloramine in water by incorporating additional environmental loss mechanisms into a comprehensive environmental fate model for monochloramine in surface waters.

The model developed by Jafvert and Valentine (1992) and Ozekin et al. (1996) describing the formation and auto-decomposition of monochloramine (Table 4.1) was used as the starting point for developing a comprehensive model for the environmental fate and transport of monochloramine. The model presented here incorporates the formation and auto-decomposition of monochloramine along with other mechanisms expected to affect the stability of monochloramine in surface waters such as volatilization, reactions with organic matter and interactions with bottom sediments.

4.2 Development of model for the fate and transport of monochloramine in surface waters

4.2.1 Formation and auto-decomposition of monochloramine

One of the first models developed to describe the persistence of monochloramine in water distribution systems was presented by Jafvert and Valentine (1992) and was later modified by Ozekin et al. (1996) (Table 4.1). Reactions 1 and 2 describe the formation and auto-decomposition of monochloramine as a reversible reaction dependent on ammonia and hypochlorous acid concentration. Reaction 3 describes the reaction between hypochlorous acid and monochloramine to form dichloramine, an unstable intermediate, which either decomposes to form monochloramine and hypochlorous acid (Reaction 4) or reacts with ammonia to form monochloramine (Reaction 6). Monochloramine is also capable of reacting with itself in a pH-dependent reaction to form dichloramine and ammonia (Reaction 5). Finally, the model describes the pH-dependent speciation of ammonia and hypochlorous acid (reactions 7 and 8). All of the rate constants for the described reactions are presented in the model (Table 4.1). Reactions 1-3 and 7-8 include

the temperature dependency of the corresponding rate coefficients. This model predicts that monochloramine will be very stable at neutral pH and room temperature, and minimum hypochlorous acid and ammonia residual, with a half-life for monochloramine of about 16 days. The loss of monochloramine in surface waters due to auto-decomposition is predicted to be of minor significance in systems with near neutral pH and become increasingly significant as pH conditions drop below neutral pH or temperatures increase.

Table 4.1. Monochloramine decay model developed by Jafvert and Valentine (1992). T in K.

	Reaction	Rate/equilibrium constants	Temperature dependency
1	$\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_1 = 1.5 \times 10^{10} \text{ M}^{-1}\text{h}^{-1}$	$k_1 = 2.37 \times 10^{12} e^{(-1540/T)} \text{ M}^{-1}\text{h}^{-1}$
2	$\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$	$k_2 = 7.6 \times 10^{-2} \text{ h}^{-1}$	$k_2 = 6.7 \times 10^{11} e^{(-8800/T)} \text{ h}^{-1}$
3	$\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_3 = 1.0 \times 10^6 \text{ M}^{-1}\text{h}^{-1}$	$k_3 = 1.08 \times 10^9 e^{(-2010/T)} \text{ M}^{-1}\text{h}^{-1}$
4	$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_2\text{Cl}$	$k_4 = 2.3 \times 10^{-3} \text{ h}^{-1}$	
5	$\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$	k_5	
6	$\text{NHCl}_2 + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_2\text{Cl}$	$k_6 = 2.2 \times 10^8 \text{ M}^{-1}\text{h}^{-1}$	
7	$\text{HOCl} \rightarrow \text{H}^+ + \text{OCl}^-$	$\text{pK}_a = 7.5$	$\text{pK}_a = 1.18 \times 10^{-4} T^2 - 7.86 \times 10^{-2} T + 20.5$
8	$\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$	$\text{pK}_a = 9.3$	$\text{pK}_a = 1.03 \times 10^{-4} T - 9.21 \times 10^{-2} T + 27.6$

$$k_d = k_H [\text{H}^+] + k_{\text{H}_2\text{CO}_3} [\text{H}_2\text{CO}_3] + k_{\text{HCO}_3} [\text{HCO}_3^-], k_H = 2.5 \times 10^7 \text{ M}^{-2}\text{h}^{-1}, k_{\text{HCO}_3} = 8 \times 10^2 \text{ M}^{-2}\text{h}^{-1}, k_{\text{H}_2\text{CO}_3} = 4.0 \times 10^4 \text{ M}^{-2}\text{h}^{-1}$$

4.2.2 Monochloramine volatilization

The tendency for monochloramine to transfer from the aqueous phase into the gas phase has been studied with results showing that monochloramine possess semi-volatile properties (Garcia and Anderson, 2018, Chapter 2). The volatility of monochloramine has been reported in terms of a dimensionless Henry's constant (Eq. 4.1). Considering that the high mixing conditions of many rivers and other surface waters will promote the loss of volatile and semi-volatile compounds into the atmosphere (Cadena et al., 1984), it is expected that some monochloramine will be lost via this mechanism. To calculate the loss

of monochloramine due to volatilization in surface waters, one can use the two-film model used to calculate the rate of loss of volatile and semi-volatile compounds (Schwarzenbach et al., 1993). The expected flux (J) of monochloramine from the aqueous phase into the gas phase is described by Eq. 4.2.

