

ACKNOWLEDGEMENTS

I would like to acknowledge many of my friends and coworkers for contributing to this project with their advice. I would also like to thank Randall Goodman and the UNC machine shop as well Dr. Vikesland's research team for technical support in constructing the Pipe Section Reactor. Thanks are due to Dr. Weidong Zhang for sharing his past experiences with the reactor and to his employer Hazen & Sawyer in agreement with the City of Raleigh for sponsoring this work.

Many thanks are owed to my advising committee for their careful consideration of my technical report in review. Their efforts not only improved the quality of my report but my critical and analytical skills as well. Special thanks are reserved for my advisor, Dr. DiGiano for teaching me how to write with more clarity and precision, how to analyze my results with greater scrutiny and for the confidence that comes with being able to defend my research. I would be remiss if I didn't also thank my advisor for teaching me the art and science behind good home-made gnocchi. I extend my warmest gratitude to my dear Roxana for her patience, encouragement and support.

ABSTRACT

Many utilities have switched from free chlorine to chloramine as a residual disinfectant to avoid formation of disinfection by-products in the distribution system (DS). While not generally appreciated, chloramines undergo autodecomposition, decaying to inert ionic species, thereby losing their disinfecting capacity. The decay process may be accelerated in the distribution system both in the bulk water phase and at the pipe wall. In the bulk phase, autodecomposition may be catalyzed by and chloramines may be reduced by natural organic matter as well as metallic species. At the pipe wall, chloramine decay may be accelerated by a complex set of catalyzing interactions and redox reactions with corrosion deposits, fresh metal surfaces, cement linings and biofilm. These facts suggest that chloramine is not a stable disinfectant and loss of residual within the DS can be problematic. Little is known about the rate of chloramine decay in the DS. Existing water quality models such as EPANET incorporate rate data of free chlorine decay to predict disinfectant residuals. The analogous rate data for chloramine decay rates in bulk water and at the pipe wall are needed for these models to predict chloramine residual throughout the DS.

A general rate model has been derived for free chlorine decay at the pipe wall in which an intrinsic wall reaction rate may be input into DS water quality models. Research thus far on free chlorine decay has shown that the wall reaction rate is much greater than the decay rate in the bulk water. It is reasonable to expect similar behavior for chloramine decay although no quantitative assessments are available in the literature. Moreover, the wall reaction rate for chloramine may depend upon several important system characteristics: 1) pipe material because corrosion releases Fe(II) that chemically

reduces chloramines, 2) water velocity because it may control mass transfer of chloramines to the pipe wall, 3) pH because many decay pathways are expected to be pH dependent and 4) temperature because reaction rates generally increase with temperature but the extent will depend on activation energies.

The purpose of this research was to measure the rate of decay of chloramines in bulk water and at the pipe wall using water and pipe samples obtained from the City of Raleigh. The rate of chloramine decay in the bulk phase was measured in batch rate tests with both finished water and water obtained from various locations in the Raleigh DS. A Pipe Section Reactor (PSR) that was developed at the University of North Carolina (UNC) for quantifying the rate of wall decay for free chlorine was used for the analogous measurement of chloramine decay rate. The PSR requires a small section of pipe (<2 ft) that is fitted with an apparatus to control water velocity thus enabling measurement of the disinfectant decay rate as a function of water velocity.

Batch samples of water from the Raleigh DS were placed into the PSR and the chloramine decay rate was measured. The effects of pipe material, pH and temperature on decay rate were measured. The two pipe materials were old tuberculated cast iron (CIP) and new cement lined ductile iron pipe (DIP). The wall reaction rate was more than one order of magnitude faster on CIP than DIP; this is expected because the presence of Fe(II) from CIP should accelerate the decay rate. Decay in both of the pipe sections, however, was significantly faster than in chloramine demand-free containers indicating that chloramine decay is greatly accelerated by either pipe wall material. As an example, 3600 hours was required for chloramine to decay from 3 to 1 mg/L in bulk water compared to only 65 hours in the presence of the DIP and only 3 hours in the

presence of the CIP wall. Increasing the water velocity from 0.26 ft/s to 1.36 ft/s caused the chloramine decay rate to double for CIP. Thus, mass transfer of chloramine between the bulk water and the wall limits the reaction rate. In contrast, the decay rate was independent of water velocity for DIP. The lack of a mass transfer limitation in DIP is because the rate of chloramine decay at the wall is slow relative to the rate of mass transfer.

Chloramine decay rates in bulk water and at the pipe were described with either first- or second-order rate models at three pH values, three temperatures and four water velocities. These decay rates were also much lower than those for free chlorine as obtained in early research at UNC. Chloramine is a weaker oxidant than free chlorine. Therefore, the decay rate both in bulk water and at the wall was expected to be lower. Nonetheless, chloramine decay especially in the presence of CI pipe material can lead to significant loss of residual in the DS. The experimental and modeling approach in this work is general and thus may be used by any water utility. Specific experiments, however, may be required because chloramine decay rates are influenced by system specific characteristics such as natural organic matter. The rate constants for chloramine decay in this particular research will be adapted by Hazen and Sawyer as input rate constants for use in the Raleigh DS water quality model to predict chloramine residuals as part of compliance with the EPA's Initial Distribution System Evaluation requirement.

Table of Contents

INTRODUCTION	6
LITERATURE REVIEW	10
Chloramination and Autodecomposition	10
Factors Affecting Chloramine Decay in the Distribution System	14
Natural Organic Matter	14
Iron	16
Pipe Materials	21
Release of Pipe Material Deposits	24
Nitrification	24
Corrosion and Biofilms	27
Chloramine Decay Models in Water Quality Models for DS	28
The EPANET Model	30
Laboratory-scale Techniques to Investigate Disinfectant Wall Reaction	37
METHODS	43
Overview of Laboratory Experiments	43
Water Treatment and Finished Water Quality Characteristics in Raleigh, N.C.	44
The Raleigh Distribution System and Selection of Sampling Locations	45
Laboratory Experiments to Measure Chloramine Decay Rates	48
Rate of Chloramine Decay in Bulk Water	48
Pipe Section Reactor Experiments	50
Pipe Section Reactor	50
Pipe Sections	52
Measurement of Water Velocity	55
Rate of Chloramine Decay in the PSR	58
Iron Release in PSR Experiments	60
Iron Release in the Raleigh DS	61
Analytical Methods	61
RESULTS	65
Decay Rate of Chloramine in Bulk Water	65
Finished Water vs. Samples Taken from Raleigh DS	65
Effect of pH	77
Effect of Temperature	80
Pipe Section Reactor Experiments	86
Measurement of Iron Release	86
Chloramine Decay in the Presence of CIP	92
Effect of Velocity on Observed Chloramine Decay Rate on CIP	96
Effect of pH on Observed Chloramine Decay Rate on CIP	103
Effect of Temperature on Observed Chloramine Decay Rate on CIP	107
Predicting Observed Rate of Decay in CIP	108
Chloramine Decay in the Presence of DIP	110
Effect of Velocity on Observed Chloramine Decay Rate on DIP	114
Effect of pH on Observed Chloramine Decay Rate on DIP	117
Effect of Temperature on Observed Chloramine Decay Rate in DIP	120
Predicting Observed Rate of Decay in DIP	122
Practical Implications of Results for Rate of Chloramine Decay	123

CONCLUSIONS.....	127
REFERENCES	131

Figures

Figure 1 Map of the Raleigh Distribution System Color-Coded by Pipe Material	47
Figure 2 Cut-away section of the Pipe Section Reactor	51
Figure 3 Photo of the cast iron pipe section.....	54
Figure 4 Photo of the cement lined ductile iron pipe section	54
Figure 5 Experimentally observed relationship between water velocity and differential head on inclined manometer	56
Figure 6 Power setting-velocity relationship in the DIP section at 23°C	57
Figure 7 Power setting-velocity relationship in the CIP section at 24°C	58
Figure 8 Test of first-order decay rate of chloramine in bulk water samples taken from the finished water of the EMJWTP and four locations within the DS	66
Figure 9 Test of second-order decay rate of chloramine in bulk water samples taken from the finished water of the EMJWTP and four locations within the DS.....	71
Figure 10 Diagnostic plot of residual error for first order model for finished water sample	73
Figure 11 Diagnostic plot of residual error for first order model for FS1 sample.....	73
Figure 12 Diagnostic plot of residual error for second order model for finished water sample	74
Figure 13 Diagnostic plot of residual error for second order model for FS1 sample	74
Figure 14 Test of first-order rate model for chloramine decay in bulk water: effect of pH and transport in DS	78
Figure 15 Effect of temperature on chloramine decay rate in bulk water at pH 6.....	81
Figure 16 Effect of temperature on chloramine decay rate in bulk water at pH 9; additional experiment included at 30°C and pH 8.5 without addition of buffer (w/o B) .	81
Figure 17 Effect of temperature on chloramine bulk decay rate: determination of activation energies for DS sample and finished water at pH 6	83
Figure 18 Effect of temperature on chloramine bulk decay rate: determination of activation energies for DS sample and finished water at pH 9	83
Figure 19 Iron release from the CIP section used as CMFR at 1.04 fps.....	89
Figure 20 Iron release from the CIP section used as CMFR at 0.22 fps.....	92
Figure 21 Chloramine decay in CIP section at pH 8, 1.36 fps velocity and 22.5°C.....	94
Figure 22 Test of first-order rate model of chloramine decay in PSR with CIP section ..	95
Figure 23 Test of second-order rate model of chloramine decay in PSR with CIP.....	96
Figure 24 Application of first-order rate model of chloramine decay at four simulated velocities in CIP section at pH 8 and 23°C.....	98
Figure 25 First-order decay rate constants versus velocity in CIP section	99
Figure 26 Intrinsic wall reaction rate coefficient, k_w , calculated from the average observed rate of chloramine decay at four water velocities in CIP at pH 8 and 23.5°C.....	102
Figure 27 Application of first-order rate model of chloramine decay at pH 7, 8 and 9 in CIP section at 1.36 fps and 23.5°C	104
Figure 28 Effect of pH on observed first-order decay coefficient in CIP section at 1.36 fps and 23.5°C	104
Figure 29 Effect of pH on the intrinsic wall reaction rate in CIP at 23.5°C	106
Figure 30 Test of first-order model of decay at three temperatures within the CIP section at pH 8 and 1.36 fps.....	107

Figure 31 Effect of temperature on intrinsic wall reaction rate in CIP section: determination of activation energies at pH 8	108
Figure 32 Chloramine decay in DIP section at pH 8, 0.91 fps velocity and 24.5°C	111
Figure 33 Test of first-order rate model of chloramine decay in PSR with DIP section	112
Figure 34 Test of second-order rate model of chloramine decay in PSR with DIP section	113
Figure 35 Application of first-order rate model of chloramine decay at four simulated velocities in DIP section at pH 8, 23.8°C	114
Figure 36 Effect of water velocity on the observed first-order decay rate in DIP at pH 8, 24.6°C	115
Figure 37 Test of first-order model of decay at three pH values within the DIP section at pH 8 and 0.91 fps	118
Figure 38 Effect of pH on observed first-order decay coefficient in DIP section at 1.36 fps and 23.5°C	118
Figure 39 Effect of pH on the intrinsic wall reaction rate in DIP at 24.5°C	119
Figure 40 Test of first-order model of decay at three temperatures within the DIP section at pH 8 and 0.91 fps	120
Figure 41 Effect of temperature on intrinsic wall reaction rate in DIP section: determination of activation energies at pH 8	121
Figure 42 Predicted first-order decay rates in bulk fluid, DIP and CIP at pH 8, 25°C and 0.26 fps simulated water velocity	124

List of Tables

Table 1 Monochloramine autodecomposition reaction scheme adapted from Jafvert and Valentine (1992)	12
Table 2 Finished water quality parameters over the study period	45
Table 3 Temperature, pH and buffer strength of each bulk water rate experiment	50
Table 4 Dimensions of DIP and CIP sections, hydraulic radius and hold-up volume.....	55
Table 5 Summary of results of batch experiments to test first order decay model for chloramine in bulk water at room temperature (22.5°C)	67
Table 6 Comparison of pseudo-first- and second-order rate models for chloramine decay in bulk water	71
Table 7 Second-order rate constants for chloramine decay in finished water samples taken from water utilities in five U.S. cities (Valentine et al. 1998)	75
Table 8 The effect of pH and transport in DS on pseudo first-order rate constant for chloramine decay in bulk water	79
Table 9 Pseudo second-order rate constants for data plotted in Figure 10: effect of pH and transport in DS	79
Table 10 Summary of pseudo-first order rate constants at three temperatures at pH 6 and pH 9.....	82
Table 11 Calculated Activation Energies for Chloramine Decay in Bulk Water Based on Rate Data at Temperatures of 12, 22.5 and 30 °C and Arrhenius Equation	85
Table 12 First-order constants for the observed rate of chloramine decay in the presence of CIP at pH 8, 1.36 fps and 22.5°C	95
Table 13 Dimensionless Groups used to calculate k_f for each simulated water velocity in CIP Section at 25°C	101
Table 14 Equations for predicting observed rate of decay in cast iron pipe	110
Table 15 First-order rate constants for chloramine decay in the presence of DIP	112
Table 16 Second-order rate constants for chloramine decay in the presence of DIP	113
Table 17 Equations for Predicting Observed Rate of Decay in DIP.....	123

INTRODUCTION

Many utilities have switched from free chlorine to chloramine as a residual disinfectant to reduce the levels of trihalomethanes and haloacetic acids formed in the distribution system (DS). While not generally appreciated, chloramines undergo autodecomposition in the absence of other oxidizable substances, decaying to inert ionic species, thereby losing their disinfecting capacity. The decay process may be accelerated in the DS both in the bulk water phase and at the pipe wall. In the bulk phase, autodecomposition may be catalyzed by and chloramines may be reduced by natural organic matter as well as metallic species.

Chloramine decay may be accelerated at the pipe wall by a complex set of catalyzing interactions and redox reactions with corrosion deposits, fresh metal surfaces, cement linings and biofilm. Reduction reactions at pipe surfaces have already been shown to increase the total loss rate of free chlorine residual by an order of magnitude or more. Iron based pipes are prone to corrosion and chlorinous disinfectants may be reduced in the corrosion process. With time, corrosion scales, consisting of ferrous and ferric minerals, may form. Dissolution of these scales is controlled by interplay among pH, carbonate and dissolved iron concentrations. Both dissolved Fe(II) and Fe(III) may accelerate chloramine decay. Cement-line ductile iron pipe may also be reactive towards chlorinous disinfectants. Aluminosilicates are the principal component of cement based pipes and are known to act as heterogeneous catalysts of certain redox reactions. While considered widely as inert, even polymeric pipe materials can cause disinfectant loss.

Although recent research has addressed free chlorine reduction at pipe surfaces, very little is known about the analogous reactions of chloramine. Existing water quality

models such as EPANET incorporate rate data of free chlorine decay to predict disinfectant residuals. The analogous rate data for chloramine decay rates in bulk water and at the pipe surfaces are needed for these models to predict chloramine residual throughout the DS.

Unlike simple rate experiments of disinfectant decay in the bulk phase, in disinfectant-demand free containers, the rate of decay caused by reaction with pipe surface material is much more difficult to measure. The rate of surface reaction, or "wall" reaction as is commonly found in the literature, has been determined indirectly from field measurements in DS whereby the total loss of free chlorine residual is measured between two points and the loss by bulk decay is subtracted. Another technique is to use such field data for total loss of residual in a water quality model of the DS that includes both bulk water and pipe wall decay rates. The model is used to find the wall reaction rate constant that best describes these field data. While this method has met with some success, it lacks a firm foundation in kinetic principles. For instance, both first- and zero-order rate models have been used to describe the same data set. A major drawback of field data in testing of rate models is that the physical and chemical conditions within the DS are seldom constant. Variations in water velocity, pH, temperature, dissolved oxygen and the chemical composition of corrosion scales and pipe materials may all strongly influence the rate of disinfectant decay.

Bench-scale reactors overcome the limitation of field-based methods by providing a well-controlled pipe surface environment. A Pipe Section Reactor (PSR) was developed at the University of North Carolina (UNC) for quantifying the rate of wall decay for free chlorine (DiGiano and Zhang 2005). This reactor requires a small section

of pipe (<2 ft) that is modified by insertion of stirrer and stirring motor in such a way as to permit measurement of the disinfectant decay rate as a function of water velocity. Small batches of water are used in which the chemical characteristics and temperature can be easily controlled.

The PSR was used by Zhang and DiGiano (2005) to show that the rate of free chlorine decay due to reaction at the surface of unlined cast iron was zero-order with respect to chlorine concentration. This rate model is reasonable if the reaction is controlled by the rate of corrosion product generation at the pipe wall. In sharp contrast, the rate of chlorine decay at the surface of cement lined ductile iron pipe was first-order with respect to chlorine concentration. Decay of free chlorine in the presence of either type of pipe material was much faster than bulk decay. This result is very important because it showed quantitatively that wall reactions can account for most of disinfectant loss in the DS.

The goal of research in this report was to adopt the PSR to explore the factors that influence reduction of chloramine at pipe surfaces and to develop a rate model. The rate model description was needed for implementation of a water quality model of the DS for the City of Raleigh, N.C. The specific objectives were:

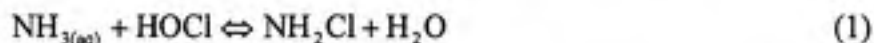
- Establish a rate model for chloramine decay in bulk water from samples of finished water at the E.M. Johnson Water Treatment Plant and at points within the DS
- Determine the effects of pH and temperature on the rate constant in the chloramine decay model for bulk water

- Establish a rate model for chloramine decay at the pipe surface using the PSR, wherein rate data were collected for an old, heavily tuberculated cast iron pipe and a new, cement lined ductile iron pipe section
- Determine the effect of water velocity, pH and temperature on the rate constant for the chloramine wall reaction
- Formulate a set of equations base on the rate model results for use in a water quality model of the DS by the City of Raleigh

LITERATURE REVIEW

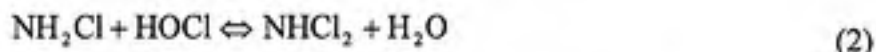
Chloramination and Autodecomposition

Monochloramine is formed in water in a process known as chloramination by a rapid reaction between hypochlorous acid and ammonia that is described by:

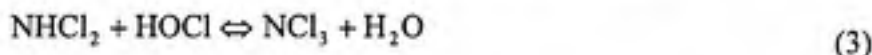


The second-order rate constant for this reaction was reported by Morris and Isaac (1983) to be $1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$ but more recent kinetic experiments using stop flow spectrophotometry (Qiang and Adams 2004) gave a smaller rate constant (1.1×10^{10} at 25°C). These later investigators noted that the rate constant given by Morris and Isaac (1983) could be inaccurate because it was determined from rate data of other researchers that was obtained over a wide range of pH and temperature. The pH is relevant because the speciation of both reactants, HOCl ($\text{pK}_a = 7.5$) and NH_3 ($\text{pK}_a = 9.3$), is pH dependent so the rate of monochloramine formation will also depend on pH.

Further reaction with hypochlorous acid will convert monochloramine into dichloramine:



and dichloramine into nitrogen trichloride (trichloramine):



The speciation of these increasingly chlorinated compounds depends on the Cl to N molar ratio. Monochloramine is the dominant species at Cl:N molar ratios below 1:1. Above 1:1 di- and trichloramine production will increase. However, the concentration of these species also depends on their stability in solution. Both di- and trichloramine are

relatively reactive and unstable in comparison to monochloramine. Trichloramine for example decays readily in solution by electron transfer leading to the oxidation of ammonia and the reduction of chlorine to the chloride ion. Thus while dichloramine may exist at measurable concentrations for high molar ratios, between 1.5:1 and 2:1, trichloramine will only ever exist in trace amounts. Above molar ratios of 2:1 all $\text{NH}_3(\text{aq})$ is oxidized to nitrogen gas or to nitrate (Snoeyink and Jenkins 1980). This is typically referred to as the breakpoint reaction where the disinfectant residual produced by combined chlorine disappears.

Jafvert and Valentine (1992) proposed a complex set of reactions that describe the autodecomposition pathways of monochloramine and these are summarized in Table 1. In this set of reactions, monochloramine autodecomposition is primarily limited by the rate of formation of the highly reactive dichloramine molecule. Dichloramine is formed by two pathways. First, hypochlorous acid that is produced by monochloramine hydrolysis in Equation 4 can react with monochloramine to produce dichloramine (Equation 2). The second pathway leading to dichloramine is the disproportionation reaction given by Equation 6 in which two monochloramine molecules are involved. The disproportionation reaction is more important if the free ammonia concentration is high. This is because hypochlorous acid produced by hydrolysis of monochloramine (Equation 4) reacts readily with free ammonia to form more monochloramine. Dichloramine formation leads to rapid chloramine loss by redox reactions (Equations 8 through 10), via formation of the unidentified product I and a slower redox reaction with monochloramine (Equation 11). Note that Equations 1 and 2 are the same as those from above and that Equations 4 and 5 are their reverse, respectively.

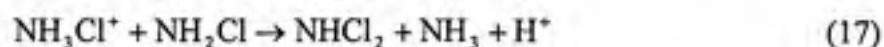
Table 1 Monochloramine autodecomposition reaction scheme adapted from Jafvert and Valentine (1992)

Equation Number and Reaction	Rate/Equilibrium Constant	Reference
1 $\text{HOCl} + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{H}_2\text{O}$	$k_1 = 1.5 \times 10^{10} \text{ M}^{-1} \text{ h}^{-1}$	Morris and Isaac (1983)
2 $\text{HOCl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{H}_2\text{O}$	$k_2 = 1.0 \times 10^6 \text{ M}^{-1} \text{ h}^{-1}$	Margerum et al. (1978)
4 $\text{NH}_2\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_3$	$k_3 = 7.6 \times 10^{-2} \text{ h}^{-1}$	Morris and Isaac (1983)
5 $\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{NH}_2\text{Cl}$	$k_4 = 2.3 \times 10^{-3} \text{ h}^{-1}$	Margerum et al. (1978)
6 $\text{NH}_2\text{Cl} + \text{NH}_2\text{Cl} \rightarrow \text{NHCl}_2 + \text{NH}_3$	k_d	Valentine and Jafvert (1988)
7 $\text{NHCl}_2 + \text{NH}_3 \rightarrow \text{NH}_2\text{Cl} + \text{NH}_2\text{Cl}$	$k_6 = 2.2 \times 10^8 \text{ M}^{-2} \text{ h}^{-1}$	Hand and Margerum (1983)
8 $\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{I}$	$k_7 = 4.0 \times 10^5 \text{ M}^{-1} \text{ h}^{-1}$	Jafvert and Valentine (1987)
9 $\text{I} + \text{NHCl}_2 \rightarrow \text{HOCl} + \text{products}$	$k_8 = 1.0 \times 10^8 \text{ M}^{-1} \text{ h}^{-1}$	Leao (1981)
10 $\text{I} + \text{NH}_2\text{Cl} \rightarrow \text{products}$	$k_9 = 3.0 \times 10^7 \text{ M}^{-1} \text{ h}^{-1}$	Leao (1981)
11 $\text{NH}_2\text{Cl} + \text{NHCl}_2 \rightarrow \text{products}$	$k_{10} = 55.0 \text{ M}^{-1} \text{ h}^{-1}$	Leao (1981)
12 $\text{HOCl} \rightleftharpoons \text{H}^+ + \text{OCl}^-$	$\text{pK}_a = 7.5$	Snoeyink and Jenkins (1980)
13 $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$	$\text{pK}_a = 9.3$	Snoeyink and Jenkins (1980)
14 $\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	$\text{pK}_a = 6.3$	Snoeyink and Jenkins (1980)
15 $\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}^+$	$\text{pK}_a = 7.5$	Snoeyink and Jenkins (1980)

The disproportionation reaction (Equation 6) is believed to be general acid catalyzed. Equation 6 represents the sum of two reactions. The first of these is a reversible reaction between a proton donor, i.e. a hydronium ion or an undissociated acid, and monochloramine that produces the monochlorammonium ion (NH_3Cl^+):



The second reaction is an irreversible reaction between the monochlorammonium ion and monochloramine to produce dichloramine and free ammonia:



Adding Equations 16 and 17 together gives Equation 6.

The rate constant for the disproportionation reaction (Equation 6) has been estimated as a function of all proton-donating molecules (Valentine and Jafvert 1988):

$$k_d = k_{H^+}[H^+] + \sum_i k_i[HA_i] \quad (18)$$

Valentine and Jafvert (1998) suggested a dependence of the monochloramine autodecomposition rate on total carbonate concentration. This dependence, which was later quantified by Vikesland et al. (2001), was attributed to the general acid catalyzed disproportionation reaction. According to the preceding reaction scheme, monochloramine decays in the absence of other reactive species by pathways that are dependent upon pH, temperature, free ammonia concentration, Cl:N molar ratio and alkalinity.