For surface waters, typical values of δ_w are expected in the range of 20 to 200 μm and typical values of δ_a on the order of 1cm (Hemond and Fechner-Levy, 2000). D_a and D_w for monochloramine can be calculated from the molecular diffusion coefficients of water and oxygen respectively considering the ratio of the molecular weight of water and oxygen to the molecular weight of monochloramine (Schwarzenbach et al., 1993).

$$H=0.0037e^{0.0759T(^{\circ}\text{C})} \quad (4.1)$$

$$J = [\text{NH}_2\text{Cl}]_0 \left(\frac{1}{\frac{\delta_w}{D_w} + \frac{\delta_a}{D_a \cdot H}} \right) \text{ M cm sec}^{-1} \quad (4.2)$$

$$\frac{D_{a\text{-water}}}{D_{a\text{-NH}_2\text{Cl}}} = \frac{\sqrt{MW_{\text{NH}_2\text{Cl}}}}{\sqrt{MW_{\text{water}}}} \quad (4.3a)$$

$$D_{a\text{-water}} = (0.2u_{10} + 0.3) \cdot \delta_a \text{ (cm}^2 \cdot \text{sec}^{-1}\text{)} \quad (4.3b)$$

$$\frac{D_{w\text{-Oxygen}}}{D_{w\text{-NH}_2\text{Cl}}} = \frac{\sqrt{MW_{\text{NH}_2\text{Cl}}}}{\sqrt{MW_{\text{Oxygen}}}} \quad (4.4a)$$

$$D_{w\text{-Oxygen}} = \left(\frac{\sqrt{4 \times 10^{-4}} + 4 \times 10^{-5} u_{10}^2}{u_w} \right) \cdot d \text{ (cm}^2 \cdot \text{sec}^{-1}\text{)} \quad (4.4b)$$

where,

$[\text{NH}_2\text{Cl}]_0$ = initial monochloramine concentration

δ_w = thickness of the hypothetical thin boundary layer of water (cm)

D_w = molecular diffusion coefficient ($\text{cm}^2 \cdot \text{sec}^{-1}$)

δ_a = thickness of the hypothetical stagnant air layer (cm)

D_a = molecular diffusion coefficient for the chemical in air ($\text{cm}^2 \cdot \text{sec}^{-1}$)

H = dimensionless Henry's constant

d = water depth (cm)

u_{10} = the wind speed measured 10m above the water surface ($\text{m} \cdot \text{sec}^{-1}$)

u_w = water velocity ($\text{cm} \cdot \text{sec}^{-1}$)

Applying the two-layer model to a hypothetical river system provides insight into the extent that volatilization will play in determining the overall environmental fate and transport of monochloramine in surface waters (Fig. 4.1). Considering a hypothetical river with depth (d) of 0.25m, water velocity (u_w) of $100 \text{ cm} \cdot \text{sec}^{-1}$, wind speed (u_{10}) of $1 \text{ m} \cdot \text{sec}^{-1}$ and an average temperature of 25°C , monochloramine will experience a volatility loss rate of about 0.01 mg/L per hour, which represents a half-life of about 4.7 days. This shows that volatilization losses will be greater than that of auto-decomposition in our shallow river scenario and that the volatilization loss rate will increase directly proportional to wind speed, water velocity and temperature. This sub-model will later be applied to represent the volatilization of monochloramine in two California rivers.

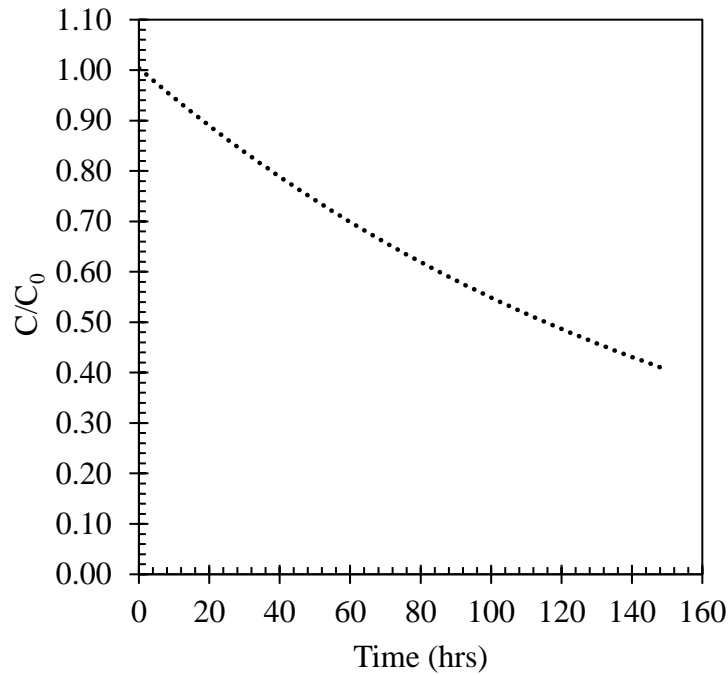


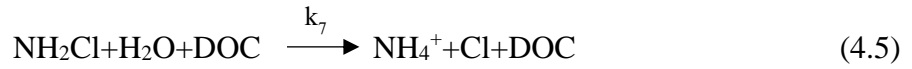
Figure 4.1. Predicted change in relative monochloramine concentration (C/C_0) over time due to transfer from the aqueous phase into the gas phase from a shallow hypothetical river. $d=0.25\text{m}$, $u_{10}=1\text{ m}\cdot\text{sec}^{-1}$, $T=25^\circ\text{C}$.

4.2.3 Monochloramine interactions with dissolved organic carbon

Monochloramine has been found to react with DOC in water distribution systems, which results in formation of undesirable byproducts (Duirk et al., 2002, 2005, 2006). Typical compounds formed by the reaction of monochloramine with DOC include chloroacetic acid, dichloroacetic acid and chloroform, compounds that are of concern due to their potential carcinogenic, mutagenic and reproductive effects (IPCS 2000, Nieuwenhuijsen et al., 2000). Due to the risk that these compounds may present, there have been numerous efforts to develop models to predict their formation in monochloramine-treated waters in the presence of typical DOC concentrations expected of water distribution systems ($0\text{-}15\text{ mg C L}^{-1}$) (Duirk et al., 2005). It has been proposed that monochloramine

reacts with DOC via two pathways, an initial oxidation of DOC by monochloramine (Eq. 4.5) followed by chlorination of DOC by the hypochlorous acid resulting from the auto-decomposition of monochloramine (Eq. 4.6) (Duirk et al., 2005). In this reaction scheme, oxidation of DOC in drinking water systems by monochloramine occurs much faster than chlorination but it is chlorination that accounts for the majority of monochloramine loss in such systems.

Models like these provide important insight into the stability of monochloramine in water distribution systems in the presence of DOC at low concentrations but may not necessarily represent what happens in surface waters where DOC concentrations are expected to be higher and of different reactivity than what is found in water distribution systems. Recently, we investigated the stability of monochloramine in the presence of DOC at concentrations more typical of surface waters ($10\text{-}45\text{ mg C L}^{-1}$) (Chapter 3). In this study, as in Duirk et al. (2005), monochloramine was found to react with DOC via two pathways, DOC oxidation followed by DOC chlorination. One important difference between our study and previous work is that it identifies the predominance of chlorination versus oxidation of DOC by monochloramine as being dependent on the aromaticity of the water sampled analyzed, described as the specific UV absorption at 280nm (SUVA_{280}). This proposes that higher initial SUVA_{280} will result in a higher proportion of DOC oxidation versus chlorination. Conversely, lower initial SUVA_{280} will result in more extensive DOC chlorination relative to oxidation. The rate expressions proposed in Chapter 3 have been used here to model the loss of monochloramine in surface waters through reactions with DOC (Eq. 4.5,4.6).



Applying this model with different initial SUVA_{280} values, at a uniform initial DOC concentration at 30 mg/L and initial monochloramine concentration of 2.0 mg/L (Fig. 4.2.), allows for predictions of the amount of monochloramine lost as a function of DOC reactivity at SUVA_{280} values representative of surface water conditions. The half-life of monochloramine in these scenarios ranges between 0.3 and 3.0 days, suggesting that small increases in SUVA_{280} can significantly affect the stability monochloramine in surface waters and that reactions with DOC will represent a major loss pathway.