Valentine et al. (1998) successfully modeled chloramine decay in real and simulated finished waters as second-order with respect to chloramine concentration:

$$-\frac{dC}{dt} = k_{vcsc} C^2 \quad (19)$$

where k_{vcsc} is referred to as the Valentine Chloramine Stability Constant. The reaction scheme of Jafvert and Valentine (1992), as given in Table 1, was used to derive a second-order rate model. In this scheme, two major pathways lead to formation of the highly reactive and unstable dichloramine molecule. These are the acid catalyzed disproportionation reaction given by Equation 6 and a reaction between HOCl and monochloramine given by Equation 2. HOCl is produced by monochloramine hydrolysis (Equation 4). These three reactions were included together with the rapid reaction between mono- and dichloramine that leads to decomposition. All were considered

elementary reactions in the kinetic analysis. The resulting observed rate constant, k_{obs} (equivalent to k_{VCS}), is :

$$k_{obs} = 3 \sum_i k_i [HA_i] + 2 \frac{k_2 (k_4/k_1)}{[NH_3]} \quad (20)$$

The first term represents the sum of all proton donors that are present in a typical drinking water:

$$\sum_i k_i [HA_i] = k_{H^+} [H^+] + k_{H_2CO_3} [H_2CO_3] + k_{HCO_3^-} [HCO_3^-] \quad (21)$$

where k_{H^+} is the specific rate constant for the hydronium ion ($2.5 \times 10^7 M^{-2} h^{-1}$);

$k_{H_2CO_3} = 4 \times 10^4 M^{-2} h^{-1}$ and $k_{HCO_3^-} = 800 M^{-2} h^{-1}$. The first term of Equation 20 accounts for acid catalysis of disproportionation and predominates in most finished waters. The second term in Equation 20 accounts for hydrolysis and the equilibrium concentration of free chlorine. As free ammonia increases, the free chlorine concentration decreases; NH_3 appears in the denominator for this reason.

Factors Affecting Chloramine Decay in the Distribution System

Natural Organic Matter

Natural organic matter (NOM) is widely present in surface waters and in some ground waters that are under the influence of surface waters. NOM has been shown to exert a significant oxidant demand that increases the rate of chloramine decomposition (Vikesland et al. 1998; Duirk et al. 2005). In addition to exerting an oxidant demand, NOM can act as a general acid catalyst (Perdue and Wolfe 1982) and hence may catalyze monochloramine autodecomposition. The reaction of monochloramine with NOM

sometimes leads to the formation of halogenated disinfection by-products (Cowman and Singer 1996; Duirk et al. 2002).

NOM has been shown to act as a bi-phasic reductant. That is, a major fraction of NOM reacts very fast with oxidants while a smaller fraction reacts much more slowly (Qualls and Johnson 1983, Vikesland et al. 1998, Duirk et al. 2002, Duirk et al. 2005). With regard specifically to monochloramine as the oxidant, the rapid initial oxidant demand may be the result of direct reactions between specific reactive sites on the NOM molecule and monochloramine. However, the slower oxidant demand may be the result of reactions between hypochlorous acid, a product of monochloramine hydrolysis, and another specific set of reactive NOM sites (Vikesland et al. 1998; Duirk et al. 2002; Duirk et al. 2005). The reactive sites on NOM are postulated to have acid-base characteristics which explains the dependency of chloramine demand kinetics on pH (Duirk et al. 2002).

Duirk et al. (2005) correlated the fraction of reactive sites on the NOM molecule that chemically reduce chloramine over long reaction periods to the specific ultraviolet absorbance at 280 nm ($SUVA_{280}$). The $SUVA_{280}$ is the ratio of the UV absorbance (with a 1 cm cell path) over the dissolved organic carbon concentration in mg/L. Hydrophobic structures within the heterogeneous molecular formation of NOM absorb UV light at 280nm. Thus, $SUVA_{280}$ is a measure of the ratio of hydrophobic structures to all chemical structures of NOM. Duirk et al. used the bi-phasic decay model and the $SUVA_{280}$ to predict the monochloramine decay kinetics in NOM bearing waters.

According to the bi-phasic reaction model, the rapid initial rate of decay of monochloramine would most likely be observed in the clear well of the water treatment

plant after addition of ammonia to free chlorine to produce monochloramine. The slower rate of monochloramine decay, would be observed within the DS and be dependent upon generation of HOCl by monochloramine hydrolysis.

NOM is typically present in the finished water of a water treatment plant. However, it may also be generated within the DS and subsequently produce a chloramine demand. One possibility is for NOM to accumulate in loose deposits on pipe walls. On instances of scouring, these deposits may exert a considerable oxidant demand (Gauthier et al. 1999).

Iron

Iron in its reduced state as Fe(II) can react with an oxidant such as chloramine. Very low concentrations of iron in oxidized form [Fe(III)] may be present in finished waters (most oxidized iron is removed by precipitation). However, iron can be generated within the DS by corrosion processes. Older cities still have a significant percent of pipe lines that are made of unlined cast iron. Newer cement-lined ductile iron pipe greatly reduces corrosion. However, the cement lining can deteriorate over time and may expose the iron surface beneath to produce corrosion.

The processes by which elemental iron on the pipe wall and reduced iron in scales formed by the corrosion activity can react with chloramine are very complex and still not well understood. Despite considerable efforts to control corrosion by addition of chemical inhibitors such as polyphosphates and by the adjustment of pH to encourage a protective scale formation, corrosion is still a major issue.

Corrosion scales are often referred to as tubercles. They form as a result of ferrous and ferric mineral precipitation over many years. Scale structure and composition

will vary depending on the finished water source. They typically consist of a reddish outer shell of mostly ferric minerals that is dense and hard. This shell can include various iron-containing minerals such as goethite (α -FeOOH), lepidocrocite (γ -FeOOH) and black magnetite (Fe_3O_4). Beneath the outer shell is a softer, relatively porous matrix comprising mostly ferrous mineral such as siderite (FeCO_3) and ferrous hydroxide ($\text{Fe}(\text{OH})_2$) (Benjamin et al. 1996; Sarin et al. 2001). Dissolution of the ferrous phases and diffusional efflux of Fe(II), or physical damage to the outer shell and exposure of ferrous minerals to the bulk water may release significant amounts of reduced iron.

Corrosion scales play a very important role in the chemical and biological quality of water particularly in older, highly corroded iron pipe sections. In most instances, corrosion scale will protect iron pipe by limiting the transfer of electron accepting species to the metal surface thereby reducing the corrosion rate. However, the scale structure comprises electrically conductive material and does not prevent corrosion entirely (Frateur et al. 1999; Sarin et al. 2001).

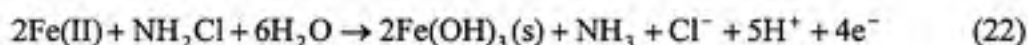
Corrosion scales may be implicated in the occurrence of red water as when pH shifts result in the dissolution of scale minerals, or when scales are hydraulically scoured. Releases of Fe(II) from corrosion scales may accelerate chloramine decay in the bulk fluid. Furthermore, corrosion scales may provide bacteria with protective micro environments, shielding the colonies from disinfectants.

Sarin et al. (2004) made the following observations concerning iron release from a pipe loop made of 70 year old galvanized iron pipe:

- Iron release occurred when ferrous minerals dissolved and water conditions were such that the ferrous ions were allowed to diffuse out of the scale.

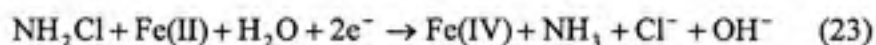
- If dissolved oxygen (DO) or another oxidant such as chloramines were present at the shell surface, they could oxidize dissolved Fe(II), causing it to precipitate at the shell and preventing its release from the scale.
- Anoxic conditions or stagnation would reduce oxidant availability at the shell allowing Fe(II) diffusion out of the scale. This effect would be minimized as water velocity increased.
- Conductivity of the scale minerals supports segregation of the anodic and cathodic components of the electrochemical corrosion couple. Anodic corrosion is balanced by cathodic reduction of either dissolved oxygen or ferric phases in the outer shell.

Not only does corrosion lead to physical destruction of the piping network but equally as important, iron has been shown to play a major role in accelerating the decay of chlorinated disinfectants (Ki  n   et al. 1998; Frateur et al. 1999; Vikesland and Valentine 2000; Vikesland and Valentine 2002). Fe(II) is readily oxidized by monochloramine, producing insoluble ferric hydroxide. Assuming all the oxidizing potential of monochloramine goes to Fe(II) oxidation, the reaction stoichiometry is:



Hydrolysis of monochloramine may produce HOCl, and HOCl may also oxidize Fe(II). However, a direct reaction with monochloramine has been shown to dominate oxidation of Fe(II) in chloraminated waters (Vikesland and Valentine 2000).

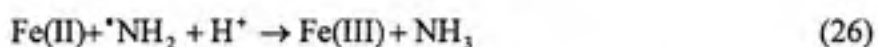
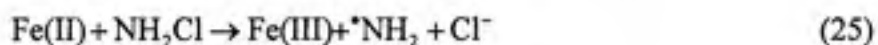
Two reactive pathways may be possible assuming a 2:1 stoichiometric ratio of Fe(II):NH₂Cl (Vikesland and Valentine 2000). In one pathway, the ferrous ion accepts two electrons from the monochloramine molecule forming the ferryl ion Fe(IV):



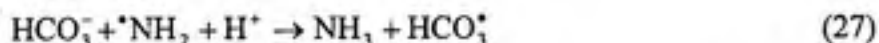
The ferryl ion would rapidly oxidize another ferrous ion.



The second reactive pathway involves sequential one electron-transfer reactions and formation of the amidogen radical, $\cdot\text{NH}_2$:



Vikesland and Valentine (2000) confirmed the existence of the amidogen radical by comparing the electron spin resonance signal produced during oxidation of Fe(II) by chloramines to a theoretical amidogen spectrum. While a 2:1 stoichiometric ratio of Fe(II) to NH_2Cl was possible, the measured ratio was frequently lower. They hypothesized that a stoichiometry ratio of less than 2:1 could be explained by a reaction that consumed the amidogen radical. A series of carefully controlled experiments was conducted in which pH and carbonate concentration were the master variables. The apparent stoichiometry at pH greater than 9.21 was 2:1 but it decreased with decreasing pH and with increasing carbonate concentration. Competing reactions with radical scavengers such as bicarbonate were hypothesized:



As a result, the stoichiometry ratio Fe(II) to NH_2Cl is typically lower than 2:1 in carbonate bearing water.

The oxidation of Fe(II) by NH_2Cl was found to be autocatalytic in that reactions proceeded more rapidly in the presence of ferric precipitate. Vikesland and Valentine (2000) suggested that Fe(II) - NH_2Cl reactions that occur on the surface of ferric

precipitate have a lower activation energy than the same reaction in solution. Thus, the iron-containing surface may act catalytically. In extending their work, Vikesland and Valentine (2002) proposed the following rate relation for the reduction of monochloramine by Fe(II) in the presence of ferric oxide precipitate:

$$-\frac{d[\text{NH}_2\text{Cl}]}{dt} = -\frac{1}{\Theta} \frac{d[\text{Fe(II)}_{\text{tot}}]}{dt} \quad (28)$$

$$= \{k_{\text{NH}_2\text{Cl, soln}} [\text{OH}^-] [\text{Fe(II)}_{\text{soln}}] + k_{\text{NH}_2\text{Cl, surf1}} [> \text{FeOFe}^+] + k_{\text{NH}_2\text{Cl, surf2}} [> \text{FeOFeOH}]\} [\text{NH}_2\text{Cl}]$$

Here, Θ is the experimentally determined reaction stoichiometry which accounts for radical scavenging, $k_{\text{NH}_2\text{Cl, soln}}$ is the rate constant for aqueous phase reactions and $k_{\text{NH}_2\text{Cl, surf1}}$ and $k_{\text{NH}_2\text{Cl, surf2}}$ are rate constants for the heterogeneous reactions between monochloramine and the corresponding surface complexes.

The primary sources of iron in the DS are iron corrosion and dissolution from corrosion deposits. Corrosion of iron based pipe materials is an electrochemical process coupling the anodic release of two electrons by a metallic phase iron atom and subsequent dissolution of that atom:



The necessary cathodic process in which electrons are accepted may include the reduction of dissolved oxygen:



Other cathodic reactions are also possible. Oxidizing disinfectants can act as electron acceptors providing another pathway for disinfectant decay in the DS. Frateur et al. (1999) found that the current density generated by the long-term corrosion of a pure iron

electrode was more anodic in the presence than absence of free chlorine. The implication is that free chlorine was being electrochemically consumed at the iron-water interface. Similarly, Cantor et al. (2003) demonstrated in pipe loop experiments that corrosivity increased in the presence of free chlorine. Equivalent concentrations of chloramine have been shown to be less corrosive towards cast iron than free chlorine (LeChevallier et al. 1990). Less corrosion would be expected by chloramine because it is a less powerful oxidant; the half-cell reduction potential for monochloramine and hypochlorite ion are 1.40 and 1.64 volts, respectively (Snoeyink and Jenkins 1980).

Corrosion of iron based metallic pipes is not the only method of iron release into bulk water in the DS. Indeed, there is often no simple relationship between iron release and iron corrosion (Benjamin et al. 1996). Iron release may be a combination of metallic iron corrosion, dissolution of corrosion scales and hydraulic scouring of corrosion deposits.

Pipe Materials

Iron-based materials include cast iron, ductile iron and steel. The term cast iron describes an iron alloy that is centrifugally cast in a sand or metal mold. Ductile iron pipe (DIP) has been increasingly used in the U.S. since the 1970's. It is a low sulfur, cast iron product with magnesium added to increase its strength (Ysusi 2000). DIP is used widely for pipe diameters ranging from 4 to 60 inches; DIP is available in larger diameters as well. Steel pipes may be manufactured with diameters ranging from 4 to 144 inches. They are primarily used in the U.S. for water mains larger than 24 inches in diameter (Ysusi 2000).

The new iron-based pipes are commonly lined to prevent corrosion and corrosion scale formation; cement mortar linings are common for DIP and for steel. Cement mortar pipes and linings are not susceptible to electrochemical corrosion. However, the lining may erode over time. A complex mixture of ceramic chemistries are used for linings and these vary depending upon the Portland cement source used in manufacturing (LeRoy et al. 1996). The primary components of Portland cement are aluminosilicates although cement also contains varying percentages of lime [$\text{Ca}(\text{OH})_2$] that can leach from the pipe wall to produce a significant increase in solution pH near the pipe wall (Schock 1999).

New shop-applied cement linings range from 1/16 to 1/8 inches thick while cast-in-place linings nominally range from 1/8 to 1/4 inch thick, depending on the pipe diameter (Ysusi 2000). Other commonly applied DIP linings, along with their AWWA material standard are: epoxy (C210), fusion-bonded epoxy (C213) and coal-tar enamel (C203). Each of these has its own potential to react with and catalyze chloramine decomposition. However, little work has been published on the direct reactivity of these materials towards chloramines.

Polyvinyl chloride (PVC) pipes are available in diameters that range from 4 to 36 inches. Many utilities have turned toward PVC for a new DS or for use within existing systems when service is extended to outlying suburban areas. The advantages of PVC over iron-based materials are: elimination of iron corrosion; smooth inner surface that reduces water head loss; and reduced loss of disinfectant at the pipe wall due to its inert nature. Nonetheless, PVC can deteriorate over time and solvents that may be present from leaking underground storage tanks can permeate the wall. High density polyethylene (HDPE) may be an alternative to PVC. Prior to 1992, AWWA approved

HDPE for water distribution only for small pipes as defined by diameters that ranged from ½ to 3 inches. In March, 1992 AWWA promulgated Standard C906 which made HDPE available for use as pipes with diameters ranging from 4 to 63 inches (Ysusi 2000). Polymeric materials in pipes or pipe linings can leach organic compounds, e.g. plasticizers, on initial installation that may be reactive towards oxidants. However, this reactivity would be significantly depleted in the short term (Gotoh 1989; Kiene et al. 1998).

Asbestos cement piping is another pipe material like cast iron that is no longer installed yet remains in service in some places (Ysusi 2000). The main concern with asbestos cement piping is the release of asbestos fibers by hydraulic erosion (Schock 1999).

Numerous authors have observed that disinfectant decay kinetics are much more rapid in real or in a simulated DS than in bulk decay rate experiments (Rossman et al. 1993; Vasconcelos et al. 1997; Maier et al. 2000; Rossman et al. 2001; Hallam et al. 2002; DiGiano and Zhang 2005). The acceleration of disinfectant decay in the DS is attributed to contributory reactions with corrosion products, biofilms and pipe surface materials. The reactivity of various pipe materials toward disinfectants has been evaluated in several studies.

Woolschlager et al. (2001) calibrated a chloramine decay model with data from a year of sampling from cement lined pipe sections in a DS in New Jersey. They found that the extent of chloramine decay was greater than predicted from batch tests conducted in chlorine demand-free glass bottles. Thus, the cement wall was a source of chloramine

decay. Autodecomposition of monochloramine was hypothesized to be accelerated on acidified aluminosilicate surfaces of the cement matrix.

Hallam et al. (2002) compared the reactivity of an array of new pipe materials and linings towards free chlorine. Experiments were conducted in stirred batch reactors made from pipe sections. The average first-order decay constants were: 0.67 h^{-1} for cast iron; 0.33 h^{-1} for ductile (spun) iron; 0.13 h^{-1} for cement lined ductile iron; 0.09 h^{-1} for PVC; and 0.05 h^{-1} for medium density polyethylene. If it can be assumed that the primary mode of disinfectant decay was oxidation of pipe surfaces, chloramines might react similarly towards these materials.

Release of Pipe Material Deposits

The processes of corrosion product generation, accumulation of carbon and nutrients in biofilms and particle settling will lead eventually to accumulation of random deposits in locations with low hydraulic scouring. Sudden changes in DS hydraulics due to intentional flushing, water main breaks or system maintenance could cause re-suspension of these deposits. Many of the chemical elements within these deposits may be expected to exert a significant oxidant demand. Chloramine or free chlorine residuals may not be able to sufficient to inactivate bacteria associated with these deposits (Gauthier et al. 1999).

Nitrification

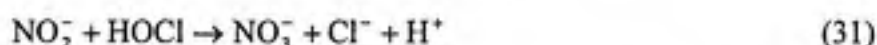
Nitrification is the microbial process in which free ammonia is converted to nitrite by autotrophic ammonia oxidizing bacteria (AOB) and subsequently to nitrate by nitrite

oxidizing bacteria (NOB). Ammonia is introduced during chloramination if it is added in excess so that the Cl:N molar ratio is less than 1:1. Ammonia is also produced in the DS by the hydrolysis of monochloramine (see Equation 4).

In a study of nitrification within a DS in South Australia, Cunliffe (1991) noticed that increased populations of nitrifying bacteria were associated with accelerated chloramine decay. Large populations of nitrifying bacteria were found to act as complete barriers to disinfectants.

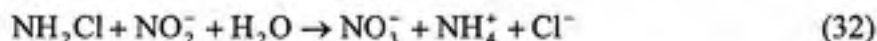
Nitrification prevents chloramine stability because:

1. AOB convert ammonia into nitrite that can reduce HOCl and disrupt the equilibrium of HOCl with chloramines.



The loss of both ammonia and hypochlorous acid in this process shifts their equilibrium with monochloramine to the left (see Equation 1) thereby contributing to chloramine loss.

2. Nitrite reduces monochloramine resulting in its oxidation to nitrate



Margerum et al. (1994) proposed the following kinetic relationship for this reaction which is pH dependent and kinetically slow.

$$\frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{NH}_2\text{Cl}]}{dt} = \frac{k_1'[\text{H}^+][\text{NH}_2\text{Cl}][\text{NO}_2^-](k_4 + k_2[\text{NO}_2^-])}{k_{-1}'[\text{NH}_3] + (k_4 + k_2[\text{NO}_2^-])} \quad (33)$$

where k_1' and k_{-1}' are forward and backward rate constants pertaining to the reversible formation of nitryl chloride (NO_2Cl), reactive intermediate, by monochloramine and nitrite. The formation of nitryl chloride is acid catalyzed

and is viewed as rate limiting. NO_2Cl may decompose to nitrite and chloride (see k_4 in Equation 33) or it may react with nitrite (see k_2 in Equation 33) to form N_2O_4 . N_2O_4 is highly unstable in aqueous solution, rapidly decomposing into nitrate and nitrite on reaction with hydroxide. Both the free chlorine reaction with nitrite and the monochloramine reaction with nitrite result in increased total ammonia levels that will in turn accelerate AOB processes.

3. Nitrifiers convert inorganic carbon into biomass and also create soluble organic products that may accelerate chloramine decay.
4. Wooschlager et al. (2001) have suggested cometabolism of monochloramine by AOB, citing a study that demonstrated the ability of nitrifiers to cometabolize the halogenated hydrocarbon trichloroethylene (Ely et al. 1995). Recently, Sathasivan et al. (2005) were able to measure microbially induced chloramine decay by comparing the decay rate in microbiologically inhibited (by the addition of silver nitrate) samples to that in uninhibited samples.

Nitrification is widespread among utilities and may pose a significant threat to chloramine stability in the DS. A 1996 survey of United States utilities discovered that roughly two-thirds of utilities that chloraminate experience nitrification and that one quarter experienced water quality problems associated with extreme levels of nitrification (Wilczak et al. 1996). Nitrification is widespread because nitrifying bacteria may be found in most surface waters and because nitrifiers can persist in many environments. Nitrification has been found to occur in systems with pH ranging from 6.5 to 10 and with temperatures that decrease to 10°C (Lieu et al. 1993; Odell et al. 1996).

Corrosion and Biofilms

Corrosivity has also been shown to lessen the effectiveness of secondary disinfectants in inactivation of bacteria in biofilms attached to a pipe wall (LeChevallier et al. 1993). The hypothesis is that corroded ferrous iron provides a competing reactive substance that limits the ability of the disinfectant to penetrate the biofilm for inactivation. LeChevallier et al. (1993) measured the corrosion rate in a pipe loop system by the linear polarization method. As the rate of corrosion increased, the ability of free chlorine to inactivate bacteria decreased. The negative effect of corrosion rate on inactivation was less for chloramines than free chlorine. The most suppression of inactivation occurred at a relatively high corrosivity associated with high concentrations of chloride and sulfate ions in solution relative to carbonate ions (this corresponds to high values of the Larson index).

The effect of corrosion and choice of secondary disinfectant was studied in the DS of two water utilities (Norton and LeChevallier 1997). The corrosion rates differed widely in the two DS. Upon switching from free chlorine to chloramine in both utilities, the heterotrophic plate counts and total coliform occurrences declined significantly. Chloramine residuals were maintained more easily than free chlorine residuals. The addition of corrosion inhibitors also assisted in reducing the corrosion rate and improving the effectiveness of disinfection.

Pipe material has also been shown to affect the extent of attachment of biofilms in the presence of secondary disinfectants (LeChevallier et al. 1993; Norton and LeChevallier 1997; Niquette et al. 2000; Rompre et al. 2000; Appenzeller et al. 2001; Camper et al. 2003; Chang and Jung 2004). Niquette et al. (2000) installed pipe coupons

in a DS with low free chlorine residuals near Brussels, Belgium. The coupons were made from an assortment of common pipe materials and the density of biofilm on each of the materials was compared after several months. Plastic materials including polyethylene and PVC had the lowest biofilm densities followed in ascending order of densities by cement-lined steel, asbestos-cement lined iron and cement lined ductile iron. Coal-tar enameled steel and unlined cast iron coupons had the highest densities. The role of cast iron in chemical reduction of disinfectants has been noted previously. This effect can lead to more extensive biofilms. However, another important factor could be pipe wall roughness. Cast iron pipe with its tubercles provides a very rough surface that can increase the bacterial attachment.

Camper et al. (2003) demonstrated that pipe material determined the efficacy of free chlorine and chloramines to limit bacterial regrowth in bench-scale annular reactors. Effluent bacterial numbers were lowest for PVC pipes, higher for cement- and epoxy-lined pipes and highest for iron-based pipes. Bacterial regrowth was also compared in field studies. The greatest extent of regrowth was found for iron pipes but there was no measurable difference among other materials. Chang and Jung (2004) recently corroborated these findings in pipe loop experiments. The results for treated groundwater, surface and desalinated brackish water were consistent: biomass production was greatest in unlined ductile iron pipes followed by galvanized steel, cement lined ductile iron, and PVC.

Chloramine Decay Models in Water Quality Models for DS

Considering all of the potential chloramine demanding substances in the DS, an important question for utility operators is the chloramine dosage in the finished water

leaving the water treatment plant. The dosage should be high enough to maintain a residual concentration that is sufficient for: disinfection of harmful microbes that may enter the DS; prevention of nitrification; prevention of bacterial regrowth; and inhibition of the growth of biofilms. Water quality models are used to predict the disinfectant residual throughout the DS. These models may be useful to establish the optimal secondary disinfectant concentration and to investigate the feasibility of disinfectant boosting stations to increase residuals in a large DS.