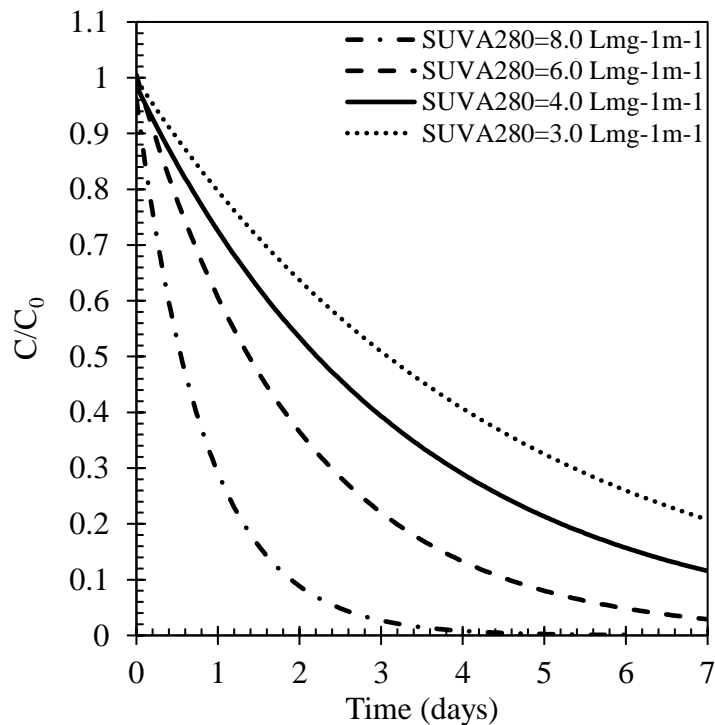


Figure 4.2. Predicted change in relative monochloramine concentration (C/C_0) over time for different initial SUVA_{280} at 30°C, [DOC]= 30mg/L, $[\text{NH}_2\text{Cl}]$ =2.0mg/L, pH=7.0.

4.2.4 Monochloramine interactions with sediments

Monochloramine present in surface waters is also expected to be in contact with sediments. Studies have shown that monochloramine will tend to react directly with carbon and other reduced species present in sediments with negligible absorption-desorption occurring (Chapter 3). In that study, the total oxidant demand of the sediment was used as a measure of all the reduced species found in sediment capable of reacting with monochloramine. This total oxidant demand was measured as the concentration of hypochlorous acid per gram of sediment needed to oxidize all of the reduced species present in the sediment. Others have successfully use this technique to determine the total oxidant demand of dissolved organic carbon in surface water samples (Duirk et. al., 2002, 2005, and 2006). Rate constants for reaction of monochloramine with bottom sediments from a number of surface waters from the region were found to vary exponentially with oxidant demand (OD), with data well-described by the equation:



Implementing the rate constant for the loss of monochloramine in sediments (Eq 4.7) with varying initial oxidant demand allows for predictions of the amount of monochloramine expected to be lost in surface waters due to interactions with sediments (Fig. 4.3). The model demonstrates that small differences in oxidant demand (0.02mMg^{-1}) can have a significant impact in the persistence of monochloramine in sediments. At an oxidant demand of 0.02 mMg^{-1} , monochloramine in overlying water is expected to have an approximate half-life of 1.4 days while at an oxidant demand of 0.04 mMg^{-1} , monochloramine is expected to have a half-life of only 0.4 days.