DS water quality models include a hydraulic component to account for macroscale transport of water by advection and a water quality component that describes the rate of chemical reaction or transformation during water transport. The hydraulic component can stand alone and is useful to water utilities for many purposes including prediction of pressure, water velocity and water age throughout the network. The water quality components developed to date are for prediction of the rate of free chlorine decay and of the production of chlorine disinfection by-products within the DS. Very little has been reported on adaptation of water quality models to describe the rate of chloramine decay.

As has been developed for free chlorine decay modeling, an analogous rate of chloramine decay in the bulk water and at the pipe surface are needed within EPANET and other similar DS water quality models. However, rate laws are not well established for either the bulk water or the wall reactions. For simplicity of modeling within existing DS model algorithms, the rate model for bulk water decay could be the same as that used for free chlorine decay. That is, a first-order rate with respect to chloramine concentration can be assumed:

$$-\frac{d[\text{NH}_2\text{Cl}]}{dt} = k_b [\text{NH}_2\text{Cl}] \quad (34)$$

The first-order decay constant, k_b , has units of inverse time (e.g., h^{-1}) and is often referred to as the bulk decay constant. There is no fundamental justification for a first-order rate process. This can be said of free chlorine decay as well. For example, the rate of free chlorine decay has been proposed as first-order with respect to free chlorine concentration and first-order with respect to chemical species that are present in a reduced state (Clark and Sivagnesan 1998). Little is known, however, about the identify and concentration of all reduced species; thus, the simpler first-order model is used by default.

Even less is known about the rate laws governing reaction of disinfectants at the pipe surface than in bulk water. Both first-order and zero-order rate models (with respect to the disinfectant concentration) have been proposed for free chlorine reaction (Vasconcelos et al. 1997, DiGiano and Zhang 2005). No rate models have been developed specifically to describe the decay of chloramines at the pipe wall for use in a DS water quality model. However, Maier et al. (2000) measured the decay of chloramine in a 1.3 km section of plastic pipe and assumed without verification that the wall reaction was first-order in the EPANET water quality model (see next section).

The EPANET Model

EPANET is a DS model that combines hydraulic and water quality components. It was developed in the early 1990s by the Water Supply and Water Resources Division of the USEPA and the software is available free of charge from the USEPA. Several other commercial software packages are available but all of these incorporate essentially

the same hydraulic and water quality modeling algorithms as EPANET. The advantage of the commercial software packages over EPANET is their user friendly features including the ability to transfer physical information about the pipe network directly from GIS databases.

The EPANET component to describe disinfectant concentration throughout the DS is based on a one-dimensional advective-reactive transport equation that accounts for decay in the bulk water and at the pipe wall:

$$\frac{\partial C_i}{\partial t} = -u_i \frac{\partial C_i}{\partial x} - k_b C_i - \frac{k_f}{r_h} (C_i - C_{i,w}) \quad (35)$$

where C_i is the concentration of the disinfectant in the bulk fluid within pipe i ; u_i is the water velocity within pipe i ; x is the distance along pipe i ; k_b is the bulk water decay coefficient; k_f is the mass transfer coefficient; r_h is the hydraulic radius of the pipe (cross sectional area divided by wetted perimeter); and $C_{i,w}$ is the disinfectant concentration at the pipe wall in pipe i . Equation 35 is unsteady state owing to several dynamic features including: variable water demand pattern each day that causes u_i to vary accordingly; variations in the disinfectant concentration entering the DS; changes in disinfectant concentration within water storage tanks over time that produce nodes in a DS with variable concentrations.

The wall concentration of disinfectant, C_w , in Equation 35 is not practical to find. However, C_w can be eliminated by assuming no build up of disinfectant at the wall after mass transfer to the wall. For the specific case in which the wall reaction is first-order, the mass balance at the wall is:

$$k_f (C - C_w) = k_w C_w \quad (36)$$

Solving Equation 36 for C_w and replacing C_w in Equation 35 gives:

$$\frac{\partial C_i}{\partial t} = -u_i \frac{\partial C_i}{\partial x} - k_b C_i - \frac{k_w k_f}{r_h (k_w + k_f)} C_i \quad (37)$$

This form of the advective-reactive transport equation illustrates the importance of the relative magnitude of the wall reaction rate constant, k_w , and mass transfer coefficient, k_f . If k_w is much larger than k_f , the loss of disinfectant at the wall is controlled by slower process of mass transfer. On the other hand, if k_w is much smaller than k_f , disinfectant loss at the wall is controlled by the decay rate at the wall. These two extremes of wall reaction rate emphasize the practical importance of rate data to quantify k_w .

Unfortunately, very few direct measurements of wall reaction rates are available (DiGiano and Zhang 2005) and these have been made exclusively for free chlorine decay.

Within EPANET (Rossman 1994), the mass-transfer coefficient is determined from a classic dimensionless mass transfer correlation given by from Edwards et al. (1976):

$$Sh = 0.023 Re^{0.83} Sc^{0.33} \quad (38)$$

where Sh is the Sherwood number, Re is Reynolds number and Sc is the Schmidt number. The Sherwood, Reynolds and Schmidt number are given by:

$$Sh = \frac{k_f d}{D} \quad (39)$$

$$Re = \frac{ud}{\nu} \quad (40)$$

$$Sc = \frac{\nu}{D} \quad (41)$$

where d is the pipe diameter, ν is the kinematic viscosity and D is the molecular diffusivity of the disinfectant. After finding the Sherwood number from Equation 38, k_f is calculated from Equation 39.

Equation 37 is solved by a finite difference technique that is referred to as the discrete volume element method (Rossman et al. 1994). A pipe segment is defined arbitrarily by the locations (nodes) along the pipe network where water demand is assigned. As an example, the EPANET model for the City of Durham, N.C. (serving about 150,000 customers) has about 11,000 pipe segments. Each pipe segment is treated as a completely-mixed flow reactor such that the independent variables are reduced from t and x to t because the concentration is uniform within each pipe segment.

The first reported application of the EPANET model to predict free chlorine residuals was a DS in Connecticut (Rossman et al. 1994). The bulk decay rate was measured directly from loss of free chlorine in a batch of finished water. These data were fit with a first-order model that produced a k_b value of 0.023 h^{-1} . Because both the rate of bulk and wall decay are first-order with respect to disinfectant concentration, an overall decay rate constant was defined from Equation 37 as:

$$K = k_b + \frac{k_w k_f}{r_h (k_w + k_f)} \quad (42)$$

Knowing k_b from the bulk decay rate tests and k_f from the mass transfer correlation (Equation 38) leaves k_w as the parameter to calibrate the EPANET model to the field measurements of free chlorine residual.

The EPANET model was run to determine the value of k_w that gave chlorine residual values that most closely matched those measured at stations throughout the DS. Rossman et al. (2004) assigned a single k_w value to the entire DS. They acknowledged

that k_w should in fact depend on pipe material, condition and age. Nevertheless, a good fit was obtained to chlorine residual data at most sampling locations by setting the global k_w between 0.006 m/h and 0.019 m/h. The importance of rate control by mass transfer or by wall reaction rate was also apparent from their model predictions. For example, the lowest k_w value (0.006 m/h) caused the overall rate constant, K , to be controlled by the wall reaction rate while the highest k_w value (0.019 m/h) shifted rate control to the mass transfer process. In a much later study, Maier et al. (2000) applied the same study design to find a k_w for chloramine decay in a 1.3 km section of pipe. The importance of the magnitudes of k_w and k_f on rate control was illustrated.

Whether water velocity affects the decay rate of the disinfectant depends directly upon the magnitudes of k_w and k_f . As can be seen from Equation 38, k_f increases with water velocity. Equation 42 shows that K will increase with k_f when k_w is much larger than k_f because the mass transfer is rate controlling (Rossman et al. 1994 and Maier et al. 2000); thus the K value should increase with velocity. Clark and Haught (2005) used a DS water quality model to predict the decay of free chlorine in a corroded, unlined ductile iron pipe loop reactor. They found that the rate of chlorine decay increased with water velocity, suggesting that k_w was fast relative to k_f and that mass transfer was limiting.

Another important aspect of rate control in wall reactions is the relative concentrations of the disinfectant and the Fe(II) that is available to react at the wall surface. If the availability of Fe(II) is limited, then the disinfectant decay reaction may appear zero-order with respect to the disinfectant concentration. A zero-order rate implies no dependency on chlorine concentration. However, the zero-order rate constant

will become larger with faster corrosion rates owing to the increase in Fe(II) concentration. This was observed for free chlorine decay in laboratory pipe section reactors (DiGiano and Zhang 2005).

If the reaction between free chlorine and Fe(II) is fast relative to the mass transfer rate of chlorine to the surface, the chlorine is immediately consumed at the wall and rate is limited by mass transfer of chlorine from the bulk water. Vasconcelos et al. (1997) modified the EPANET water quality model to account for zero-order reaction rates by expressing the decay reaction rate as:

$$\frac{dC}{dt} = -k_b C - \min\left(\frac{k_{w,0}}{r_b}, \frac{k_r C}{r_b}\right) \quad (43)$$

where $k_{w,0}$ is the zero-order intrinsic wall reaction rate. This equation states that the smaller of the two rates (wall reaction or mass transfer to the wall) determines the observed wall reaction. If the wall reaction is slow relative to the mass transfer rate, then the rate is independent of the disinfectant concentration reaching the wall. The implicit assumption is that the wall reaction is zero-order with respect to chlorine concentration.

The modified EPANET model developed by Vasconcelos et al. (1997) was applied for prediction free chlorine residuals in five DS. The pipe characteristics that could affect the decay rate at the wall differed widely among these five DS. After calibrating hydraulic models for each system and determining a first-order rate constant, k_b , in bulk decay tests, the EPANET model was calibrated to fit field data of chlorine residuals by using both a zero-order and a first-order wall reaction, each in combination with mass transfer to the wall. Three methods were evaluated for assigning k_w values within the DS: 1) all pipe segments with same k_w as used by Rossman et al. (1994); 2) different k_w values for each zone of pipe segments based on the qualitative assessment of

pipe characteristics; and 3) different k_w values for each pipe segment by assuming an inverse proportionality to the Hazen-Williams C-factor:

$$k_w = \frac{\alpha}{CF} \quad (44)$$

where α is the roughness constant that served as the calibrating parameter in the EPANET model and CF is the C-factor in Hazen-Williams equation. The lower the C factor, the higher is k_w consistent with rougher pipe surfaces causing greater wall demand.

The EPANET modeling assumptions that gave the best prediction were first-order bulk decay combined with zero-order wall reaction wherein the k_w values were calculated by an inverse proportionality with the Hazen-Williams C-factor. However, the fit of both the zero-order and first-order rate models to the field data for chlorine residuals were fairly similar.

The success shown by Vasconcelos et al. (1997) in use of an inverse proportionality with Hazen-Williams C-factor to predict k_w values led others to use the same model. However, DiGiano and Zhang (2005) pointed out that a different proportionality constant was needed for each of the five DS. Therefore, the C-factor failed to account for all factors that control the wall reaction rate.

A field-scale experimental method was used by Doshi et al. (2003) to find k_w in the DS of Detroit, Mich. without any use of EPANET. A long section of pipe with no water withdrawal points was located. The change in residual due to only decay of chlorine in bulk water was known from independent measurements in a batch of water. The difference between the total decrease in chlorine residual measured over the pipe length and that due to bulk decay was attributed to the loss due to wall reaction. The

extent of wall reaction was measured at different water velocities by adjusting the wastage rate of water at a fire hydrant. This experiment failed to corroborate an inverse relationship between the C-factor and the wall reaction rate as suggested by Vasconcelos et al. (1997).

Vasconcelos et al. (1997) conceded that comparison of EPANET model predictions with field measurements in a DS is an indirect method for calculation of k_w that is likely to lead to misspecification of governing relationships. All of these field studies reveal the same deficiencies. Foremost, the calculation of k_w requires a high degree of confidence in the values of all other hydraulic and mass transfer parameters that must be specified. In addition, the DS is highly dynamic such that many measurements of chlorine residual over time and space are needed for accurate fitting of k_w . Furthermore, the reactivity of each pipe material towards disinfectants may vary widely depending upon its age and condition.

Laboratory-scale Techniques to Investigate Disinfectant Wall Reaction

Given all of the shortcomings of field-based methods to deduce the rate of disinfectant decay at pipe walls, well-controlled laboratory-scale reactors provide a better choice. Baribeau et al. (2001) attached coupons of pipe material to the wall of a polycarbonate annular reactor to determine the effect of pipe material on biofilm growth in chlorinated water. The annular reactor is a flow-through device that contains an inner drum. Rotation of the inner drum imparts shear-induced velocity in the annular space, thereby allowing control of water velocity across the surface of the pipe coupons. While Baribeau et al. (2001) did not use the reactor to measure the effects of pipe material or water velocity on chlorine decay, the potential to do so exists.

The use of pipe coupons to measure disinfectant decay is limited by the fact that pipe coupons are not necessarily representative of a continuous pipe surface. For example, studies of coupons that contain protective coatings such as a cement lining can be invalidated if the unlined, cut edge of the coupons is also exposed to the water. Disinfectant decay on tuberculated pipe surfaces are also difficult to simulate with pipe coupons. Coupons would have to be many times larger than tubercle sizes, which can be on the order of cm in diameter, to capture the spatially averaged features of a tuberculated surface. The structural integrity of corrosion deposits is also difficult to maintain in cutting a pipe coupon. For all of these reasons, the pipe coupon method may be limited to new pipe materials that do not have corrosion deposits and this almost defeats the intended purpose of a comprehensive study of disinfectant decay rates.

Pipe loop reactors provide a more realistic simulation of the DS environment than pipe coupons. They consist of intact sections of DS pipe that form a closed loop wherein water velocity is controlled by an in-line pump. Rossman et al. (2001) constructed a pipe loop reactor with an 88 ft section of 6-inch diameter, unlined-ductile iron pipe that was heavily tuberculated. Water was circulated through the pipe loop at a sufficiently high water velocity to eliminate mass-transfer effects. Rossman et al. assumed that both bulk decay and wall reaction kinetics were first-order such that the rate of disinfectant decay was described by:

$$\frac{dC}{dt} = -(k_b + K_w)C \quad (45)$$

where

$$K_w = k_w / r_h \quad (46)$$

If first-order kinetics apply, the slope of a logarithmic plot of the disinfectant concentration with time yields the sum of the decay rate constants. Rossman et al. (2001) used bottle decay tests to determine k_b and then subtracted that value from the slope of the logarithmic plot to obtain K_w . In general, they found that K_w was much greater than k_b , i.e., the chlorine-wall reaction accounted for a much greater fraction of total decay than that attributed to decay in the bulk water. The value of the wall reaction rate was only determined for a single water velocity although experiments at lower velocity where mass transfer was made rate controlling would have tested previously presented ideas concerning the effect of Hazen-Williams C factor on the wall decay rate.

Pipe loop reactors also have disadvantages. They require large sections of homogenous pipe as well as large volumes of water to operate and are cumbersome in this regard. Short pipe sections are an attractive alternative in that they are more manageable than pipe loop reactors while still more representative of the DS than pipe coupons. Hallam et al. (2002) used stirred batch reactors made from pipe sections to measure the free chlorine decay rate. They calculated K_w for each of the pipe materials based on bulk decay studies and the observed rate of chlorine decay in the pipe sections. Pipe materials were classified as highly reactive, moderately reactive and non-reactive depending upon K_w . The rate of decay was generally found to increase with water velocity which was simulated by more vigorous mixing by the stir bar; thus, mass-transfer was rate controlling. Hallam et al. admitted that the hydraulics of the batch reactors in their study were not very well characterized.

Kiéne et al. (1998) developed the Propeller Loop Reactor (PLR) for determining the effect of cast iron pipe corrosion on chlorine decay. The outer wall of the PLR was

made from a segment of cast-iron pipe and a slightly shorter length of smaller diameter, comparatively non-reactive stainless steel pipe was positioned inside. The rotation of an impeller, positioned along the central axis of both pipes, induced water flow through the inner pipe and back around in the annular space between the pipes. The corrosivity, C_r , of the sample water was varied in the PLR by increasing the concentration of Cl^- ions in solution. The rate of chlorine decay was measured and compared to the corrosivity as measured electrochemically. The following empirical relationship was established.

$$C_t = C_0 \left(1 - k_{PLR} \left(\frac{C_r}{d} \right) t \right) \quad (47)$$

where k_{PLR} is the empirically determined rate constant for chlorine decay in the PLR and d is the inner pipe diameter.

The Propella™ reactor was developed by Appenzeller et al. (2001) using the same principle as the PLR. This reactor was used for investigation of the effect of corrosion inhibitors on bacterial growth on pipe surfaces. In this design, baffling was attached to the inner pipe to prevent vortexing and the water velocity in the annular space is of interest. The hydrodynamics of the Propella™ reactor show that water velocity near the pipe surface can be quantified (Blenke 1978). While a single annular velocity was selected for study, the Propella™ reactor could be used to measure the effects of velocity on disinfectant decay.

DiGiano and Zhang (2005) adopted the Propella™ design to develop a pipe section reactor (PSR). The advance over the Propella™ design was to vary the speed of the impeller motor with a rheostat in order to vary water velocity. A pitot tube was inserted in the annular space for direct confirmation of water velocity at the pipe wall. The decay rate of free chlorine at the pipe wall was measured in a section of unlined cast

iron pipe (CIP) that was heavily tuberculated and in a section of cement-lined, ductile iron pipe (DIP). The results showed that the rate of chlorine decay was zero-order with respect to chlorine concentration in the CIP section but first-order with respect to chlorine concentration in the DIP section. The zero-order rate expression is:

$$-\frac{dC}{dt} = k_{obs} = \frac{K_{w,o}}{r_h} \quad (48)$$

where k_{obs} is the observed zero-order decay rate. Increasing the water velocity caused k_{obs} to increase. This effect was explained by faster iron release as proposed by Sarin et al. (2004) wherein a high water velocity may damage the tubercle shell releasing reactive Fe(II) stored beneath.

Because the rate of decay in bulk water is not eliminated in the PSR, DiGiano and Zhang (2005) acknowledge that the zero-order rate constant, $K_{w,o}$, is only an approximation of the intrinsic wall reaction rate, k_w , because the bulk decay rate, k_b , was first-order, and could not be subtracted out of a zero-order rate model. However, 92% of chlorine loss during the first two hours of an experiment was attributable to pipe-wall reactions. This showed that the wall reaction dominated over the decay rate in bulk water and thus, $K_{w,o}$, was a close approximation of the intrinsic wall reaction rate. PSR experiments showed that $K_{w,o}$ increased at lower pH due to higher corrosion rates and dissolution of corrosion scale minerals that resulted in higher rates of iron release. $K_{w,o}$ also decreased with lower DO because of increased iron release as expected from exposure of the reduced iron beneath the oxidized hard shell of the tubercle as proposed by Sarin et al. (2004). PSR experiments with DIP gave a different rate law to describe chlorine decay rate at the pipe wall. In this case, the decay rate was first-order such that the rate constant for the wall reaction was calculated by

$$\frac{k_w}{r_h} = k_{obs} - k_b \quad (49)$$

Decay in the DIP was first-order because the cement lining prevented corrosion. Thus the decay rate was dependent on the chlorine concentration and not limited by the rate of corrosion at the pipe wall.

METHODS

Overview of Laboratory Experiments

The overall goal of this work was to measure rate constants to describe chloramine decay within the Raleigh distribution system (DS). As noted in the Literature Review, chloramine decay occurs both in the bulk water and at the pipe wall. While the rate of decay in bulk water is easily observed in batch reactor experiments, there is no standard procedure for measuring the rate of decay at the pipe wall. Neither of these processes has been studied in enough detail thus far to draw firm conclusions on the most appropriate rate models; this is particularly true for the wall reaction rate. The pipe section reactor (PSR) was originally used by DiGiano and Zhang (2005) to simulate the DS environment for observing the rate of free chlorine decay. This same reactor was adopted to measure the rate of chloramine decay in this research.

Samples of finished water were collected at the E. M. Johnson Water Treatment Plant (EMJWTP) and of water from several locations within the Raleigh DS. These samples were used to measure the rate of chloramine decay in bulk water independently and also to fill the PSR for determination of the rate of decay at the pipe wall. An old, tuberculated cast iron pipe (CIP) section from the Raleigh DS and a new, cement lined ductile iron pipe (DIP) section were used in the PSR.

Both pH and temperature were master variables in the bulk water and PSR experiments in order to confirm chloramine decay mechanisms suggested by the literature. Dissolved oxygen (DO) was monitored given its importance in iron oxidation reactions. The observed rate of decay in the PSR is the summation of the rates in the bulk water and at the wall, the latter possibly limited by mass transfer of chloramine from

the bulk water to the wall. The goal of the experimental work with the PSR was to deduce the intrinsic rate of chloramine reaction at the wall by accounting for both the rate of decay in the bulk water and the effects of mass transfer. Water velocity was varied to determine the effect of mass transfer. The initial chloramine concentration was varied to test zero-, first-order and second-order rate models of decay.

Water Treatment and Finished Water Quality Characteristics in Raleigh, N.C.

The EMJWTP has a maximum production capacity of 85 MGD. It is the sole water treatment plant for over 250,000 people throughout Raleigh and surrounding communities. The raw water source is the Falls Lake Reservoir which lies along the Neuse River. Raw water drawn from Falls Lake may be stored on-site in two 80 MG impoundments where plain sedimentation is achieved.

Ozone is added to the raw water for the main purpose of meeting regulations for removal of *Cryptosporidium* although the purported secondary benefits include increased coagulation efficacy and oxidation of reduced forms of iron and manganese. Ozone has not been in use consistently throughout the year due to various reasons, including modifications to design. KMnO_4 is added alternatively, when the ozone process is not functioning, for oxidation of iron and manganese. The DO concentration in the finished water during periods of ozonation is very high because pure oxygen is used for ozone generation and, thus, oxygen supersaturation occurs within the ozone contactors. The daily average concentration of DO in finished water over the course of this study was 8.85 mg/L. DO was also fairly high (> 6.2 mg/L) at the sampling locations in the DS although the decrease from the finished water suggests important reduction reactions

could be occurring given that the DO saturation level at typical water temperatures was in excess of 8 mg/L.

Ferric sulfate and cationic polymer are used as the coagulant and coagulant aid, respectively. Powdered activated carbon may also be added for additional removal of natural organic matter. After flocculation, sedimentation, chlorination and multi-media filtration, the water is stored in a clearwell with an average detention time of 8 hours (DiGiano et al. 2002). After the clearwell, additional free chlorine is dosed and ammonia is added to form chloramines prior to entering the DS; samples collected at this point are referred to as "finished water" samples. The average and range of concentrations of relevant water quality parameters measured by EMJWTP staff during the period of this study are listed in Table 2. This study was conducted between April and December of 2005.

Table 2 Finished water quality parameters over the study period, 03/05 to 12/05

Parameter (units)	Average	Range
Total Residual Chlorine (mg/L Cl ₂)	3.9	3.4 – 4.4
pH	8.4	7.8 – 8.6
Temperature (°C)	24.4	14.9 – 31.2
DO (mg/L)	8.85	8.01 – 9.21
TOC (mg/L)	4.28	1.10 – 6.12
Turbidity (NTU)	0.082	0.039 – 0.249

The Raleigh Distribution System and Selection of Sampling Locations

DIP comprises roughly 75 to 80 percent of the DS. Roughly 20 percent of the DS is unlined CIP and this area is concentrated downtown (DiGiano et al. 2002). A small fraction of the DS is PVC and exists on the fringes of the DS, mostly to the South. Water samples were collected at either the EMJWTP or from within the DS. The samples

within the DS were collected at four fire stations hereafter referred to as FS1, FS2, FS17 and FS20; their locations are shown in Figure 1. The locations were selected to obtain a range of dominance of different pipe material. As is shown by the color coding of pipe material in Figure 1, FS17 is surrounded primarily by DIP while FS1 is surrounded by CIP. FS2 is surrounded by a mix of DIP and CIP. FS20 is surrounded mostly by DIP; however, the CIP section downtown lies between the EMJWTP and FS20. Therefore, water arriving at FS20 may have traveled through the downtown section.

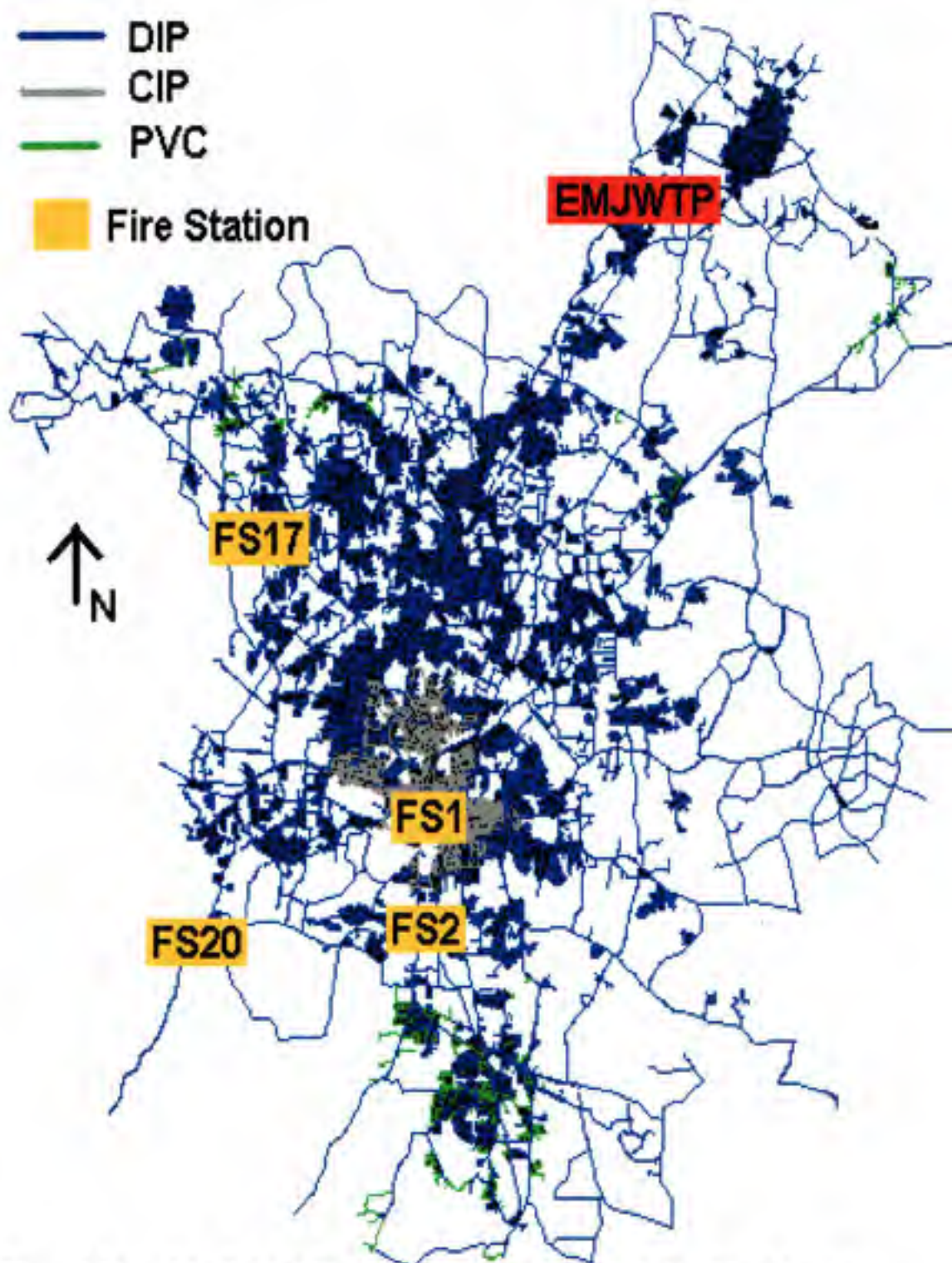


Figure 1 Map of the Raleigh Distribution System Color-Coded by Pipe Material

Laboratory Experiments to Measure Chloramine Decay Rates

Rate of Chloramine Decay in Bulk Water

The rate of chloramine decay was measured in either 1- or 0.5 L glass bottles filled with Raleigh finished water or with samples collected in the DS. It was assumed that bottles were made chlorine demand-free by soaking overnight in a 50 mg/L free chlorine bath. After the chlorine bath, they were rinsed thoroughly in laboratory grade water and air dried prior to use. Laboratory grade water was produced by a purification system made by Dracor Water Systems (Durham, NC) which includes an activated carbon bed, mixed ion exchangers and a 1 μm filter. When collecting samples in the field, bottles were rinsed twice with the sample, filled to the neck with sample water (some head-space remained) and sealed by a Teflon-lined cap or by glass stopper. After collection, samples were stored in a cooler at ambient temperature for transportation back to the laboratory where total chlorine, pH and temperature were measured.

Upon arrival at the laboratory, samples were either buffered to pH 6 or pH 9 or not buffered to test the effect of pH and pH buffering on the rate of chloramine autodecomposition. Samples were buffered to pH 6 by addition of a 10^{-1}M phosphate ($\text{KH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4$) stock solution to produce a 10^{-3}M buffer strength in solution. To buffer at pH 9, a 10^{-1}M borate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ and H_3BO_3) stock solution was added to produce a 10^{-3}M buffer strength in solution. New 10^{-1}M phosphate buffer stock solutions were prepared monthly, prior to experimentation by dissolution of 99.5% by weight KH_2PO_4 crystals and 99% by weight Na_2HPO_4 crystals (Malinckrodt, Paris, K.Y.). New borate buffer solutions were prepared by dissolution of 99.8% by weight

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ crystals and 100.0% by weight H_3BO_3 crystals (Fisher Chemical, Fairlawn, N.J.).

The addition of phosphate and borate buffers can raise possible concerns for interpretation of chloramine decay rates. Protonated phosphate and borate species may act as acid catalysts to promote monochloramine autodecomposition (Jafvert and Valentine 1988). However, initial experiments to measure the rate of chloramine decay without addition of a buffer showed that pH increased from 6 to 7 in a period of 200 h (as was necessary to measure the decay rate). Thus, the decision was made to add buffer in each rate experiment. The consequence of pH buffering could be that the measured bulk decay rate was higher than expected in finished water. The rate of chloramine decay in buffered and un-buffered samples was compared.

The pH, buffer strength and temperature of each experiment are listed in Table 3. The average pH is given for those experiments in which no buffer was added. The temperatures selected for experimentation were 12, 22.5, and 30°C because this spans the range of temperatures most common to the Raleigh DS. These temperatures were maintained by storing the samples in a constant temperature room. Total chlorine, temperature and pH were measured periodically over a period of several hundred hours.

Table 3 Temperature, pH and buffer strength of each bulk water rate experiment

Source	Temperature (°C)	pH	Added Buffer Strength (M)
EMJWTP	12	6, 9	10 ⁻³
	30	6, 9	10 ⁻³
	22.5	6, 9	10 ⁻³
		8.5	None
FS1	12	6, 9	10 ⁻³
	30	6, 9	10 ⁻³
	22.5	6, 9	10 ⁻³
		7.9	None
FS2	22.5	7.9	None
FS17	22.5	8.2	None
FS20	22.5	8.0	None

Pipe Section Reactor Experiments

Pipe Section Reactor

The PSR is shown schematically in Figure 2. The outer cylindrical wall of the PSR is a section of 6-inch inner diameter (ID) pipe that was either taken from the distribution network or cut from fresh pipe stock. CIP and DIP sections were used because, together, they represent over 90 percent of Raleigh's DS. Stainless steel plates were attached to either end of the pipe section by four threaded steel rods and wing nuts. A seal between the plates and the pipe ends was formed with o-rings cut from Teflon sheets.

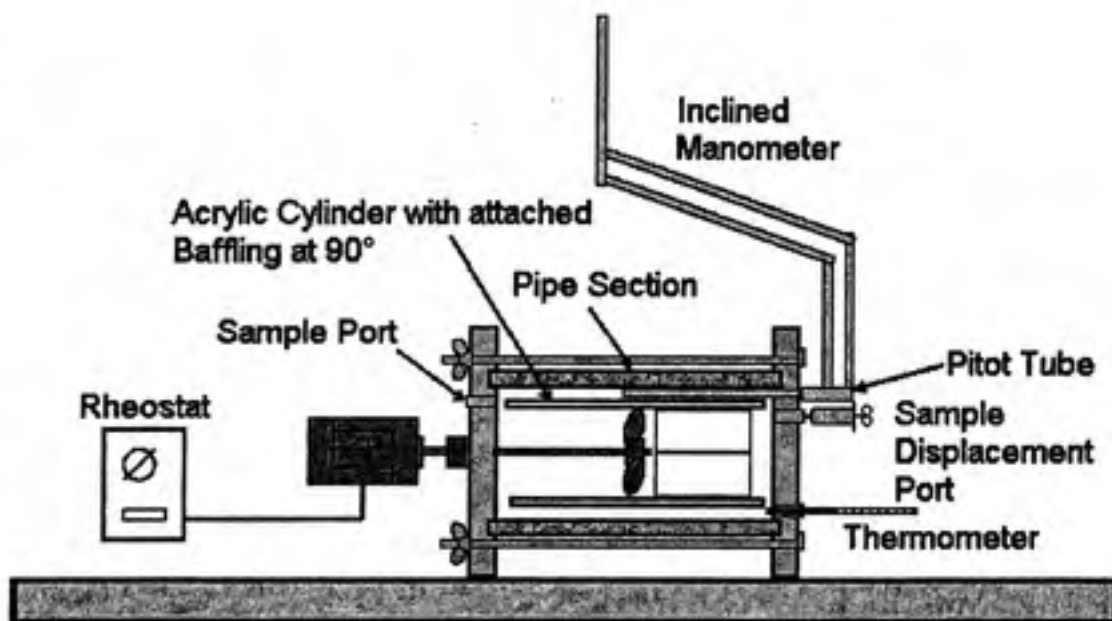


Figure 2 Cut-away section of the Pipe Section Reactor

As is also shown in Figure 2, an annular space was created by insertion of a smaller diameter acrylic cylinder within the pipe section. Stainless steel set screws were used to center and suspend the acrylic cylinder inside of the pipe section. The acrylic cylinder was approximately 25 mm shorter than the pipe section (12.5 mm at each end). Two flat acrylic baffling plates, oriented at 90° to one another, were fit tightly inside the acrylic cylinder at the right end in the schematic.

A shaft with an impeller was inserted horizontally along the central axis of the concentric cylinders. A 4-in diameter impeller was used for the DIP section. However, heavy tuberculation of the CIP section reduced the pipe's diameter such that a smaller diameter acrylic cylinder (88.3 vs. 115 mm) was needed to keep the annular space the same; this reduced the impeller diameter from 4- to 3-in. The shaft was connected by a coupling sleeve that was inserted into stainless steel end-plate to a 1/8 HP electric motor (Model No. 4Z140, Dayton Electric & Manufacturing Company, Niles, Il.). The electric

motor was connected to a rheostat (No. 5X412D, Dayton Electric & Manufacturing Company, Niles, Il.) for control of motor speed. The mixing action of the impeller caused a circulation pattern of water from the inner acrylic cylinder to the annular space between the inner and outer cylinders. The purpose of the baffles was to prevent vortexing of water as it circulated through the inner cylinder.

The velocity of the water in the annular space was measured directly by a Pitot tube and inclined manometer as shown in Figure 2. The Pitot tube was inserted directly through a port in the right-side end-plate into the annular space. A stagnation point forms at the tip of the Pitot tube and the resulting pressure is known as the velocity head (Olson and Wright 1990). Hydraulic conditions may vary along the length of the pipe, especially near the end-plates. Therefore, the positioning of the tip is important for measuring water velocity. The position of the stagnation point was selected as the approximate middle of the pipe length.

Each end-plate was equipped with a sampling port. To collect samples during batch operation, the desired volume of water was injected into one sample port by a syringe to displace the same volume through the opposite port. A third port on one of the end-plates was fitted to accommodate a thermometer for direct temperature measurement.

Pipe Sections

Photographs of the 70-year old, heavily tuberculated, CIP and the new DIP sections used in the PSR are presented in Figures 3 and 4, respectively. This CIP section was cut from a location in the Raleigh DS during routine maintenance. Care was taken to preserve physical integrity of the tubercles. A significant fraction of the cross sectional area of the CIP section is shown in Figure 3 to be occluded by tuberculation. After a

partial drying, the two ends of the pipe section were coated with an epoxy to prevent reaction with chloramines. Once the epoxy hardened, the pipe section was re-wetted and left submerged in local, chloraminated tap water (Orange County Water and Sewer Authority - OWASA) until testing. The water was changed once per week. The end-plates of the PSR were attached to the CIP ends one month prior to testing. OWASA tap water was then passed continuously through the reactor at a flow rate of about 1 L/min to acclimate the tubercles to chloraminated water.

Unfortunately, a DIP section with a 6-inch diameter was not made available during routine maintenance of the Raleigh DS during this study period. Thus, a fresh stock of DIP was used instead. The ends of the DIP section were coated with epoxy in the same manner as for the CIP section. Once the epoxy had cured, the end-plates of the PSR were attached. Finished water at the EMJWTP was passed through the pipe section at about 1 L/min for three weeks before the PSR experiment to acclimate the cement lining to chloraminated water.



Figure 3 Photo of the cast iron pipe section



Figure 4 Photo of the cement lined ductile iron pipe section

The estimated inner diameter of the pipe section, the hydraulic radius, r_h , and the volume of water held within the pipe section are listed in Table 4. The inner diameter and volume of the CIP sections are very rough estimates because they were affected by

heavy tuberculation. The hydraulic radius is generally defined as the cross-sectional area divided by the wetted perimeter. Thus, the hydraulic radius in the PSR is one-half the ID.

Table 4 Dimensions of DIP and CIP sections, hydraulic radius and hold-up volume

Material	Length (mm)	ID (mm)	r_h (mm)	Volume (mL)
DIP	346	152	38.0	6280
CIP	355	139	34.8	5390

Measurement of Water Velocity

The Pitot tube allows measurement of the head loss, h , caused by the fluid flow around the tip of the tube (Olson and Wright 1990). The fluid velocity, v , is calculated from h by the following equation that can be derived from fundamentals of fluid flow (i.e., no empirical assumptions are required):

$$v(m/s) = \sqrt{2gh} = \sqrt{2(9.81/1000)h(mm)} = 0.14\sqrt{h} \quad (50)$$

where g is the acceleration due to gravity.

Flow rate tests were conducted to check the accuracy of the Pitot tube-manometer set. The Pitot tube was installed in a section of 1-inch diameter PVC pipe and the flow rate, in the PVC pipe, was determined from the time taken to fill a volumetric flask. Water velocities were calculated from the pipe diameter at various volumetric flow rates. The relationship between water velocity and differential head, as measured by the inclined manometer, is shown in Figure 5. A power law equation (exponent = 0.5) was fitted to the data with $R^2 = 0.99$:

$$v(m/s) = 0.08\sqrt{h} \quad (51)$$

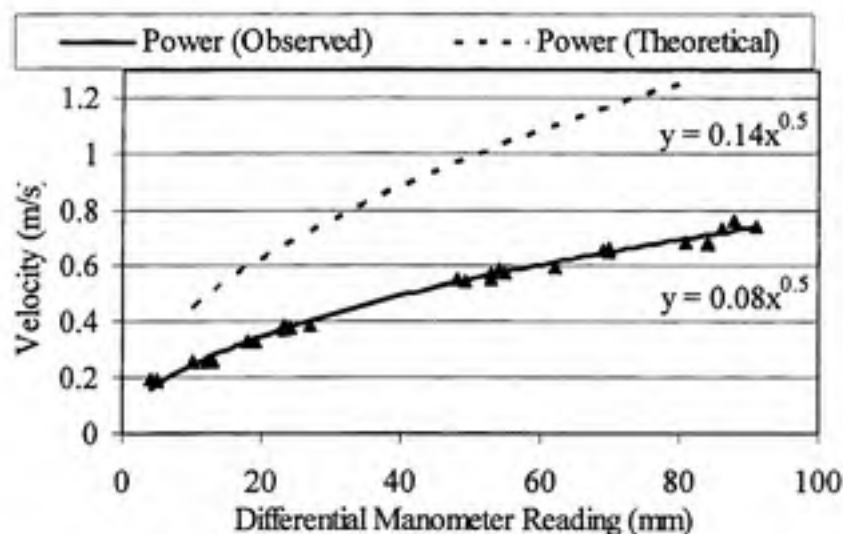


Figure 5 Experimentally observed relationship between water velocity and differential head on inclined manometer

While experimental error may have played a role, there is a systematic deviation from theory in the observed relationship between water velocity and differential head in the manometer. The pre-exponential coefficient was found to be 0.08 while in theory it should have been 0.14. This deviation suggests a flaw in the design or the condition of the Pitot tube. However, the Pitot tube was precise and measurements were successfully fit by a power law function with exponent 0.5 as evidenced by the high R^2 value. Thus Equation 51 was deemed suitable for relating differential head in the manometer to water velocity.

A calibration curve was derived between the power setting (PS) of the rheostat in the PSR (as a percentage of maximum impeller rotational speed) and the water velocity generated in the annular space of the CIP and DIP sections. Water velocity is calculated from the differential head reading of the inclined manometer by using Equation 51. The calibration curve is different for the CIP and the DIP sections because of differences in

both the diameter of the inner acrylic cylinder and the impeller size that determine the impeller speed to produce a given water velocity.

The power setting-velocity relationship for the DIP pipe section is shown in Figure 6. Each data point represents the velocity calculated from the differential head reading at each of ten power settings on the rheostat. The third-order polynomial fit, in fps, with $R^2 = 0.998$, is

$$v = -2.21 \times 10^{-6} (PS)^3 + 3.47 \times 10^{-4} (PS)^2 + 0.006 (PS) \quad (52)$$

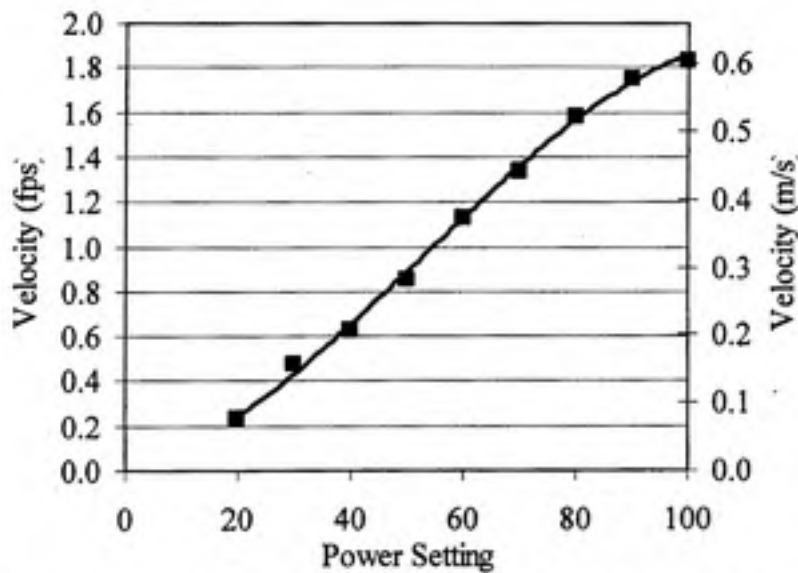


Figure 6 Power setting-velocity relationship in the DIP section at 23°C

For comparison, the time averaged water velocity throughout the Raleigh DS is 0.26 fps with a standard deviation of 0.5 fps according to a hydraulic model. The maximum velocity in the DS model is 5.5 fps.

The power setting-velocity calibration for the CIP section is given in Figure 7. Unlike the DIP section, the surface of the CIP section was very rough (see Figure 3). The

velocity in the annular space on the CIP varied greatly and depended on the size and shape of the nearest tubercle. Three sets of data are plotted in Figure 7 corresponding to three Pitot tube tip locations along the pipe length. An average of these three data sets is used for the velocity calibration. The third-order fit of that average in fps, with $R^2 = 0.998$, is

$$v = -1.08 \times 10^{-6} (PS)^3 + 1.82 \times 10^{-4} (PS)^2 + 0.007(PS) \quad (53)$$

The Pitot tube-manometer was not sensitive enough to measure velocity head at a power setting of 20. The velocity plotted at a power setting of 20 is extrapolated from the polynomial fit, Equation 53.

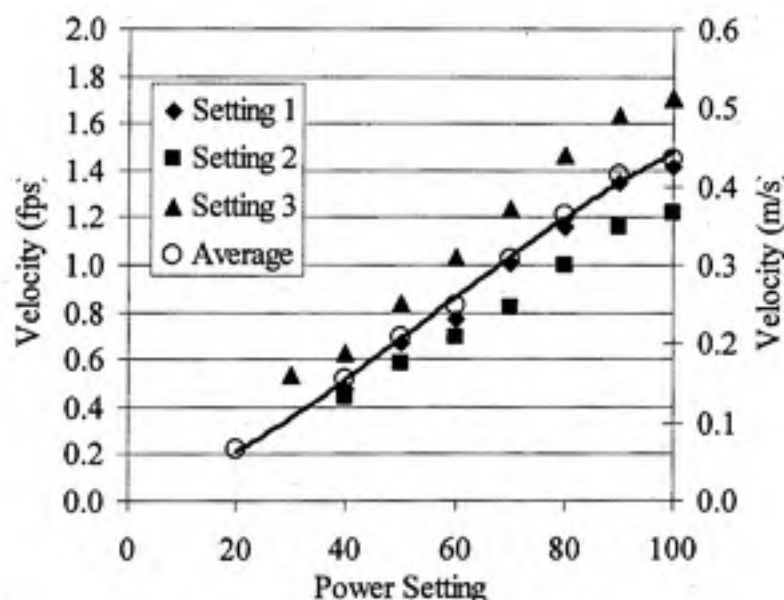


Figure 7 Power setting-velocity relationship in the CIP section at 24°C

Rate of Chloramine Decay in the PSR

Finished water from the EMJWTP was collected in 20 L chlorine demand-free, glass carboys and transported back to Chapel Hill for use in PSR experiments. These

samples were stored at room temperature (22.5°C) in a dark cabinet. Immediately prior to experimentation, a 10^{-3} M pH buffer was added to each batch by dissolving phosphate crystals directly in the sample to target pH 7 and pH 8. After dissolution of phosphate crystals was complete, the pH was measured. In most cases, a small amount of HCl was required because the alkalinity of the finished water was high enough to give a pH of about 8.6. To achieve the desired pH, 1.0 N or 0.1 N HCl was added drop-wise. Stock acid solutions were prepared by diluting concentrated (37.4%), non-trace metal HCl (Fisher Chemical, Fairlawn, N.J.). If the target pH was 9, a 10^{-3} M borate buffer (borax/ H_3BO_3) was added to the sample. The desired pH was then achieved by small additions of a 10.0 N NaOH solution. Stock base solutions were prepared by dissolving 99.0% by weight NaOH crystals (Malinckrodt, Paris, K.Y.).

After pH buffering, total chlorine was measured. If the concentration was above a target concentration, small volumes of a 1020 mg/L stock solution of sodium metabisulfite ($Na_2S_2O_5$) were added to reduce the chloramine concentration. Experimentation demonstrated that 25 mL of a 1020 mg/L $Na_2S_2O_5$ solution would reduce 1.0 mg/L total chlorine in a 20 L batch of finished water with high reproducibility. New $Na_2S_2O_5$ solutions were prepared daily, prior to each experiment by dissolving 99.0% by weight $Na_2S_2O_5$ crystals (Fisher Chemical, Fairlawn, N.J.). Total chlorine residuals were measured spectrophotometrically after $Na_2S_2O_5$ addition (see *Analytical Methods*). Monochloramine was not added in any experiments.

DO and temperature were measured prior to each experiment. DO was also measured after any $Na_2S_2O_5$ addition. After initial measurements of pH, temperature, DO and total chlorine, a gear pump was used to transfer the sample through a port on one

of the end-plates of the PSR. The PSR was oriented vertically and filled from the bottom up while the impeller rotated at a low speed in order to reduce the volume of air trapped inside.

Once the reactor was filled and air bubbles were removed, the reactor was vigorously mixed for a few seconds and the initial total chlorine concentration for the experiment was measured. The rheostat was then adjusted to the desired setting and the timer was started. Total chlorine and temperature were measured periodically within the PSR.

Temperature control within the PSR was problematic. The impeller motor produced a significant amount of heat, particularly at higher power settings and when the 4-inch impeller was used in the DIP section. This heat was conductively transferred into the PSR increasing the temperature. To minimize the effect of heat transfer, the experiments were conducted in a constant temperature room that was set to a lower temperature than desired for the experiment in order to balance out heat gain by the PSR from the impeller motor.

At the end of an experiment, the reactor was vertically oriented and ports were opened on both ends. Sample water was emptied through a port in the lower end-plate, through a tubing section and into a Büchner flask. DO was measured as the flask filled and as water flowed out through the side port on the neck of the flask. The pH was also measured in the flask at the end of each experiment.