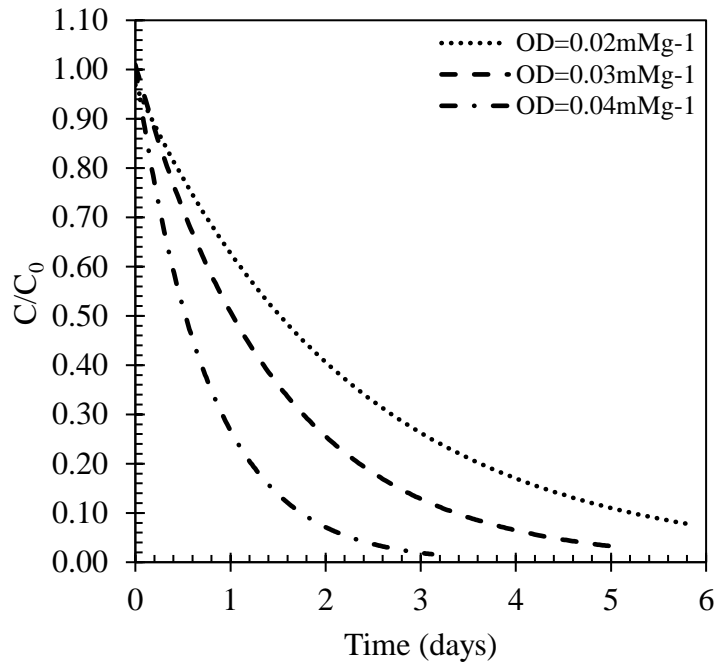


Figure 4.3. Predicted change in relative monochloramine concentration (C/C_0) over time for different total oxidant demand (OD) at 25°C.

At the same time, in Chapter 3 it was introduced the notion that the loss of monochloramine due to interactions with sediments may be limited by the transport of monochloramine across the benthic boundary layer, which will be affected by different mixing conditions. As a result, it was necessary to introduce a transport correction factor of $\tau = 1.4$ to the original rate expression (Eq.4.8). We present model predictions for two hypothetical scenarios, one with constant rapid mixing and another with minimum periodical mixing (Fig. 4.4.). Just as the experimental results presented in Chapter 3, the model predicts that constant rapid mixing will necessarily increase the rate of reaction of monochloramine with sediments.

$$\frac{d[NH_2Cl]}{dt} = \tau k_{sed} \quad (4.8)$$

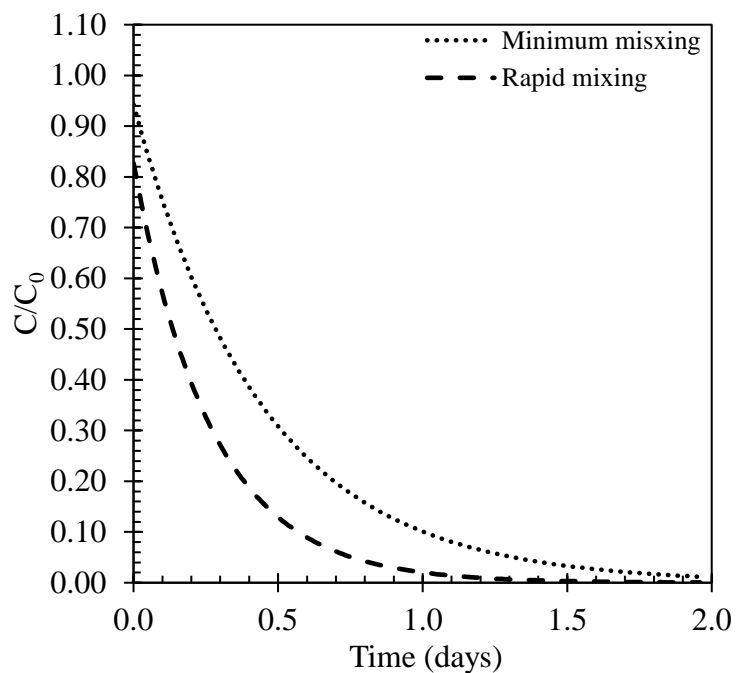


Fig. 4.4. Predicted change in relative monochloramine concentration (C/C_0) in sediment under two different mixing conditions. Oxidant demand = 0.04 mg^{-1} , $T=25^\circ\text{C}$.

4.3 Model for the environmental fate and transport of monochloramine in surface

waters

A comprehensive model for the environmental fate and transport of monochloramine is presented here. The model builds on previous models describing the formation and auto-decomposition of monochloramine by incorporating other monochloramine loss mechanisms of environmental relevance. The stability and persistence of monochloramine in surface waters described here is thus being determined by several processes, including the formation and auto-decomposition of monochloramine (Jafvert and Valentine, 1992; Ozekin et al. 1996). Equations 3-6 of Table 4.1 were not considered given that those reactions are negligible under environmental conditions. Monochloramine transfer from the aqueous phase into the gas phase was also incorporated

(Garcia and Anderson, 2018, Chapter 2), along with monochloramine reactions with dissolved organic carbon and monochloramine interactions with sediments (Chapter 3). The key differential equations making up the model (Eq.4.9-4.11) were solved using the second-order Heun method with a time step of 0.001minutes.