Iron Release in PSR Experiments

A set of PSR experiments was conducted to measure the rate of iron release from the tuberculated CIP walls. The hypothesis was that the rate of iron release was related to

the rate at which chloramine decayed within the PSR. Each 20 L batch of Raleigh finished water, for iron release experiments, was buffered by 10^{-3} M phosphate to achieve either pH 7 or 8. Chloramines were totally reduced prior to the PSR experiment by addition of 25mL of a 1020 mg/L $\text{Na}_2\text{S}_2\text{O}_5$ solution for every 1.0 mg/L total chlorine. After $\text{Na}_2\text{S}_2\text{O}_5$ addition, total chlorine was measured spectrophotometrically to ensure complete reduction. A peristaltic pump was used to pump 50 mL/min through the PSR while the impeller was rotating rapidly enough to produce a completely mixed-flow reactor (CMFR). Total iron in the water leaving the PSR was measured periodically. No attempt was made to differentiate iron oxidation states.

Iron Release in the Raleigh DS

The iron concentration was measured in finished water and DS water from Raleigh to determine if a relationship existed with the rate of chloramine decay that was measured in bulk water experiments. Samples from FS1, FS17 and the EMJWTP were filtered through a 0.22 μm polyethersulfone disc filters. The disc filters were stored in Petri dishes at ambient temperature and transported back to laboratory for iron analysis. Each disc filter was immersed in 100 mL solutions for iron digestion as described later (see *Analytical Methods*). Total iron was then measured spectrophotometrically with the DR 2000 Method 8008. The iron concentration in solution was used to calculate the approximate concentration of iron in the sample water.

Analytical Methods

DO was measured by the membrane probe technique (YSI Model 55DO, Yellow Springs, Ohio). The DO meter was manually calibrated to atmospheric oxygen

concentration before each measurement. Measurements made by the membrane probe technique are reported to the nearest 0.1 mg/L.

The pH was measured with an Accumet pH Meter 10 (Fisher Scientific Co., Hampton, N.H.). A two point calibration was performed with buffered solutions at pH 4 and pH 10 prior to each use. Measurements are reported to the nearest 0.1 pH units.

Total chlorine was measured with the Hach™ DPD (*N,N*-diethyl-*p*-phenylenediamine) colorimetric method and a Hach™ DR 2000 spectrophotometer (Hach Chemical Co., Loveland, Colo.). The Hach™ DPD chemistry is equivalent to *Standard Methods for the Examination of Water and Wastewater* method 4500-Cl G (Clesceri 1999). The powdered chemical pillows provided for total chlorine determination were suitable for 25 mL samples with a maximum detection of 2.00 mg/L as Cl₂.

The free chlorine concentration is assumed to be negligible at the typical chlorine to ammonia weight ratio of less than 5:1 at the EMJWTP (corresponding to a maximum molar ratio of 1:1) that are used in water treatment practice to form chloramines. The equilibrium constant for monochloramine formation, Equation 1, is 1.7×10^{11} (Snoeyink and Jenkins 1980). Thus the fact that free ammonia concentrations are typically around 0.7 mg/L after chloramines are formed at the EMJWTP is evidence that free chlorine cannot be significantly present. The measurement of total chlorine concentration, which is the summation of the free chlorine and combined (chloramine) concentrations, was therefore reported as the chloramine concentration. In addition, no measurement of free chlorine concentration was made because of the difficulty in correct interpretation due to: 1) color development by the chloramine reaction with DPD that could start before a reading is taken that is supposed to equal the free chlorine concentration and 2) some

organic forms of combined chlorine may react with DPD to give a false free chlorine reading (Jensen 1988). Throughout this report, the terminology for combined chlorine will be *chloramine*, keeping in mind that monochloramine is the principle form of combined chlorine that was present.

Ten replicate measurements were made of total chlorine concentration on samples of finished water from Raleigh to measure the precision of the method. It was assumed that the total chlorine residual concentration was higher than the detection limit of the DR 2000, thus samples were diluted prior to measurement. The average and standard of the ten measurements deviation was 2.01 ± 0.011 mg/L. To determine the accuracy of the DR 2000, measurements were made of free chlorine solutions prepared by diluting a 69.1 mg/L stock solution (Hach Chemical Co., Loveland, Colo.). 1.93 percent error was obtained when measuring a 2.07 mg/L as Cl_2 solution. 5.07 percent error was obtained when measuring a 1.38 mg/L as Cl_2 solution where percent error was calculated as the difference between the predicted and the measured value divided by the predicted value. This accuracy was deemed sufficient for this work. Chloramine concentrations are reported to the nearest 0.1 mg/L in this report.

Total iron was also measured spectrophotometrically using DR 2000 Method 8008 with the same Hach™ DR 2000 spectrophotometer (Hach Chemical Co., Loveland, Colo.) as used for total chlorine. Powdered chemical pillows of FerroVer™ were used for 25 mL samples to give a maximum detection of 3.00 mg/L as Fe. The total iron measurement was adapted from *Standard Methods for the Examination of Water and Wastewater* method 3500-Fe B (Clesceri 1999). Before measuring total Fe, the samples were digested in a 50 ml solution to ensure that all iron, including colloidal ferric

particles, was brought into solution prior to measurement. The digestion procedure involves addition of a NH_2OH solution and excess (2 ml, 37.4%) HCl (Fisher Chemical, Fairlawn, N.J.) to the sample, boiling until the sample volume is reduced by 50 percent, allowing the sample to cool, and dilution of the sample back to 50 ml with laboratory grade water. The NH_2OH solution was prepared by dissolving NH_2OH crystals (Fisher Chemical, Fairlawn, N.J.) in laboratory grade water. The solution pH was increased to between 3.2 and 3.5 by NaOH before FerroVerTM reagent was added. The Hach manual for the DR 2000 method states a standard deviation of ± 0.006 mg/L as Fe when measuring a 1.00 mg/L as Fe stock solution. No effort was made to confirm this accuracy in this work. Hach Chemical Co. reports that the lowest average concentration of iron that is different from zero with a 99% confidence interval is 0.02 mg/L by this method.

Temperature was measured by a -1 to 51°C, in 0.2°C increments, alcohol thermometer.

All mass measurements were made with an analytical balance (Ohaus Adventurer, Model No. AR2140 Ohaus Corp. Pinebrook, N.J.) which has a sensitivity of 0.0001 g. Balance calibration was ensured at the beginning of the study with a set of calibration weights.

RESULTS

Decay Rate of Chloramine in Bulk Water

Finished Water vs. Samples Taken from Raleigh DS

The decay rate of chloramine in bulk water was measured in batch experiments at room temperature (22.5°C) with samples taken from finished water and from four locations in the Raleigh DS. The hypothesis was that the rate of decay may depend on reactants produced with travel time in the DS. Although chloramine decay is accelerated by natural organic matter, it was not expected that the amounts of organic materials would change significantly within the distribution system. DiGiano et al. (2000) and DiGiano et al. (2002), for example, found no evidence of an increase in total organic carbon concentration with travel time in the Raleigh DS. Iron, however, may be generated in the DS and this would accelerate chloramine decay. Corrosion of distribution system pipes may generate Fe(II) that could be subsequently oxidized by chloramine, thus causing chloramine to be reduced. Upon oxidation, iron would precipitate as ferric hydroxide, thereby lowering solution pH, and pH has been shown to affect chloramine stability (Valentine et al. 1998). Additionally, as discussed in the literature review, colonies of ammonia-oxidizing bacteria may remove ammonia with residence time in the DS. Free ammonia levels may also affect rate of chloramine decay (Valentine et al. 1998). If iron, pH and ammonia can play such an important role in chloramine stability, it would be important to know how their variation in the DS affects the bulk chloramine decay rate.

Finished water samples were collected from the EMJWTP and at four fire stations throughout the DS and monitored periodically for chloramine decay. The distribution network samples were collected in sections either dominated by unlined cast iron pipe (CIP) or cement lined ductile iron pipe (DIP) or some combination of the two (see Experimental Methods). The chloramine concentration, normalized by initial concentration in the batch rate tests, is plotted semi-logarithmically against time in Figure 8 so as to test a first-order kinetic relationship as given in Equation 29. The slope of the best fit line is the bulk first-order decay coefficient, k_b .

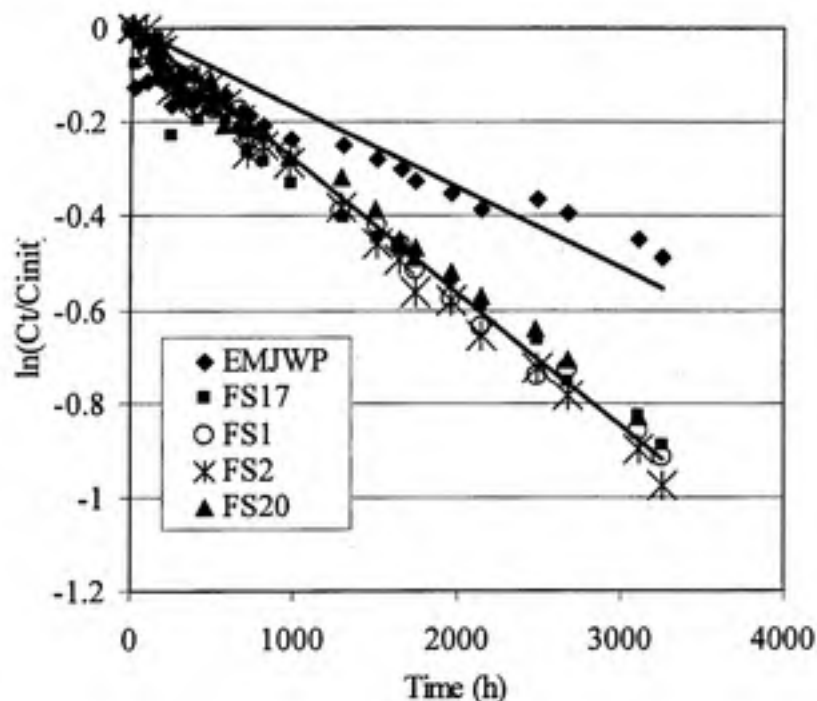


Figure 8 Test of first-order decay rate of chloramine in bulk water samples taken from the finished water of the EMJWTP and four locations within the DS

The initial pH and total chlorine concentration for each rate test and the k_b values taken from Figure 8 are presented in Table 5. In addition, the total iron concentration retained on a 0.22 μm disc filter for samples taken at FS1, FS 17 and finished water were

included. These samples were all collected on the same day. Variation in the initial total chlorine concentration may reflect temporal changes in total chlorine leaving the water treatment plant, differences in residence time in the DS, or differences in pipe materials in the sections of the DS where each of the sample sources was located. For instance, FS1 is located downtown in a section of primarily CIP whereas the other samples were taken from areas dominated by DIP. Iron corrosion from the CIP wall may have caused chloramine residuals to decay faster there than in other locations.

Table 5 Summary of results of batch experiments to test first order decay model for chloramine in bulk water at room temperature (22.5°C)

Sampling Location	Initial Total Cl ₂ (mg/L as Cl ₂)	Fe (mg/L)	pH	$k_{b,1}$ (h ⁻¹)	R ²
EMJWTP	4.3	0.004	8.50	1.7×10^{-4}	0.73
FS17	3.6	0.010	8.21	2.8×10^{-4}	0.96
FS1	3.0	0.024	7.94	2.9×10^{-4}	0.99
FS2	3.6	No Data	7.90	3.0×10^{-4}	0.99
FS20	3.8	No Data	7.96	2.7×10^{-4}	0.99

While the bulk water rate data shown in Figure 8 appear to fit a first order relationship, the $k_{b,1}$ value was measurably higher for the samples taken from the DS than from the finished water. However, if the reaction was truly first-order, all of the $k_{b,1}$ must be same. The fact that the initial concentration of chloramine is different in each rate test is not the explanation for the difference in $k_{b,1}$ values. The fundamental nature of a first-order relationship is such that the rate constant is independent of the initial concentration of the reactant. Thus, these data show a pseudo- rather than true first-order dependence on chloramine concentration. One explanation is that the reaction rate depends on another reactant concentration in addition to chloramine. Given that reaction involves both the oxidant and a reductant, rate dependency on both has been proposed for

describing the decay of a disinfectant (Clark and Sivaganesan 1998; DiGiano et al. 2000). The effect of the additional reactant(s) on rate is incorporated into the observed first-order rate constant, $k_{b,f}$ which is thereby defined as a "pseudo" first-order rate constant. The specific reactants or catalysts that could be involved in chloramine decay and that could be generated within the DS are unknown. Fe was the only potential reductant that was measured and these values appear in Table 5. The fact that the iron concentration in the FS1 sample is more than double that in the FS17 sample but $k_{b,f}$ is the same for both samples suggests that iron does not explain a faster rate of decay in the DS samples. Many more experiments would be needed to conclude that the rate of chloramine decay is independent of the iron concentration.

DiGiano et al. (2000) also noted a pseudo-first-order decay rate of free chlorine decay in bulk water for samples taken from the Raleigh DS. An overall second-order rate model was proposed, wherein the rate is first-order with respect to chloramine and first-order with respect to some unknown collection of reduced forms of reactants. This same type of model has been proposed by Clark and Sivaganesan (1998) for free chlorine decay. At certain ratios of free chlorine to reduced reactant concentrations, a first-order rate model may appear to fit the data (DiGiano et al. 2000). However, the $k_{b,f}$ value would not remain constant if the concentrations of the reduced reactants changed.

In contrast to the free chlorine decay observed by DiGiano et al. (2000) and Clark and Sivaganesan (1998), chloramine decay is much slower. Using the example of the decay rate for the sample taken from FS 1, about 1.7 months were required for chloramine to decay from 2.0 mg/L to 1.4 mg/L. For a sample collected by DiGiano et al. (2000) at the same site, the time required for the same extent of free chlorine decay

amounts to only 60 hours. The difference in free chlorine and chloramine decay rates is important because the unknown reduced reactants would need to be fairly stable to remain over the four months of the chloramine decay test. Therefore, one possibility is that the substance generated in the DS acts as catalyst rather than as a reactant.

Autodecomposition is another possible pathway for loss of chloramine in which the presence of reductants would not affect the rate. The data presented in Figure 8 were tested with a second-order rate with respect to chloramine concentration. This model has been shown appropriate to describe autodecomposition of monochloramine in the absence of major oxidizable reactants (Valentine et al. 1998). Autodecomposition involves highly reactive and unstable dichloramine that forms when hypochlorous acid, produced by hydrolysis (Equation 4) reacts with monochloramine (Equation 2) or by a disproportionation reaction involving two monochloramine molecules (Equation 6). The disproportionation reaction is more important at lower pH values as it begins to dominate dichloramine formation. The hydrolysis pathway is important at low ammonia concentrations because hypochlorous acid, produced by hydrolysis, reacts readily with free ammonia. In either sequence leading to dichloramine formation, two monochloramine molecules are consumed, and as Valentine et al. (1998) suggested, monochloramine autodecomposition should be second-order.

$$-\frac{dC}{dt} = k_{d,2}C^2 \quad (54)$$

After separating variables, the integral form is

$$-\int_{C_0}^C \frac{dC}{C^2} = \int_0^t k_{d,2} dt \quad (55)$$

where the limits of integration are the initial concentration, C_0 and the concentration at any time, C_t . Upon integration, a linear relationship is obtained.

$$\frac{1}{C_t} = \frac{1}{C_0} + k_{b,2}t \quad (56)$$

The linear form of the second-order model shown in Equation 56 was tested in Figure 9. While the fit appears reasonably good, there may be a systematic deviation from linearity at longer times for data from the locations within the DS but not for data from the finished water. Once again, however, a unique $k_{b,2}$ did not describe all rate experiments as should be obtained for a true second-order rate expression. Visual inspection suggests that the $k_{b,2}$ values for the sample from the DS are greater than for the finished water sample. Thus, the second-order model is still deficient in explaining the rate of chloramine decay. Here again, the implication of a variable rate constant is that there are un-accounted for reactants or catalysts generated within the DS that affect the rate of chloramine decay.

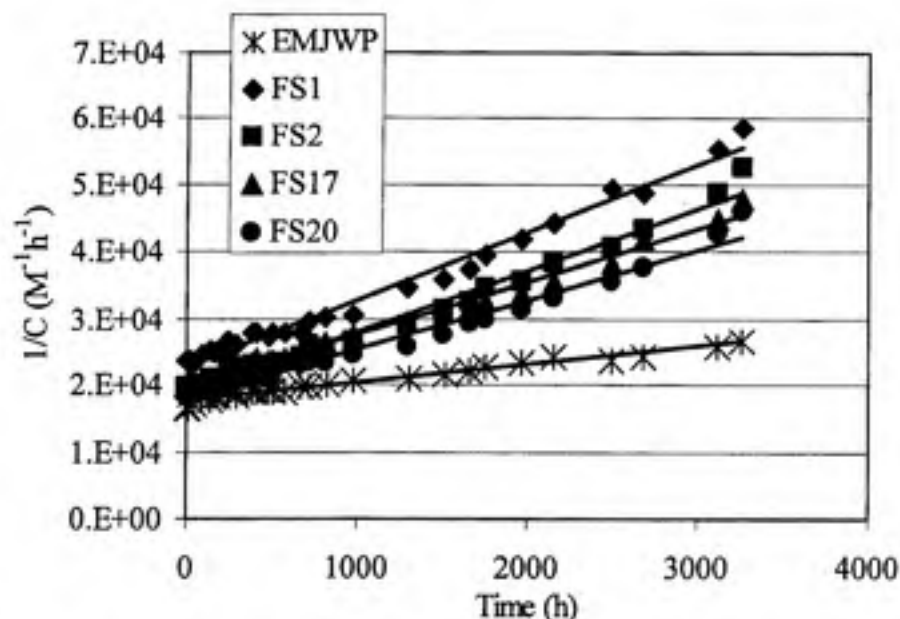


Figure 9 Test of second-order decay rate of chloramine in bulk water samples taken from the finished water of the EMJWTP and four locations within the DS

The $k_{b,2}$ values are compared with $k_{b,1}$ values in Table 6. While the R^2 values were about the same for both models for samples taken from the DS, the R^2 value was higher for the second-order model than for the finished water sample. Far more data would be needed to conclude that one pseudo rate model was better than another. For instance, rate data with different initial chloramine concentrations should be included.

Table 6 Comparison of pseudo-first- and second-order rate models for chloramine decay in bulk water

Sampling Location	pH	First-Order Model		Second-Order Model	
		$k_{b,1}$ (h^{-1})	R^2	$k_{b,2}$ ($M^{-1}h^{-1}$)	R^2
EMJWTP	8.5	1.7×10^{-4}	0.73	2.7	0.96
FS17	8.2	2.8×10^{-4}	0.96	7.8	0.98
FS1	7.9	2.9×10^{-4}	0.99	10.	0.99
FS2	7.9	3.0×10^{-4}	0.99	9.2	0.98
FS20	8.0	2.7×10^{-4}	0.99	7.4	0.98

A useful diagnostic tool for determining quality of a model fit is a plot of residual error against the regressor variable which is time. These diagnostic plots are useful for two reasons: (1) they can demonstrate failure of the regression model assumption that residuals are normally distributed with a mean of zero, and (2) they can provide additional insight into how the independent variable relates to the dependent variable. Diagnostic plots for the first-order model are given in Figure 10 (for finished water) and Figure 11 (for FS1) and for the second-order model in Figure 12 (for finished water) and Figure 13 (for FS1). If a model does not fit the rate data, the residual error would systematically vary over time. This was true of the residual error (varies from positive to negative with increased time) in the tests of the first-order model for the finished water sample (Figure 10) and the second-order model for the FS1 sample (Figure 13). In contrast, residual error appears to vary randomly with time for the first-order model for the FS1 sample (Figure 11) and the second-order model for the finished water (Figure 12). Thus, not all of the data are consistently fit by either the first-order or second-order model. A common feature of the four diagnostic plots is that the variance of residuals depends on time; this feature is known as heteroscedasticity. As a result of heteroscedasticity, the R^2 values reported in Table 6 may be deflated and are not a good indication of quality of fit.

One possible explanation for a difference in goodness of fit between the first- and second-order rate models is that the same model is not appropriate for both the finished water and the DS water. Chloramine decay in the finished water may be dominated by autodecomposition and is therefore second order while decay in the distribution system may be dominated by reactions with an unidentified set of reductants and is therefore first

order. Many more experiments would be needed to conclude that one model is better than another for either finished water or water in the DS.

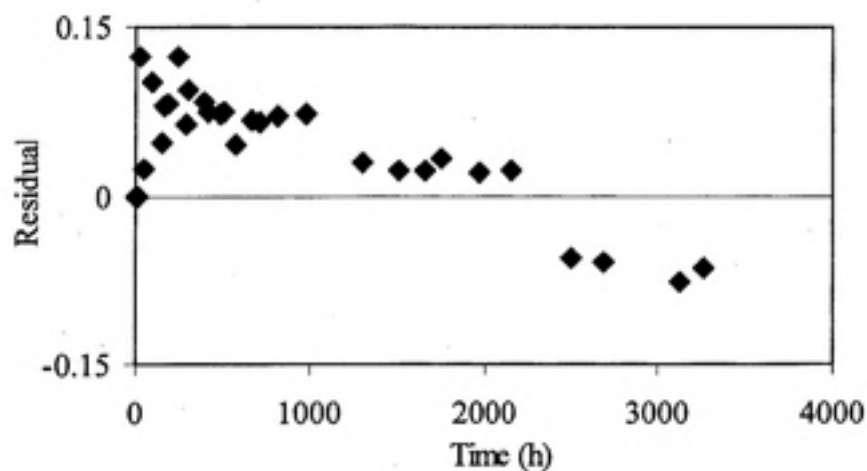


Figure 10 Diagnostic plot of residual error for first order model for finished water sample

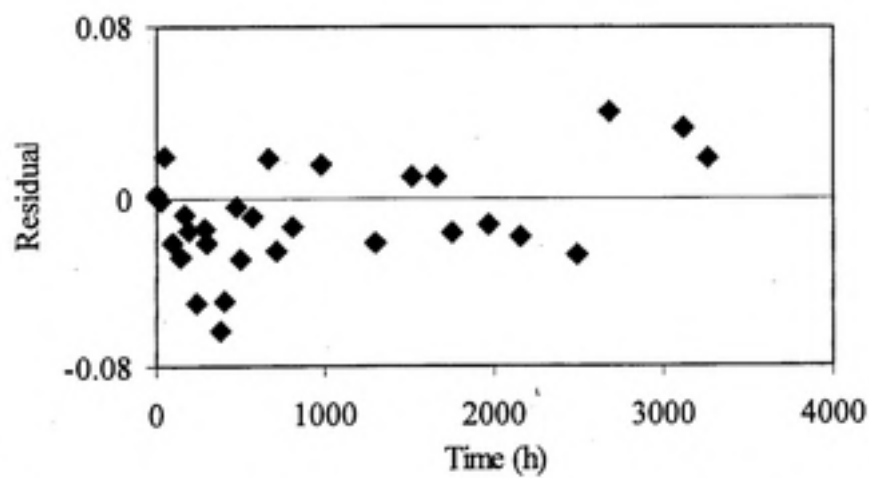


Figure 11 Diagnostic plot of residual error for first order model for FS1 sample

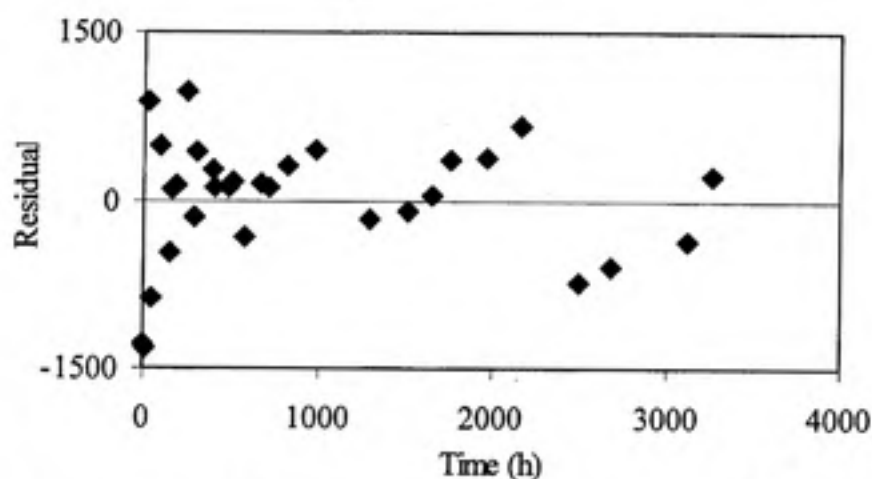


Figure 12 Diagnostic plot of residual error for second order model for finished water sample

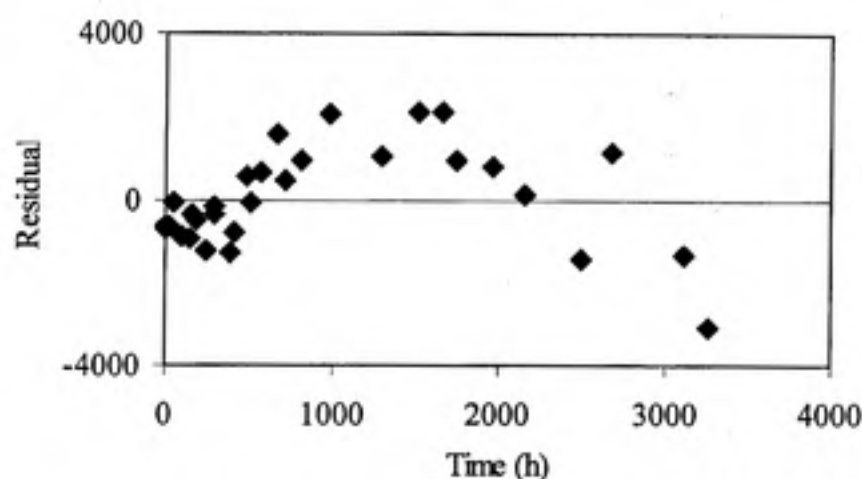


Figure 13 Diagnostic plot of residual error for second order model for FS1 sample

The $k_{d,2}$ values from the Raleigh finished water and DS were compared to the second-order rate constant for autodecomposition that was obtained by Valentine et al. (1998) for finished water samples that were collected from water utilities in five cities. The $k_{d,2}$ values reported by Valentine et al. were calculated from the line of best fit of data in the linear form of Equation 56 and are summarized in Table 7. For comparison to Table 7, the average TOC in Raleigh finished water in 2004 was 2.2 mg/L and alkalinity

was 0.34 mM HCO_3^- (City of Raleigh EMJWTP, 2004). Because $k_{b,2}$ depends strongly upon pH, comparisons between the values obtained for Raleigh and those from the five cities given in Table 7 were restricted to those from a similar pH range, i.e., pH above 7.9. The order of magnitude of $k_{b,2}$ values is similar between Table 6 and 7.

Table 7 Second-order rate constants for chloramine decay in finished water samples taken from water utilities in five U.S. cities (Valentine et al. 1998)

Location	TOC (mg/L)	Alkalinity (mg/L HCO_3^-)	pH	$k_{b,2}$ ($\text{M}^{-1} \text{h}^{-1}$)
Iowa City, IA	1.2	1.76	6.5	282 ± 36
			7.5	40 ± 9
			8.3	18 ± 7
Cedar Rapids, IA	1.5	1.30	6.5	111 ± 7
			7.5	19 ± 7
			8.3	12 ± 1
Belle Glade, FL	12.2	0.78	6.5	417 ± 49
			7.9	54 ± 15
Minneapolis, MN	3.4	0.48	6.5	503 ± 54
			7.5	79 ± 26
			8.3	29 ± 17
Joseph Jensen, CA	1.8	1.88	6.5	532 ± 82
			7.5	67 ± 3
			8.3	26 ± 4

Another useful aspect of the results given in Table 7 is the reporting of 95 percent confidence intervals for $k_{b,2}$ values from replicate batch decay experiments.

Unfortunately, replicate experiments were not conducted to obtain the $k_{b,1}$ values in Table 6. Thus, one possible explanation for higher $k_{b,1}$ values in the DS samples than in the finished water samples could have been experimental error in the rate measurement. At pH above 7.9, which is closest to the pH values in this study, the confidence intervals in Table 7 range from ± 8 percent to ± 59 percent of the mean. The $k_{b,2}$ value for the finished water sample in Table 6 is 70 percent lower than the average $k_{b,2}$ for the DS samples. While not as satisfactory as replicate experiments with the Raleigh samples, the

standard deviations obtained by Valentine et al. (1998) suggest that the higher values of $k_{b,2}$ that were determined in the DS water than in finished water samples are not explained by experimental error.

The results in Table 7 also could suggest that the higher $k_{b,2}$ values in the DS samples could be due solely or in part to pH changes within the DS. As shown in Table 7, monochloramine autodecomposition is accelerated at lower pH. The pH of the finished water sample from Raleigh was 8.5 whereas the pH of the DS samples was notably lower, ranging from pH 7.9 to 8.2. Therefore, faster decay in the DS samples may be partially explained by the lowering of pH. The extent of increase in $k_{b,2}$ brought about by a lower pH can be quantified from the results provided by Valentine et al. (1998) in Table 7. For instance, the decrease in pH from 8.3 to 7.5 in the Cedar Rapids samples caused the average $k_{b,2}$ to increase by $7 \text{ M}^{-1}\text{h}^{-1}$; expressed as ratio, the $\Delta k_{b,2} : \Delta \text{pH}$ is 9:1. Similar calculations for the Iowa City and Joseph Jensen samples give ratios of 28:1 and 51:1, respectively. Performing this same calculation for rate data taken from the finished water and DS samples from Raleigh gives an average $\Delta k_{b,2} : \Delta \text{pH}$ ratio of 10:1. Thus, the lower pH in the DS samples in Raleigh could possibly explain the difference in observed bulk decay rates. However, subsequent rate experiments conducted at different pH values (see Effect of pH) still imply a role for a second reactant or a catalyst.

The presence of reduced species that may be generated within the DS and then be oxidized by chloramine cannot be ignored as a contributing factor. Below 1 to 2 mg/L of free ammonia, the hydrolysis pathway of monochloramine autodecomposition is significant (Valentine et al. 1998). This pathway contributes increasingly as free

ammonia levels decrease (see Equation 31). DiGiano et al. (2002) found that free ammonia levels in the Raleigh DS are consistently lower than in the finished water. Therefore, it is possible that lower free ammonia concentrations in the DS samples also contributed to a faster bulk decay rate.

Effect of pH

The general acid catalyzed disproportionation reaction (Equation 6) that leads to the formation of dichloramine plays an important role in monochloramine autodecomposition. Hence, pH was expected to influence the rate of autodecomposition as had been shown by Valentine et al. (1998) and summarized in Table 7. A series of batch rate experiments was conducted to test the effect of pH. Initial attempts to adjust pH by addition of HCl proved unsuccessful as noted by a steady rise of pH over the course of the experiment, in samples initially adjusted to a pH of 6. This effect could be attributable to the release of ammonia in monochloramine disproportionation given that the pKa of ammonium is 9.3. To avoid pH change, pH was buffered with either 10^{-3} M phosphate or borate depending upon the pH of interest. However, either buffer complicates interpretation of rate data. Phosphoric and boric acids along with their deprotonated forms (except for the phosphate and borate ions) are general acid catalysts with regards to monochloramine decomposition (Valentine and Jafvert, 1988).

The rate data at pH 6 (buffered with phosphate) and 9 (buffered with borate) for both the finished water and one sample taken from the DS at FS1 are shown in Figure 14. These tests were each conducted at room temperature (22.5°C). The pseudo-first order rate model was tested again with these data and gave good agreement.

The $k_{b,1}$ values obtained from the first-order model test are summarized in Table 8. They are more than an order of magnitude greater at pH 6 than at pH 9 for both the finished water and the FS1 sample. The effect of pH is consistent with the acid catalyzed disproportionation of monochloramine (see Equation 6). All protons and proton donating molecules catalyze disproportionation by increasing the activity of the monochlorammonium ion (see Equation 16). This in turn increases the number of interactions between monochlorammonium and monochloramine producing more dichloramine (see Equation 17). The autodecomposition scheme presented as Equations 1 through 15 underscore the importance of dichloramine production for chloramine loss.

The results in Table 8 also corroborate evidence in Table 6 for the effect of catalysts generated in transport through the DS on chloramine decomposition rate. The $k_{b,1}$ values shown in Table 8 at FS1 for pH 6 and pH 9 are each about twice those of the finished water sample.

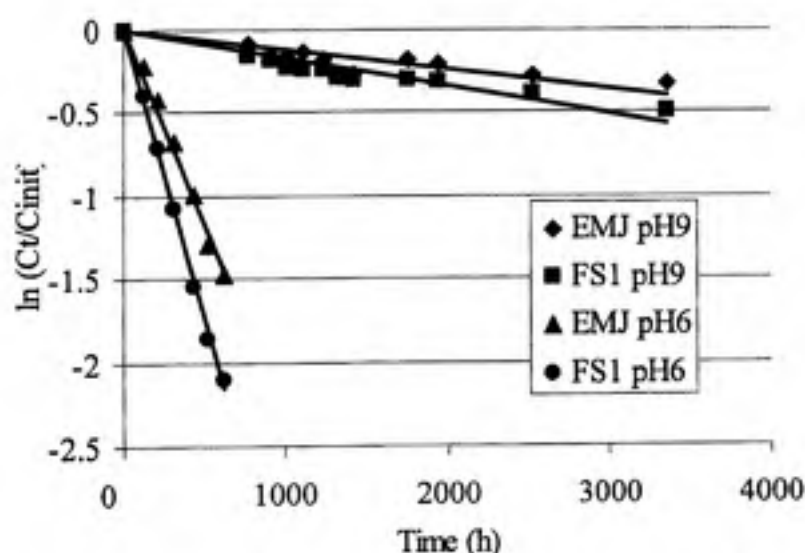


Figure 14 Test of first-order rate model for chloramine decay in bulk water: effect of pH and transport in DS

Table 8 The effect of pH and transport in DS on pseudo first-order rate constant for chloramine decay in bulk water

Sampling Location	pH	$k_{b,1}$ (h ⁻¹)	R ²
EMJWTP	9	1.2×10^{-4}	0.65
FS1	9	1.7×10^{-4}	0.85
EMJWTP	6	2.3×10^{-3}	0.99
FS1	6	3.5×10^{-3}	0.998

As noted above, the addition of phosphate or boric acid buffers could possibly have influenced the rate of chloramine decomposition. However, the extent of this effect is minor as evidenced by comparison of the $k_{b,1}$ values of the finished and FS1 samples obtained at pH 9 with buffer ($k_{b,1} = 1.2 \times 10^{-4}$ to 1.7×10^{-4} h⁻¹) to those of the corresponding field samples without buffering at a pH of about 8 as given in Table 6 ($k_{b,1} = 1.7 \times 10^{-4}$ to 2.9×10^{-4} h⁻¹).

The second-order rate model was also tested with the same data sets as above. A good fit was obtained as expected from the proposed mechanism of autodecomposition. The pseudo second-order values, $k_{b,2}$, are listed in Table 9. These are in fairly good agreement with those listed in Table 7 for similar pH values and measured in finished waters for five cities (Valentine et al. 1998). The effect of transport through DS on chloramine decay rate is once again apparent; the pseudo second-order coefficient values increase by a factor of two.

Table 9 Pseudo second-order rate constants for data plotted in Figure 10: effect of pH and transport in DS

Location	pH	$k_{b,2}$ (M ⁻¹ h ⁻¹)
EMJWTP	6	110
FS1	6	230
EMJWTP	9	1.8
FS1	9	2.9

The difference in rates at pH 6 and 9 can be related to the proton donating species that are present (see Equation 31). Carbonic acid and bicarbonate have a significant bearing on the rate constant in drinking water environments. At pH 6, total carbonate is predominantly bicarbonate or carbonic acid; both forms contribute to the acid catalysis of monochloramine disproportionation. At pH 9 only bicarbonate exists substantially, carbonic acid will not contribute to acid catalysis. Moreover, Equation 31 shows that the proton activity is directly proportional to the second-order rate constant. Thus, reducing the pH from 9 to 6 should increase the second-order rate constants by two orders of magnitude. The results given in Table 9 are in agreement with this prediction.

Effect of Temperature

Additional chloramine decay rate experiments were conducted at 12°C and 30°C. Given that the effect of pH is also important, rate experiments for both pH 6 and pH 9 were repeated at these temperatures. A test of the first-order rate model is presented in Figure 15 for data collected at pH 6 at temperatures of 12, 22.5 and 30°C. The first-order rate model was applied to data collected at pH 9 for the same three temperatures and the results are presented in Figure 16. An additional experiment was included at 30°C to investigate the effect of buffer. In this test, the unadjusted pH was 8.5. All of these plots confirm that pseudo-first order rate model fits the data well. Moreover, the rate increases with temperature at pH 6 and at pH 9 as should be expected from the fundamentals of reaction kinetics. Buffer addition was shown to have no significant influence on rate, which is consistent with previous findings.

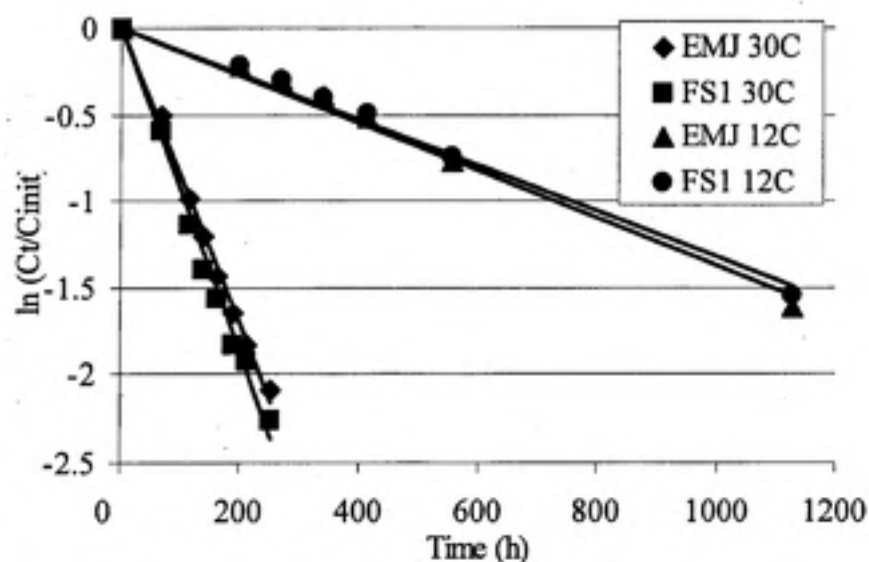


Figure 15 Effect of temperature on chloramine decay rate in bulk water at pH 6

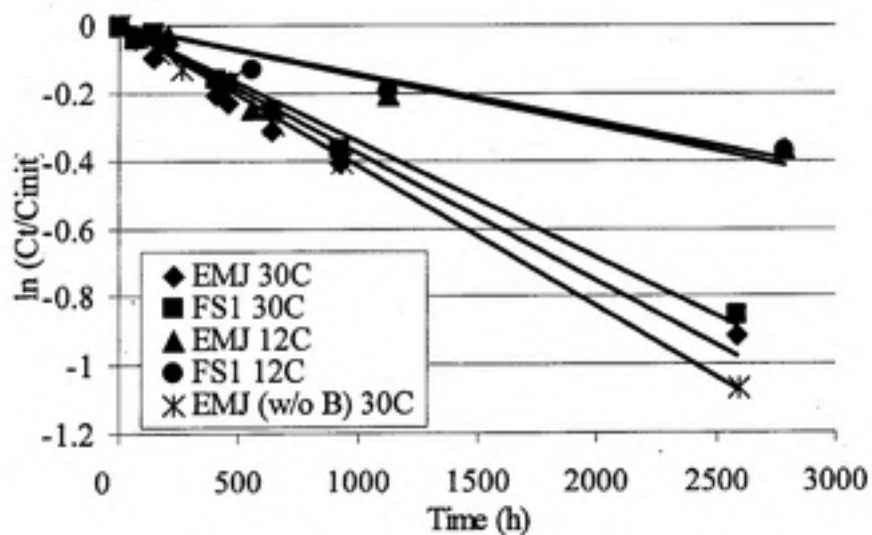


Figure 16 Effect of temperature on chloramine decay rate in bulk water at pH 9; additional experiment included at 30°C and pH 8.5 without addition of buffer (w/o B)

Table 10 Summary of pseudo-first order rate constants at three temperatures at pH 6 and pH 9

Sampling Location	Temperature (°C)	pH = 6		pH = 9	
		$k_{d,1}$ (h ⁻¹)	R ²	$k_{d,1}$ (h ⁻¹)	R ²
EMJWTP	12	1.3×10 ⁻³	0.98	1.5×10 ⁻⁴	0.66
FS1		1.2×10 ⁻³	0.98	1.4×10 ⁻⁴	0.94
EMJWTP	22.5	2.3×10 ⁻³	0.99	1.2×10 ⁻⁴	0.65
FS1		3.5×10 ⁻³	0.998	1.7×10 ⁻⁴	0.85
EMJWTP (w/o B)	30	-	-	4.1×10 ⁻⁴	0.997
EMJWTP		8.5×10 ⁻³	0.99	3.8×10 ⁻⁴	0.97
FS1		9.4×10 ⁻³	0.98	3.4×10 ⁻⁴	0.99

All of the first-order rate constants determined from Figure 15 and Figure 20 are summarized in Table 10. As with any rate data, the Arrhenius equation may be applied to quantify the effect of temperature on the rate constant:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (57)$$

where A is the Arrhenius constant, E_a is the activation energy, R is the universal gas constant (8.314 × 10⁻³ kJ mol⁻¹K⁻¹) and T is the temperature in degrees Kelvin.

Equation 57 in logarithmic form is:

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (58)$$

The data listed in Table 10 were plotted according to Equation 58 in Figure 17 (pH 6) and in Figure 18 (pH 9).

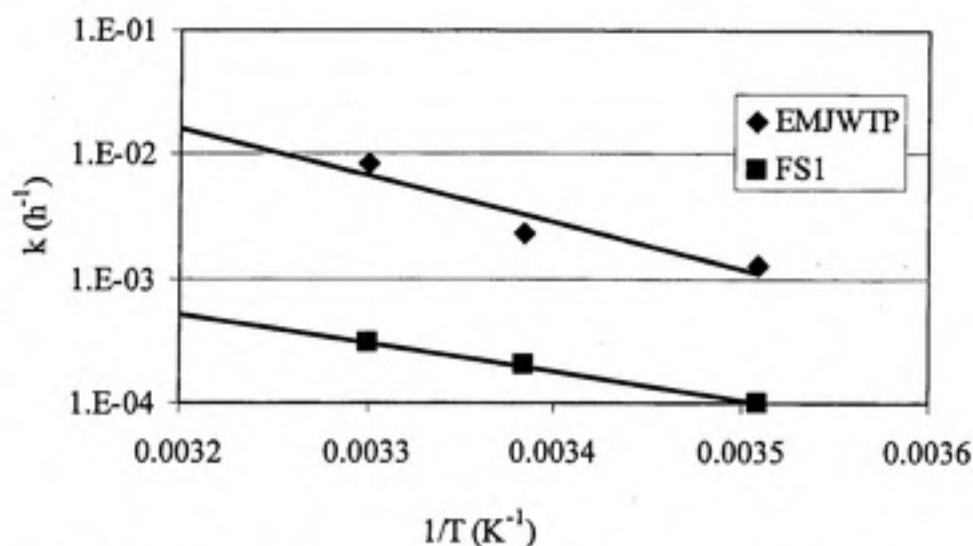


Figure 17 Effect of temperature on chloramine bulk decay rate: determination of activation energies for DS sample and finished water at pH 6

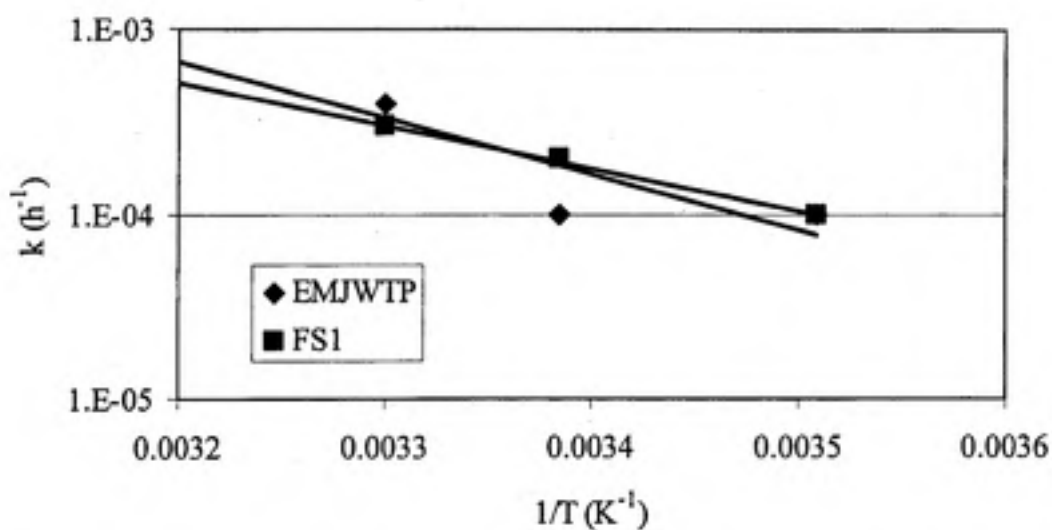


Figure 18 Effect of temperature on chloramine bulk decay rate: determination of activation energies for DS sample and finished water at pH 9

The activation energies calculated from the slopes of the plots in Figure 17 and Figure 18 are presented in Table 11. Activation energies are instructive as to the rate limiting step in a reaction scheme. In the case of monochloramine autodecomposition,

the rate limiting step is the formation of the unstable dichloramine molecule. As discussed, two reactive pathways are available for dichloramine formation: production of HOCl through monochloramine hydrolysis (Equation 5) acid catalyzed disproportionation of monochloramine (Equation 6). As to which of these two pathways prevails will depend on solution pH as well as free ammonia concentrations (see Equation 20). At pH 6, it is expected that the acid catalyzed disproportionation reaction will dominate dichloramine formation kinetics. At pH 9 both pathways may play an important role. Dominance of different decomposition pathways is evidenced by different activation energies at pH 6 (72 to 81 kJ/mol) versus pH 9 (44 to 58 kJ/mol). The difference in E_a values at pH 6 and 9 also suggests that the activation energy of acid catalyzed disproportionation is higher than that of monochloramine hydrolysis.

A common procedure used in environmental engineering is to provide an equation that can be used to calculate the rate constant at any temperature by knowing the rate constant at a reference temperature. Dividing the Arrhenius equation (Equation 57) at any temperature, T , by a reference of temperature of 20°C (293°K) gives

$$\frac{k_T}{k_{20}} = \frac{A}{A} e^{(-E_a/RT + E_a/R(293))} \quad (59)$$

Taking the $\log_{10}$ of both sides gives:

$$\log\left(\frac{k_T}{k_{20}}\right) = 0.4343 \frac{E_a(T - 293)}{RT(293)} \quad (60)$$

For T that is within $\pm 10^\circ\text{K}$ of 293°K, $0.4343 E_a / RT(293)$ will remain relatively constant, and can be approximated by $\beta = 0.4343 E_a / RT(293)$:

$$\log \frac{k_T}{k_{20}} = \beta(T - 293^\circ \text{K}) \quad (61)$$

The antilog of this equation is

$$\frac{k_T}{k_{20}} = \theta^{[T(^{\circ}K) - 293^{\circ}K]} = \theta^{[T(^{\circ}C) - 20^{\circ}C]} \quad (62)$$

where $\theta = 10^{\beta}$ and β is calculated from E_a , R and $T = 303^{\circ}K$. Note that temperature may be expressed for convenience in degrees Celsius; either $^{\circ}C$ or $^{\circ}K$ is acceptable in this form of equation to calculate the temperature effect. The values of θ and k_{20} are given in Table 11 for convenience of use.

Table 11 Calculated Activation Energies for Chloramine Decay in Bulk Water Based on Rate Data at Temperatures of 12, 22.5 and 30 $^{\circ}C$ and Arrhenius Equation

Location	pH	E_a kJ/mol	R^2	k_{20}	θ
EMJWTP	6	72	0.89	2.5×10^{-3}	1.104
	9	58	0.73	1.5×10^{-4}	1.083
FS 1	6	81	0.99	2.9×10^{-3}	1.118
	9	44	0.999	1.7×10^{-4}	1.062

Valentine et al. (1998) measured monochloramine autodecomposition at 4, 25 and 35 $^{\circ}C$, at pH 7.5, with 10 mM total carbonate and with 0.015 mM free ammonia. From the change in the second order rate constants they observed, an activation energy of 41 kJ/mol could be calculated. This value is very close to the E_a observed in the DS sample at pH 9: 44 kJ/mol. The first acid dissociation constant for carbonic acid is $pK_a = 6.3$. Therefore, in both the DS samples at pH 9 and those of Valentine et al. at pH 7.5, bicarbonate is the dominant form of alkalinity and the E_a values would be similar. A slightly lower E_a in the experiments of Valentine et al. could be explained by noting that the total carbonate in the solutions used by Valentine et al. was 10 mM, which is considerably higher than the average alkalinity of 0.34 mM in Raleigh finished water,

(City of Raleigh EMJWTP, 2004). Bicarbonate is a catalyst of monochloramine autodecomposition. Thus, lower total carbonate in Raleigh finished water could translate into higher observed activation energies.