$$\frac{d[NH_2Cl]}{dt} = +k_1[HOCl][NH_3] - k_2[NH_2Cl] - k_7[NH_2Cl][DOC] - \tau k_{sed}[NH_2Cl] - [NH_2Cl] \left(\frac{1}{\frac{\delta_w}{D_w} + \frac{\delta_a}{(D_w \cdot H)}} \right) / d \quad (4.9)$$

$$\frac{d[NH_3]}{dt} = -k_1[[HOCl][NH_3] + k_2[NH_2Cl] + k_7[NH_2Cl][DOC] \quad (4.10)$$

$$\frac{d[HOCl]}{dt} = -k_1[HOCl][NH_3] + k_2[NH_2Cl] - k_8[HOCl][DOC] \quad (4.11)$$

4.4 Model validation

In order to validate the proposed model, monochloramine concentrations were measured in the Santa Ana River and the New River in California to assess monochloramine attenuation as it was transported in these two rivers. Samples were collected from the Santa Ana River and the New River on May 15th, 2016 and May 26th, 2016, respectively. There were five different sampling locations in the Santa Ana River covering 4.8 km and 6 different sampling locations in the New River covering 5.63 km (Fig. 4.5). 1L amber glass bottles were filled with water and placed in ice for transportation. Physicochemical properties of these two rivers were measured 3hrs after collection, results are shown in Table 4.2. The Santa Ana River constantly receives tertiary treated wastewater and the New River receives chlorinated primary-treated wastewater from Mexico with some secondary treated wastewater from the US. The average flow rate of each river along with the distance of sample collection from an arbitrary starting point serve as the basis for calculating transport times. The physicochemical conditions were used in the model to

compare model predictions with field data (Fig. 4.6). The model was found to be in good agreement with the Santa Ana River and the New River, with relative root-mean-square error values below 0.06.



Figure 4.5. Sample location in a) Santa Ana River and b) New River

Table 4.2. Characteristics of sampled rivers

Water	Flow velocity (m/sec)	Temp. (°C)	[DOC] (mg/L)	SUVA ₂₈₀ (Lm ⁻¹ mg-C ⁻¹)	Oxidant Demand (mM/g)	pH	Avg. depth (m)	Wind speed (cm/sec)
Santa Ana River	0.38	31	42.4	2.7	0.02	7.5	0.30	100
New River	1.04	24	27.2	7.5	0.13	7.2	1.00	50

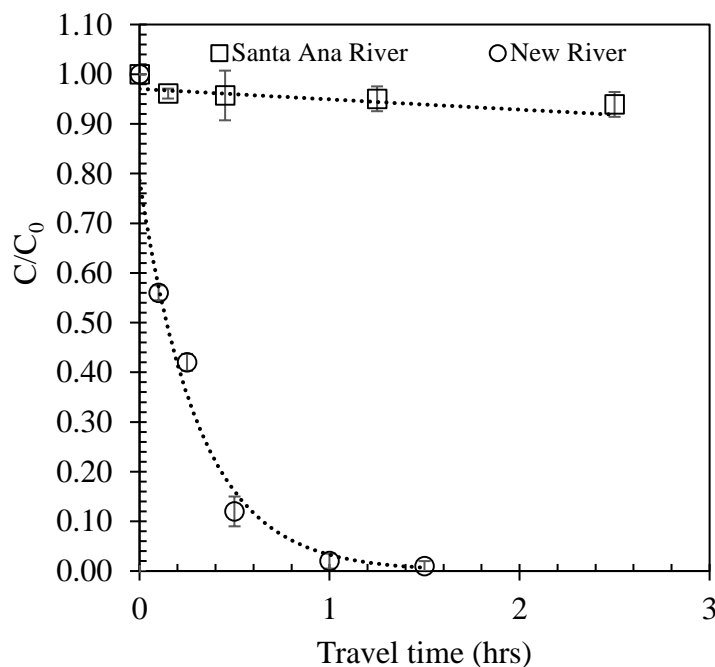


Fig 4.6. Change in relative monochloramine concentration (C/C_0) over time in the Santa Ana River ($[\text{NH}_2\text{Cl}] = 16 \mu\text{g/L}$) and the New River ($[\text{NH}_2\text{Cl}] = 72 \mu\text{g/L}$). Dotted lines represent model predictions.