The E_a for samples collected in the DS (FS 1) at pH 9 is about 20 percent lower than the E_a for finished water samples at pH 9. Whether this difference is explained mechanistically or by experimental error is difficult to determine without more measurements. A lower activation energy could be explained by a shift from the disproportionation pathway (Equation 6) to the hydrolysis pathway (Equation 2 and Equation 5) of dichloramine formation. The latter is favored at lower ammonia concentrations that may exist at FS1. While ammonia concentration was not measured in any samples, DiGiano et al. (2002) found that free ammonia levels at FS 1 were roughly half of those in the finished water over a six month period. Free ammonia in the finished water can combine readily with hypochlorous acid that is produced by monochloramine hydrolysis and thus suppress the hydrolysis pathway (see Equation 20). That is, the ammonia-HOCl reaction prevents HOCl from reacting with monochloramine thereby lessening the formation of dichloramine. If the free ammonia level declines within the DS, the hydrolysis pathway of dichloramine formation will become more important and the disproportionation pathway will become less important. Far more experimental evidence is needed, however, to confirm this hypothesis.

Pipe Section Reactor Experiments

Measurement of Iron Release

Iron, in both its oxidized and reduced forms, accelerates the rate of chloramine decay. Fe(II) can react directly with, thereby reducing, monochloramine. Ferric oxide

surfaces have been implicated in catalyzing reduction of monochloramine by Fe(II) (Vikesland and Valentine 2000). The direct reaction with Fe(II) and the catalyzing interaction with ferric oxides are both pH dependent (Vikesland and Valentine 2000; Vikesland and Valentine 2002). The reactivity and catalytic potential of iron towards chloramine imply that chloramine decay may depend upon the rate of iron release from pipe walls.

Iron release from DS pipe walls is the combined result of metallic iron corrosion, dissolution of ferric and ferrous minerals from corrosion scales and hydraulic scour. Corrosion scales, which are often referred to as tubercles, are iron-based mineral deposits. Their solubility is pH dependent. Iron corrosion rates are also known to be pH dependent.

The PSR has been shown in previous work to be very useful for measuring the rate of free chlorine decay in the presence of pipe wall material (DiGiano et al. 2004). However, the PSR had not been used to measure the rate of iron release. It was postulated that if the iron release rate could be measured as a function of pH by the PSR, a method may be established to estimate the rate of chloramine decay produced by wall reactions. That is, the reactivity of Fe(II) towards monochloramine and the catalytic effect of ferric precipitate on monochloramine-Fe(II) redox reactions are known. These are both dependent upon solution pH. Thus, the rate of chloramine decay may be predicted by measuring the pH and estimating the iron release rate as a function of pH.

A preliminary experiment was conducted to determine if the PSR could be used to measure the rate of iron release from the tuberculated CIP walls. Because chloramine can increase the rate of iron corrosion, chloramine was removed from Raleigh finished

water to avoid affecting iron release. Chloramine was removed by addition of sodium meta-bisulfite prior to each experiment (see Experimental Method for details). Finished water samples were then phosphate buffered at pH 8 and passed through the PSR at a rate of 50 mL/min. At this flow rate, hydraulic residence time within the PSR was 107 minutes. The total iron concentration and the DO in the feed water (Raleigh finished water) were 0.02 mg/L and 8.1 mg/L, respectively. The experiment was conducted at room temperature (22.5°C) and the stirring motor was set to achieve a simulated water velocity of 1.04 fps. With the stirring motor on, the PSR can be assumed to behave as a completely-mixed flow reactor (CMFR). The mass balance on iron within the PSR is thus:

$$QC_{in} - QC_{out} + rV = V \frac{dC_{out}}{dt} \quad (63)$$

where C_{in} is the feed concentration, C_{out} is the exit concentration, r is the rate of iron release (mg/L/min) and V is the volume of the PSR. The reaction is unsteady state because C_{out} is initially the feed concentration of the tap water but will increase over time due to iron release.

The initial assumption was a zero-order rate of iron release. If r is independent of iron concentration, Equation 63 can be integrated by separation of variables to give:

$$C_{out} = C_{in} + \frac{Vr}{Q} \left(1 - e^{-\frac{Q}{V}} \right) \quad (64)$$

The validity of the model was tested by finding the value of r that gave the best fit to the experimental data of C_{out} with time in the PSR experiment. A good fit is shown in Figure 19. This fit corresponds to an iron release rate of 0.009 mg/L-min.

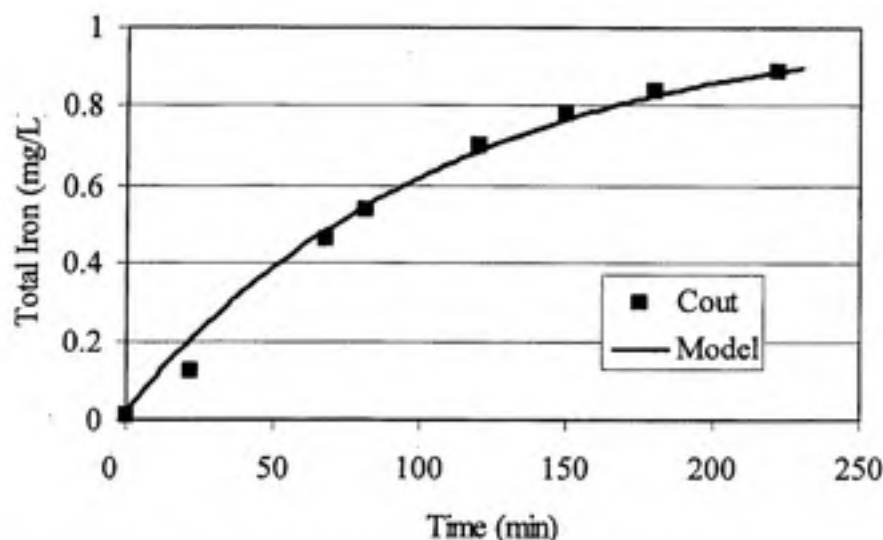


Figure 19 Iron release from the CIP section used as CMFR at 1.04 fps

An iron release rate per unit thickness of a corrosion layer is found by:

$$r_{Th} = r \left(\frac{V}{A} \right) \left(\frac{1}{\rho_{Fe(s)}} \right) \quad (65)$$

where A is the surface area of the pipe section and $\rho_{Fe(s)}$ is the density of iron within the surface layer. Surface area was calculated from an estimate of the average internal diameter of the tuberculated surface. It was assumed that most of the iron released during this experiment was released from the tubercles (a reasonable assumption given the complete, uniform coverage of metallic surface by tuberculation). The bulk density of the tuberculation was assumed to be 1.90 g/cc (40% porosity) based on measurements of the bulk tuberculation density in 90-year old sections of CIP in the Boston, MA distribution system (Sarin et al. 2000). Using these estimates of surface area and iron density, the rate of iron release on a thickness basis is 0.089 mm/yr, 3.5 mpy (mils per year), or 0.001 inches per year.

The rate of iron release from the tubercle surface is within the range reported for field tests of corrosion. DiGiano et al. (2004) measured corrosion rates in the field by inserting corrosion probes into the effluent stream of hydrants in North Chatham County and Durham, NC. The corrosivity of water in these distribution systems, with respect to iron, was 4.3 to 5.1 mpy and 6.1 to 6.4 mpy, respectively. Metallic iron, however, is much denser than corrosion scale: 7.86 g/cc versus 1.90 g/cc (Sarin et al. 2000). Thus, 3.5 mpy corrosion of metallic iron releases much more iron than 3.5 mpy of iron release from corrosion scale. Under these experimental conditions, corrosion scale is protective of the cast iron pipe surface releasing far less iron into solution than fresh, corroding pipe surface.

While the observed iron release matched expectations, subsequent experiments revealed a serious drawback. As in the preliminary iron release experiment, chloramine was removed from the Raleigh finished water by addition of sodium meta-bisulfite. A 10^{-2} M phosphate buffer was used to maintain pH 7 in one experiment and pH 8 in another. This was of interest because the rate of iron release by corrosion has been shown to depend upon pH. For example, Sarin et al. (2002) showed that iron release from tuberculated cast iron pipe loop decreased from 1.5 to 0.3 mg/L by increasing solution pH from 7.6 to 9.5. The simulated water velocity in each experiment was set to 0.22 fps which was considerably lower than 1.04 fps as used in the preliminary experiment. DO, which was proposed to play a key role in iron release by Sarin et al. (2002), was initially above 7.8 mg/L in each experiment.

The results of the PSR experiments are shown in Figure 20. Total effluent iron did not increase as was expected from the preliminary experiment. In fact, the iron

concentration appeared to decrease with time to 0.02 mg/L or below. According to the spectrophotometer manual, the lowest average concentration that can be resolved from zero with a 99% confidence interval is 0.02 mg/L. One possible explanation for a decrease in concentration would be initial re-suspension of loosely deposited iron particles just after the stirring motor was started. The main point, however, is that these data provide no evidence of iron release. The only substantial difference between the preliminary experiment, Figure 19, and the follow up experiments, Figure 20, was that the simulated water velocity was five times higher for the preliminary experiment. A higher velocity could have caused much more scouring of ferric particles from the tubercle shell. This implies physical disruption in contrast to iron release by corrosion or dissolution.

Chemically induced release of iron by corrosion or dissolution is much different than physical disruption of tubercles. Sarin et al. (2004) postulated a complex mechanism by which soft, porous ferrous minerals may be encapsulated by a denser ferric oxide shell. Breaks in the shell can cause release of reduced iron as can the onset of anoxic conditions (e.g., during stagnation) which then causes the outer shell to dissolve allowing the release of reduced iron. The preliminary experiment at high velocity may have produced hydraulic scour of the shell that caused iron release by breakage of the protective shell on tubercles. Therefore, while measurement of iron in the preliminary experiment was promising, follow up work suggested that a relationship between the chemistry of corrosion and iron release would be very difficult to measure in the PSR. For this reason, iron release experiments were discontinued.

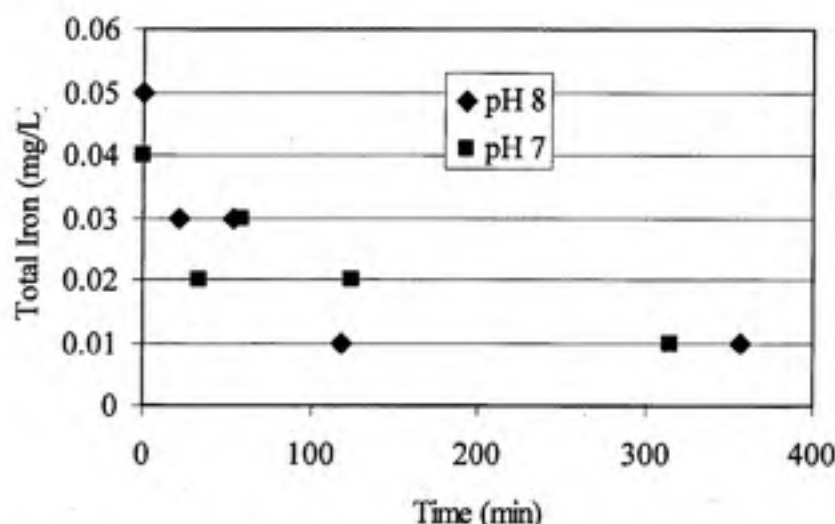


Figure 20 Iron release from the CIP section used as CMFR at 0.22 fps

Chloramine Decay in the Presence of CIP

A series of batch experiments was performed in the PSR to simulate the DS environment with a CIP section. The first set of experiments was designed to test rate models to describe chloramine decay. As discussed in the literature review, free chlorine as well as chloramine decay in the DS is due to the combination of decay in the bulk fluid (bulk decay) and decay at the wall. The presence of the wall material complicates rate analysis because of the need to account for mass transfer between the wall and the bulk water. Thus, the intrinsic reaction rate between chloramine and iron on the pipe wall may be masked by a mass transfer limitation. While the bulk decay rate can be measured directly, as described in the previous section, the intrinsic wall reaction rate must be deduced from the observed rate of decay in a simulated DS environment. The design of PSR experiments is such that the bulk decay of chloramine cannot be simply subtracted so as to measure only the decay by wall reaction. Nonetheless, a method from the

literature (Rossman et al. 1994) will be discussed to determine the intrinsic wall reaction rate from an observed decay rate by accounting for bulk water decay.

A zero-order model of observed decay rate, k_{obs} , was tried first because this had been shown valid for description of the free chlorine decay rate by wall reaction in CIP (DiGiano and Zhang, 2005). Zero-order decay occurs when the reaction rate is not controlled by the oxidant concentration but rather by the reductant (ferrous ion) concentration. In their experiments DiGiano et al. observed that the bulk decay accounted for a very small fraction of free chlorine decay. Therefore, the wall reaction was much faster than bulk decay. If the wall reaction is much faster than bulk decay the approximation can be made to description of the data by the wall reaction alone.

A zero-order wall reaction rate model is simply:

$$\frac{dC}{dt} = k_{obs,0} \approx k_{w,0} \quad (66)$$

Integration of Equation 66 yields:

$$C = C_o - k_{w,0}t \quad (67)$$

Plots of chloramine concentration over time for three different initial chloramine concentrations are provided in Figure 21. These experiments were conducted at room temperature (22.5°C), pH 8 with 10^{-3} M phosphate buffering and with a simulated water velocity of 1.36 fps. Initial DO concentrations were in the range 7.8 to 8.3 mg/L. The rate of chloramine decay was fairly rapid. In one experiment, chloramine decayed from 3.8 mg/L to 1.1 mg/L in two hours. According to the results of earlier experiments concerning bulk water decay rates (see Table 6) the time required to observe this same extent of decline would be roughly 4000 hours. Thus, the rate of wall reaction in CIP is far greater than the rate of bulk water reaction.

If the zero-order rate model is appropriate, the data sets in Figure 21 should appear as parallel, straight lines. It is apparent from Figure 21 that a zero-order model does not describe these data.

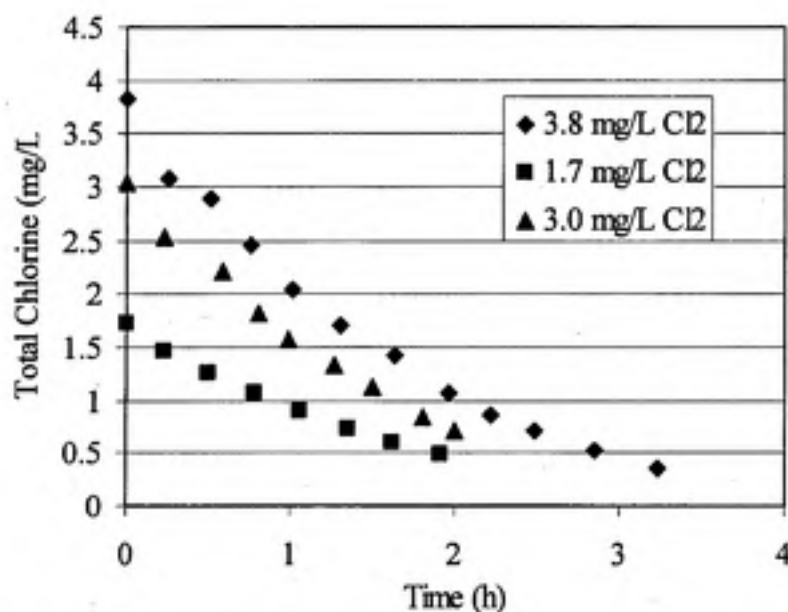


Figure 21 Chloramine decay in CIP section at pH 8, 1.36 fps velocity and 22.5°C

The data were next plotted to test a first-order decay rate. As shown in Figure 22, the first order model gave an excellent fit to the data. An essential test of a true first-order model is that the normalization of concentration by the initial concentration results in superimposition of each data set for the three different initial concentrations of chloramine as is clearly apparent in Figure 22. The $k_{obs,i}$ values and R^2 values are given in Table 12. All three rate constants agree very closely.

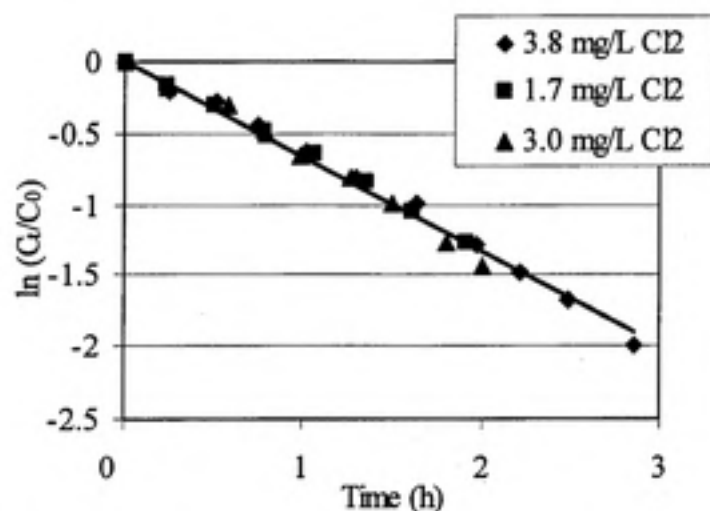


Figure 22 Test of first-order rate model of chloramine decay in PSR with CIP section

Table 12 First-order constants for the observed rate of chloramine decay in the presence of CIP at pH 8, 1.36 fps and 22.5°C

Initial Concentration (mg/L)	$k_{obs,1}$ (h ⁻¹)	R ²
3.8	0.68	0.99
1.7	0.64	0.996
3.0	0.72	0.99

The linearized form of a second-order rate model was also tested with the same data sets in the same way as for decay rate studies in bulk water. The curvilinear nature of each of three plots presented in Figure 23 is evidence that a second-order rate model is not appropriate.

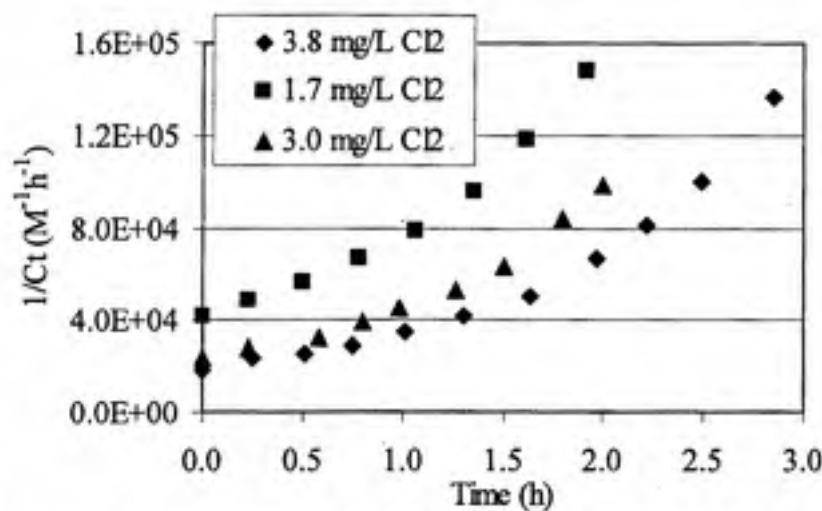


Figure 23 Test of second-order rate model of chloramine decay in PSR with CIP

The difference in rate behavior between the PSR and the bulk water rate experiments is important. The bulk decay rate of chloramine was not clearly shown to be either pseudo first-order (a second reactant was likely involved) or second-order (this being justified by autodecomposition involving two monochloramine molecules). However, the decay rate of chloramine in the presence of the CIP material was very clearly a first-order process with respect to chloramine concentration. Chloramine decay in the PSR differs from decay in the bulk water because of the intrinsic wall reaction rate that occurs in the PSR. This wall reaction requires accounting for the rate at which chloramine transfers from the bulk water to the wall where the reaction takes place. The next step in the investigation of kinetics, therefore, was to examine the effect of water velocity on the observed decay rate.

Effect of Velocity on Observed Chloramine Decay Rate on CIP

Hallam et al. (2002) and DiGiano and Zhang (2005) showed that the free chlorine decay rate increases with water velocity if the wall reaction rate is limited by mass

transfer of the reactant to the pipe wall. Whether this same effect would be observed for the chloramine decay rate depends on the relative magnitude of the rates for the intrinsic reaction at the wall and mass transfer. Rossman et al. (1994) proposed that three rate constants are needed to predict the observed decay rate (see Equation 37): the bulk decay rate, k_b , the intrinsic reaction rate at the wall, k_w , and the rate of mass transfer, k_f . The bulk decay rate is slow in comparison to the intrinsic wall reaction rate and accounts for only a small fraction of decay. If the wall reaction rate is fast relative to mass transfer, k_f controls the observed reaction rate and it will increase with water velocity. However, if the wall reaction rate is slow relative to the rate of mass transfer, k_w controls and the observed rate is independent of water velocity. If the two rate constants are similar in magnitude, both will contribute to the determination of the overall rate of decay.

A series of PSR experiments was performed in the CIP section over simulated water velocities that ranged from 0.22 to 1.36 fps. Initial DO ranged from 7.2 to 8.8 mg/L, the average temperature for each experiment was between 22.5 and 23.5°C and each batch of feed water was buffered by 10^{-3} M phosphate to pH 8. The linearized first-order rate model was applied successfully for all four experiments as shown in Figure 24. The observed rate of chloramine decay can be seen to increase with velocity suggesting mass transfer limitation of the reactant in this velocity range.

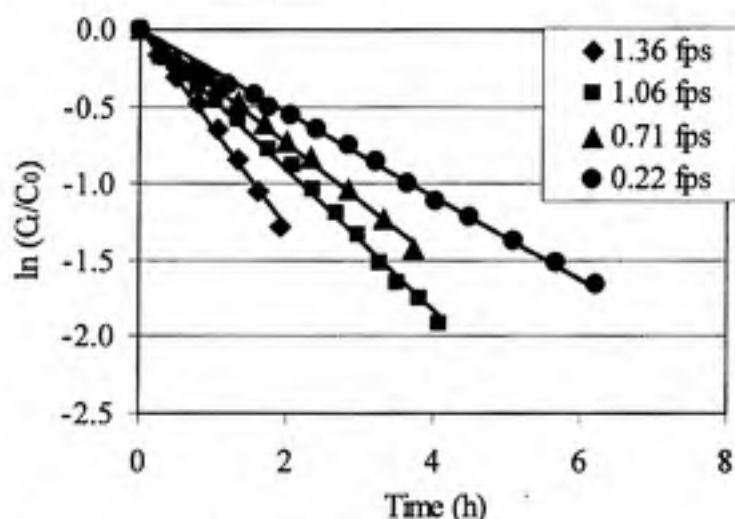


Figure 24 Application of first-order rate model of chloramine decay at four simulated velocities in CIP section at pH 8 and 23°C

The same series of four experiments presented in Figure 24 was repeated twice. The resulting observed rate constants from all twelve experiments are plotted against the simulated water velocity in Figure 25. Initial DO in all experiments ranged from 6.8 to 8.9 mg/L, the average temperature for each experiment was between 22.5 and 24.5°C and each batch of feed water was buffered by 10^{-3} M phosphate to pH 8. The data point for each velocity setting is the average of three experiments; the bars show the 95 percent confidence intervals with two degrees of freedom.

The results in Figure 25 show that $k_{obs,l}$ only increases slightly until a threshold value of water velocity of about 0.6 fps. Above this threshold value, $k_{obs,l}$ increases more rapidly with water velocity as may be expected if mass transfer is rate limiting. Similar results were obtained by DiGiano and Zhang (2005) in their PSR experiments with free chlorine. The rate of chloramine decay depends on water velocity because decay is dominated by reactions with the tuberculated CIP wall and because the wall reaction rate

is either greater than or comparable to the rate of chloramine mass transfer from the bulk fluid to the wall.