Monochloramine was found to be much more persistent in the Santa Ana River than in the New River (Fig. 4.6), with half-life values of about 30 hrs and 0.2 hrs respectively. The predicted contribution of each loss mechanism is shown in Table 4.3. This model predicts that monochloramine auto-decomposition accounted for approximately 10% of monochloramine loss in both rivers. Loss due to volatilization differed strongly for the two systems with volatilization accounting for 30% of monochloramine loss in the Santa Ana River while just 5% loss in the New River. The reaction of monochloramine with DOC was found to be a more important loss mechanism in the New River than the Santa Ana

River. This was expected, given that the New River water has DOC of higher reactivity. Monochloramine reactions with DOC accounted for 15% of the loss in the Santa Ana River and 42% in the New River. Finally, monochloramine losses through interactions with sediments were comparable in both rivers (45% in the Santa Ana River and 43% in the New River) (Table 4.3).

A notable difference between the results presented here and previous models describing the persistence of monochloramine in water distribution systems is the significance of auto-decomposition in the overall loss rate of monochloramine. Models like this assume monochloramine loss to be driven by auto-decomposition and reactions with DOC. While Duirk et al. (2005) indicate auto-decomposition accounting for 35.9-27.9% of the total monochloramine loss in samples with $SUVA_{280}$ values between 1.6 and 3.2 $m^{-1}L\ mg-C^{-1}$, our results show that monochloramine auto-decomposition will only account for about 10% monochloramine loss in surface waters with $SUVA_{280}$ values of 2.7-7.5 $m^{-1}L\ mg-C$. In addition to this, Duirk et al. (2005) reported monochloramine losses due to reactions with DOC in water distribution systems as accounting for 64.1-72.1% of the total loss. Our study suggests that reactions with DOC will account for 15%-42% of total monochloramine loss in surface waters. With this in mind, it is clear that environmental loss mechanisms such as volatilization, reactions with sediments, and reactions with DOC of higher concentration and reactivity lower the expected persistence of monochloramine compared to the case in water distribution systems where monochloramine is assumed to decay only due to auto-decomposition and reactions with DOC.

Table 4.3. Percent monochloramine loss for different mechanism

Loss mechanism	Santa Ana River	New River
Auto-decomposition	10%	10%
Volatilization	30%	5%
Reactions with DOC	15%	42%
Reactions with sediments	45%	43%
Half-life (hrs)	30	0.2

These results can also provide some clues to the monochloramine byproducts being formed in surface waters. In the Santa Ana River, there was a total of 60% monochloramine lost through reactions with DOC and reduced species in sediments. Of that amount, the model predicts that only 4% of monochloramine will oxidize organic matter while the remaining 96% will contribute to DOC chlorination. Chlorination reactions with DOC can be expected to yield chloroacetic acid, chloroform, and other compounds. On the other hand, in the New River there was a total of 84% monochloramine lost through reactions with DOC and reduced species in sediments. Of the amount reacting with DOC and sediments, the model predicts that 88% of monochloramine will oxidize organic matter while the remaining 12% will contribute to DOC chlorination. These estimates indicate that of the total monochloramine present in the Santa Ana River, approximately 2% will oxidize DOC and 57% will contribute to the formation of chlorinated organic compounds. In the New River, 74% of the total monochloramine will oxidize DOC while 10% will contribute to the formation of chlorinated organic compounds.

4.5 Conclusions

Development and application of a model for monochloramine loss that incorporates auto-decomposition, volatilization, reactions with DOC, and interactions with sediments provides new insights into the persistence and fate and transport of monochloramine in surface waters. The model developed in this study was found to be in good agreement with field data for the Santa Ana River and the New River, with relative root-mean-square error values below 0.06. Monochloramine auto-decomposition accounted for 10% monochloramine loss in both rivers. The loss of monochloramine due to volatilization was 5.5 times more significant in the Santa Ana River than in the New River. This can be explained by the shallowness and higher average wind velocity of the Santa Ana River at the time of sampling. The model suggests that monochloramine loss due to interaction with sediments has the potential to be a significant competing mechanism with monochloramine loss due to reactions with dissolved organic carbon in the water phase. However, this may be of significance only in shallow river systems, where the close proximity of the sediment surface and rapid mixing conditions will permit constant contact between monochloramine and the sediments. In the case of deep waters such as lakes, the loss of monochloramine due to interactions with the sediments will be of less importance.

Previous models for the fate and transport of monochloramine in water distribution systems do not take into consideration environmental loss pathways such as volatilization, reactions with DOC of higher concentration and reactivity than found in treated drinking water, and interactions with sediments. As a result, those models predict that monochloramine oxidation is almost negligible and that the majority of monochloramine

is lost through chlorination of DOC, resulting in the formation of chlorinated organic compounds. The model presented here proposes that the predominance of DOC oxidation versus chlorination and thus the predominance in formation of chlorinated organic compounds varies among different surface waters with DOC of different reactivity. In the case of the Santa Ana River, 2% of the total monochloramine is expected to oxidize DOC while 57% is expected to contribute to DOC chlorination. In the New River, of the total monochloramine, 74% is expected to oxidize DOC while only 10% is expected to contribute to DOC oxidation. This indicates that in the presence of DOC of relative low reactivity, such as in the Santa Ana River, monochloramine will be more stable than in a system containing DOC of higher reactivity, such as in the New River. This suggest that monochloramine has the potential of forming almost six times more chlorinated organic compounds in the Santa Ana River than in the New River where the majority of monochloramine is consumed rapidly through DOC oxidation. With this in mind, the effect of chlorinated organic compounds would be more of a concern in the Santa Ana River than the New River and the longer persistence of monochloramine may result in greater downstream impacts to bacterial and algal communities.

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Chapter 5: General Conclusions and Future Work.

5.1 The Henry's Constant of Monochloramine

Although volatilization has been ignored when assessing the stability of monochloramine in close environments such as in water distribution systems, the work presented here hints at the possibility that monochloramine volatilization can be an important loss mechanism in open environmental systems. The obtained non-dimensional Henry's constant of monochloramine suggests that monochloramine possesses semi-volatile properties and that it is considerably more volatile than ammonia. With this in mind, it is expected that the high mixing conditions of many rivers and other surface waters will promote considerable losses of monochloramine into the air.

The dimensionless Henry's constant for monochloramine has been reported once before at a value considerably lower than the results of this study. In this study, the experimentally obtained Henry's constant for monochloramine was found to be in better agreement with a value estimated from structure-activity relationships than the previously reported value.

5.2 Monochloramine interactions with organic matter from surface waters.

Many studies have reported models for the interactions between monochloramine and organic matter in water distribution systems. However, none of these models have considered environmentally relevant conditions and how higher dissolved organic carbon concentrations and of different reactivity will affect the stability of monochloramine in surface waters. This study conducted an assessment of the stability of monochloramine in surface waters samples with DOC concentrations ranging from 19.7 to 47.1 mg/L. The

specific UV absorption of the water samples at 280nm (SUVA₂₈₀) was found as an adequate proxy to estimate the reactivity of monochloramine towards DOC. Results confirmed that monochloramine reacts with DOC via two pathways, DOC oxidation followed by DOC chlorination. Monochloramine only participates in the oxidation of DOC while the generated hypochlorous acid is responsible for DOC chlorination.

Unlike previous studies reporting the stability of monochloramine in the presence of DOC in water distributions systems, results here suggest that the degree of oxidation versus chlorination is dependent on the specific aromaticity of the sample in questions. It was found that lower initial SUVA₂₈₀ will tend to favor chlorination of organic matter while higher initial SUVA₂₈₀ will favor oxidation of organic matter.

5.3 Model for the fate and transport of monochloramine in surface waters.

Previous models describing the stability of monochloramine were developed to predict the persistence of monochloramine in water distribution systems with the goal of ensuring proper chlorine residuals and minimizing the formation of undesirable disinfection byproducts. Unfortunately, very few efforts have been dedicated to assessing the stability of monochloramine in natural systems where monochloramine and its byproducts can negatively affect aquatic environments. Current models consider monochloramine formation and auto-decomposition, have neglected monochloramine volatilization and interaction with sediments and have only represented monochloramine interactions with organic matter under relatively low DOC concentrations. The model presented here has better represented the environmental fate and transport of monochloramine by incorporating monochloramine volatilization and interactions with

sediments as relevant loss mechanisms and by assessing the stability of monochloramine in the presence of DOC under more environmentally relevant conditions. The model presented here was validated with field data from the Santa Ana River and the New River in Southern California. The model was found to be in good agreement with field data with root-mean-square error values below 0.06.

5.4 Future work

The results presented here have broadened our understanding of the environmental, persistence fate and transport of monochloramine in surface water receiving treated wastewater. The presented model is capable of accurately predicting the stability of monochloramine in different surface waters and has the potential to predict the formation of monochloramine byproducts. Future work should be focused on applying the results presented here to predict the concentration and specific type of monochloramine byproducts that have the potential to form in surface waters receiving treated wastewater. This knowledge has the potential to assist toxicologists in determining the specific effects that monochloramine may have on aquatic environments.