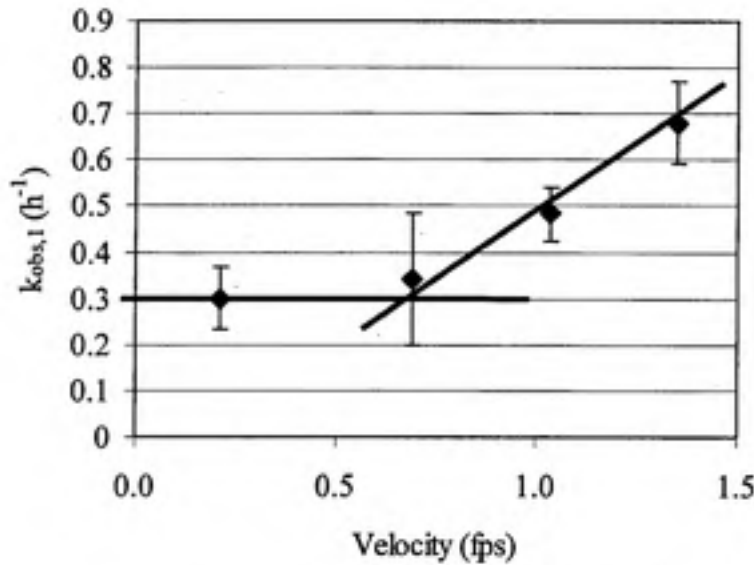


Figure 25 First-order decay rate constants versus velocity in CIP section

The rate of decay of chloramine at the wall, k_w , can be calculated from $k_{obs,1}$. The nature of the PSR in fundamental terms is a batch recycle reactor wherein the surface of the pipe material represents a “differential reactor” because the spatial gradient of chloramine concentration (dC/dx) is small enough to be ignored (Weber and DiGiano, 1996). Thus, the fundamental mass balance given by Equation 37 reduces to:

$$\frac{dC}{dt} = -k_b C - \frac{k_w k_f}{r_h (k_w + k_f)} C = - \left(k_b + \frac{k_w k_f}{r_h (k_w + k_f)} \right) C \quad (68)$$

where the rate constants within the brackets are collectively the observed first-order rate of decay of chloramine in the PSR. Given that k_b and k_f are known, k_w can be found by rearrangement of the rate constants:

$$k_w = \frac{(k_{obs,l} - k_b)r_h k_f}{k_f - r_h(k_{obs,l} - k_b)} \quad (69)$$

The rate constant for decay in bulk water, k_b , was assumed equal to $2.9 \times 10^{-4} \text{ h}^{-1}$ based on rate data from bulk water testing. A Sherwood-Reynolds-Schmidt number correlation is provided in Equations 38 through Equation 41 from which k_f can be calculated as a function of simulated water velocity. Rossman et al. used the Sherwood-Reynolds-Schmidt relationship for turbulent fluid flow in pipes given by Edwards et al. (1976). This same relationship was also given by Geankoplis (1978). Others have given a slightly different correlation; Cussler (1984) used $Sh = 0.026(Re)^{0.8}(Sc)^{0.333}$. However, to remain consistent with the method of Rossman et al. (1994), the dimensionless relationship of Edwards et al. and Geankoplis was used to determine k_f .

The hydraulic nature of the PSR differs from that of a section of pipe in a DS and deserves comment. The presence of the acrylic cylinder inside the PSR is hydraulically analogous to placing a solid cylinder of equal diameter within the PSR: water flowing against the pipe wall is confined to the annular space. However, the confinement of flow has no bearing on the formulation of Equation 68. The hydraulic radius in Equation 68 derives from the ratio of the total volume within the PSR to the internal surface area of the pipe wall, neither of which is affected by the presence of the hollow acrylic cylinder. Likewise, the Sherwood-Reynolds-Schmidt number correlation in Equations 38 through 41 is not affected by the presence of the acrylic cylinder. Cussler (1984) explained that the characteristic length for turbulent fluid flow in a pipe which is typically the diameter, is important because only the pipe wall region is involved. The pipe wall region is unaffected by the acrylic cylinder; thus, the characteristic length is also unaffected.

Mass transfer correlations are implicitly temperature dependent in that the molecular diffusivity of the component being transferred and the viscosity of the water must be specified for the temperature of interest. In these calculations, a temperature of 25°C was assumed such that the molecular diffusivity of chloramine in water is 1.87×10^{-9} m²/s (based on the Wilke-Chang equation) and the dimensionless Schmidt number is 481. The Reynolds and Sherwood numbers corresponding to the simulated velocities in each experiment and resulting mass transfer coefficients are listed in Table 13.

Table 13 Dimensionless Groups used to calculate k_f for each simulated water velocity in CIP Section at 25°C

Velocity (fps)	Re	Sh	k_f (m/h)
1.35	6.41×10^4	1.73×10^3	8.35×10^{-2}
1.04	4.92×10^4	1.39×10^3	6.71×10^{-2}
0.69	3.27×10^4	9.86×10^2	4.78×10^{-2}
0.21	1.00×10^4	3.70×10^2	1.79×10^{-2}

After substitution of k_f , k_b and the hydraulic radius of the pipe section, r_h , the k_w values were determined from the average observed decay rate at each velocity setting using Equation 69. These k_w values are plotted against water velocity in Figure 26. The variation in k_w is not large, nor is there a systematic relationship with water velocity. This is strong evidence of k_w being independent of water velocity as should be expected. The average k_w for this data set (four measurements) is 2.4×10^{-2} m/h with a standard deviation of 7.1×10^{-3} m/h. Given that the mass transfer coefficients in Table 13 are on the same order of magnitude as the wall decay rate in CIP, both would control the observed chloramine decay rate or k_{obs} in Equation 68.

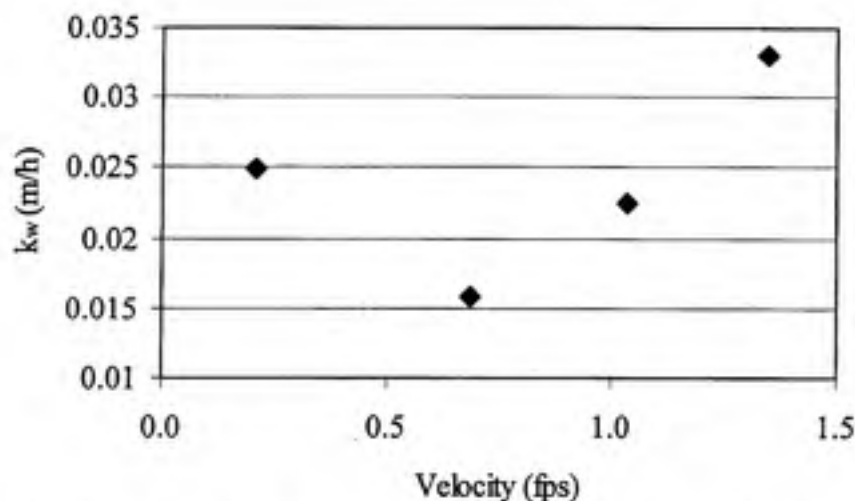


Figure 26 Intrinsic wall reaction rate coefficient, k_w , calculated from the average observed rate of chloramine decay at four water velocities in CIP at pH 8 and 23.5°C

The complexity of the iron-monochloramine reaction system makes it impossible to conclude a specific reaction mechanism leading to chloramine decay from the type of kinetic study performed here. The results presented in Figure 18 indicate that the observed decay rate is well approximated by a first-order relationship. Assuming that the observed decay rate is dominated by the intrinsic wall reaction, the intrinsic reaction rate can also be assumed as first-order. The intrinsic rate for chloramine decay by wall reaction could be first-order if there is a direct reaction with Fe(II). Fe(II) would be introduced by corrosion or ferrous mineral dissolution from the corrosion scale. In the iron release scheme proposed by Sarin et al. (2004), DO reacts rapidly with Fe(II) at the tubercle surface thus preventing iron release. Monochloramine could also be reacting with Fe(II) at that same surface.

The rate of chloramine decay in the presence of CIP in the PSR was first-order while DiGiano and Zhang (2005) found that the rate of free chlorine decay was zero-order using the same experimental setup, i.e., the rate of decay was independent of free

chlorine concentration. DiGiano and Zhang (2005) attributed this behavior to the rate limiting generation of the corrosion product Fe(II). If the rate of corrosion product generation was slow relative to the rate of reduction of free chlorine by Fe(II), the rate of Fe(II) generation would control the overall redox reaction rate and thus, the reaction rate would not depend on the chlorine concentration. Conversely, the first-order dependence of decay on chloramine in CIP indicates that the rate of corrosion product generation is as fast or faster than the rate of reduction of monochloramine by Fe(II). This explanation seems intuitively correct given that the decay rate of chloramine in bulk water is much slower than that of free chlorine.

Effect of pH on Observed Chloramine Decay Rate on CIP

Chloramine decay can occur by reactions with NOM and iron as well as by autodecomposition. Each of these classes of reaction is pH dependent and each can occur in the distribution system. Thus, quantification of the effect of pH on chloramine decay rate in the presence of CIP is of practical importance. A series of PSR tests was conducted with Raleigh finished water at pH 7 and 8, using the same phosphate buffering system as described earlier; a 10^{-3} M borate buffer was used to achieve pH 9. The simulated water velocity was set at 1.36 fps, average operating temperature was between 23.2 and 23.9°C and initial DO for all three experiments was in excess of 7.0 mg/L.

The observed rate of chloramine decay at each of three pH values was well described by a first-order model as illustrated in Figure 27. The first-order rate constants are shown to increase linearly with decreasing pH in Figure 28. The decrease in pH from 9 to 8 increases the observed rate constant by 60 percent; the increase in rate constant is 120 percent when comparing the results of pH 9 to pH 7 experiments.

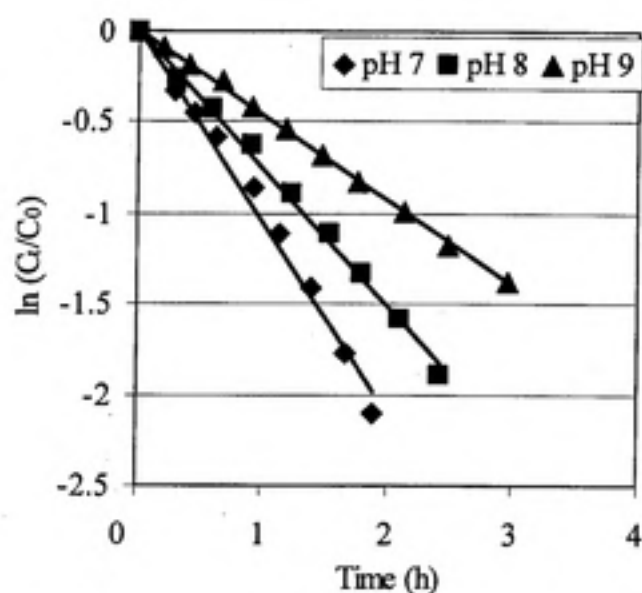


Figure 27 Application of first-order rate model of chloramine decay at pH 7, 8 and 9 in CIP section at 1.36 fps and 23.5°C

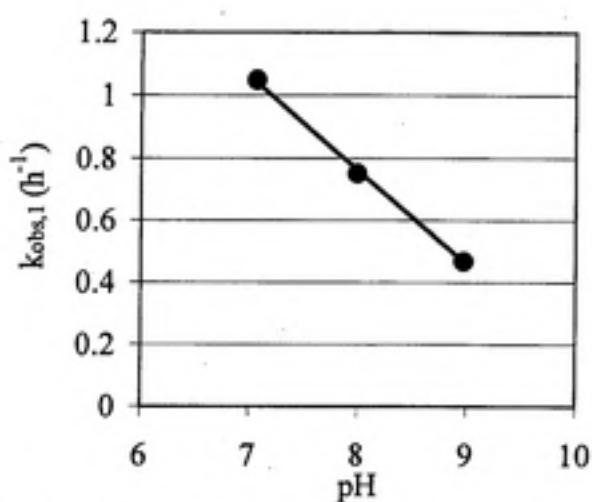


Figure 28 Effect of pH on observed first-order decay coefficient in CIP section at 1.36 fps and 23.5°C

An increase in $k_{obs,1}$ with decreasing pH is opposite to expectations from the literature with regard to the bulk water reaction between chloramine and Fe(II) (Vikesland and Valentine 2000). It is also opposite to what is expected from the

literature when considering the iron oxide surface-catalyzed reaction between chloramine and Fe(II) (Vikesland and Valentine 2002). However, neither the bulk water nor iron oxide surface-catalytic mechanisms consider the availability of Fe(II) as is necessary when tubercles are present. Dissolution of Fe(II) is favored by lower pH. If more iron was being dissolved at pH 7 but all of it was oxidized at the tubercle surface, iron released from the corrosion deposits into the bulk fluid would not increase. However, more Fe(II) may be available at lower pH for reaction at that surface. The increase in Fe(II) could then accelerate chloramine decay at the tubercle surface, i.e., at the pipe wall.

The siderite (FeCO_3) model of iron release was proposed by Sontheimer et al. (1981). FeCO_3 is the least soluble ferrous mineral in the anoxic tubercle interior. In the presence of siderite, dissolved Fe(II) concentrations inside the tubercle will be determined principally by pH and alkalinity. Sarin et al. (2003) performed equilibrium calculations for the dissolved Fe(II) concentrations in equilibrium with FeCO_3 based on thermodynamic relationships and plotted the concentrations as a function of pH and alkalinity.

The average alkalinity in Raleigh finished water in 2004 was 33.8 mg/L as CaCO_3 . Based on the work of Sarin et al. (2003), the equilibrium concentration of dissolved Fe(II) within the tubercle is about 8.5 mg/L at pH 7, 1.7 mg/L at pH 8 and 0.7 mg/L at pH 9. In other words, when the pH is lowered from 9 to 8, a 140 percent increase in equilibrium concentration of Fe(II) within the tubercle would be expected. Likewise, an 1100 percent increase is expected by decreasing the pH from pH 9 to pH 7. The corresponding change in Fe(II) concentration at the tubercle surface would depend

on the diffusivity of Fe(II), the porosity of the tubercle shell and the rate of oxidation of Fe(II) by DO. Therefore, the concentration of Fe(II) available for reaction with chloramines will not increase in direct proportion with the concentration of Fe(II) at the tubercle interior. Nonetheless, more dissolved Fe(II) within the tubercle could account for the faster rate of chloramine decay at the tubercle surface.

An increase in observed chloramine decay rate at lower pH because of increased concentrations of reactive ferrous atoms at the ferric oxide wall should also mean a corresponding increase in the intrinsic rate of reaction at the wall. The k_w was calculated from the observed rate of chloramine decay at each pH using the same method as presented earlier (see Equation 69). The resulting k_w values are plotted against pH in Figure 29. As expected, k_w increases with decreasing pH: decreasing the pH from 9 to 8, increases k_w by 88 percent and decreasing pH from pH 9 to pH 7 increases k_w by 220 percent. The line of best fit with an $R^2 = 0.984$ is:

$$k_w = -0.023(\text{pH}) + 0.225 \quad (70)$$

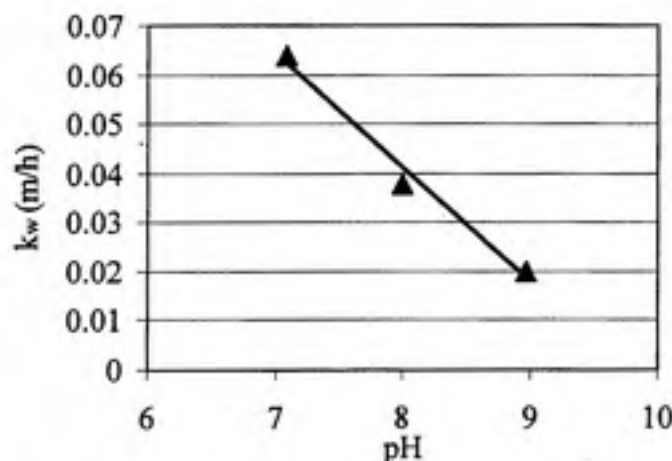


Figure 29 Effect of pH on the intrinsic wall reaction rate in CIP at 23.5°C

Effect of Temperature on Observed Chloramine Decay Rate on CIP

As shown in Figure 30, rate data from the PSR conformed to the first-order model at temperatures of 15.1, 23.5 and 29.5°C. The simulated water velocity was 1.36 fps, the pH was buffered to 8 and the initial DO was in excess of 7.8 mg/L for these tests. As expected, chloramine decays more rapidly at higher temperatures. The observed reaction rate constant includes mass transfer effects that will not be affected by temperature in the same way as the decay reaction. Therefore, the activation energies cannot be calculated from $k_{obs,t}$ values. Instead, k_w values must be used.

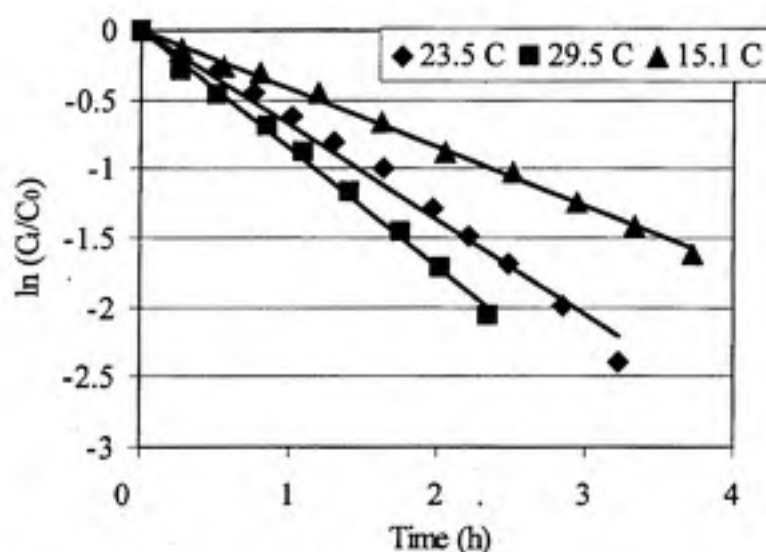


Figure 30 Test of first-order model of decay at three temperatures within the CIP section at pH 8 and 1.36 fps

Intrinsic wall reaction rate constants from each experiment are plotted semi-logarithmically according to the Arrhenius equation, Equation 58, in Figure 31. The activation energy calculated from the slope of the line of best fit is 67 kJ/mol with an $R^2 = 0.998$. For comparison, the E_a for decay in bulk DS samples at pH 9 was 44 kJ/mol.

and in bulk finished water at pH 9 was 58 kJ/mol (see Table 11). These E_a values are different enough to conclude that different mechanisms are dominating chloramine loss in bulk decay and PSR experiments.

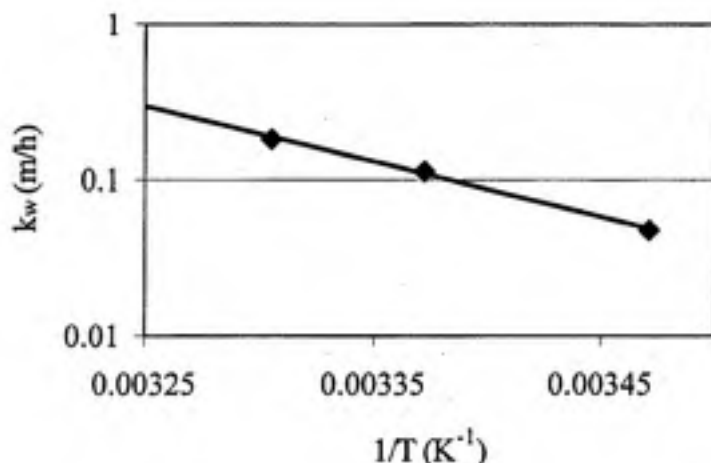


Figure 31 Effect of temperature on intrinsic wall reaction rate in CIP section: determination of activation energies at pH 8

As with the bulk decay rate (see Equation 62), the intrinsic wall reaction rate in CIP can be calculated from the intrinsic rate at a reference temperature of 20°C. Using $\theta = 1.10$ and $k_{w,20} = 0.078 \text{ m/h}$, the intrinsic wall reaction rate can be calculated at any temperature from 283 to 303°K (10 to 30°C).

Predicting Observed Rate of Decay in CIP

The observed rate of chloramine decay in CIP, $k_{obs,I}$ can be predicted by Equation 68. The relationships needed to evaluate each of the constants in Equation 68 are provided in Table 14. The bulk decay rate, k_b , can be estimated from the rate of decay observed in the DS samples either at pH 6 or at pH 9. Typically, finished water pH is high enough so that the bulk decay rate will be closer to k_b for pH 9. However, pH can

decrease with residence time in the DS (DiGiano et al. 2002), and if the finished water pH is less than 7.0, carbonic acid speciation could accelerate monochloramine autodecomposition. In that case, the bulk decay rate may be closer to the k_b observed at pH 6. The bulk decay rate may be adjusted for temperature by the Arrhenius relationship, Equation 58. However, in the typical DS temperature range (from 10 to 30°C), the bulk decay constant would not vary greatly (from $1.4 \times 10^{-4} \text{ h}^{-1}$ to $3.4 \times 10^{-4} \text{ h}^{-1}$). Furthermore, chloramine decay will be dominated by reactions with the CIP wall. Accordingly, the bulk decay rate has been assumed for simplicity of use to be independent of temperature. The calculation of k_f has been explained in previous sections based on the well known Sherwood-Reynolds-Schmidt number correlation. Below the correlation in Table 14 is given an equation to find k_f at a reference temperature of 20°C as a function of water velocity and pipe diameter. To use the equation for other temperatures requires substitution of the temperature adjusted viscosity and diffusivity into the Reynolds and Schmidt number. The equation given for k_w in Table 14 is based on the experiments conducted in this research that showed its dependency on both pH and temperature wherein the reference pH is 8 and the reference temperature is 20°C.

Table 14 Equations for predicting observed rate of decay in cast iron pipe

Parameter	Variable Dependency	Equation(s)	Units
k_b	pH, Temp.	$\approx 4.3 \times 10^{-3} \text{ h}^{-1} \text{ (pH 6)}; \approx 2.9 \times 10^{-4} \text{ h}^{-1} \text{ (pH 9)}$ $= 0.121 [v(m/s)]^{0.83} [d(m)]^{-0.17}$	h^{-1}
k_f	Velocity, Temperature	where: $\text{Sh} = 0.023 \text{ Re}^{0.83} \text{ Sc}^{0.33}$; $\text{Re} = \frac{\rho V d}{\mu}$ $\text{Sc}^* = 481$; $D^* = 1.87 \times 10^{-9} \text{ m}^2/\text{s}$	m/h
k_w	pH	$= -0.023(\text{pH}) + 0.225$	m/h
	Temperature	$= 0.078(1.10^{(T-20)})^\dagger$	m/h
$k_{obs,l}$	pH, Vel., Temp.	$= k_b + \frac{k_w k_f}{r_h(k_w + k_f)}$	h^{-1}

* Schmidt number and diffusivity at 25°C are given and should be recalculated if temperature varies more than $\pm 10^\circ\text{C}$

† Temperature should be input as degrees Celsius

Chloramine Decay in the Presence of DIP

Three rate tests were conducted with different initial concentrations of chloramine in a PSR that contained DIP. In all three experiments, the temperature was 24.5°C, the pH was buffered to 8, the velocity was 0.91 fps and initial DO was in excess of 8.1 mg/L. DO only decayed slightly in all of the DIP experiments. The zero-order rate model (Equation 48) was tested with these rate data as shown in Figure 32. The deviation from linearity of these plots is large enough to conclude that a zero-order rate model is not appropriate.

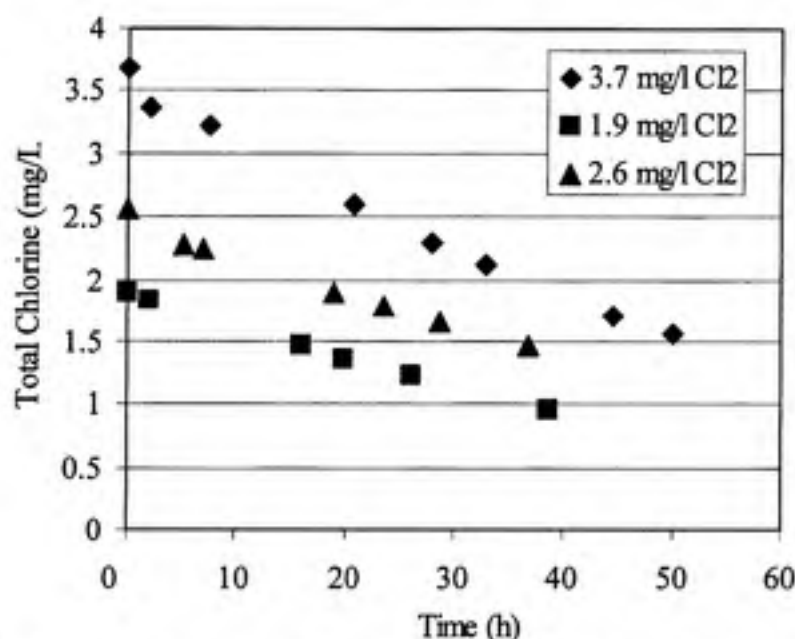


Figure 32 Chloramine decay in DIP section at pH 8, 0.91 fps velocity and 24.5°C

The rate of chloramine decay in the presence of DIP was slower compared with that in the presence of CIP (see Figure 21). Whereas chloramine decreased from 3.8 to less than 1 mg/L as Cl₂ in two hours in the CIP section, it took much longer (two days) for chloramine to decrease from 3.7 to 1.5 mg/L as Cl₂ in the DIP section. As expected from the lack of availability of reactive iron, chloramine decay is much slower in the DIP than in the CIP section. However, decay in the DIP section is sufficiently fast in comparison to the bulk decay experiments to conclude that interactions with the pipe wall are contributing to chloramine loss. For example, it would take roughly 125 days for chloramine to decay from 3.7 to 1.5 mg/L by the bulk decay rate.

The same three data sets were tested with a first-order rate model as depicted in Figure 33. As was found for the CIP section, a first-order rate describes all three data sets very well. The first-order rate constants for each data set along with the R² values are listed in Table 15. The difference among these rate constants is very small.

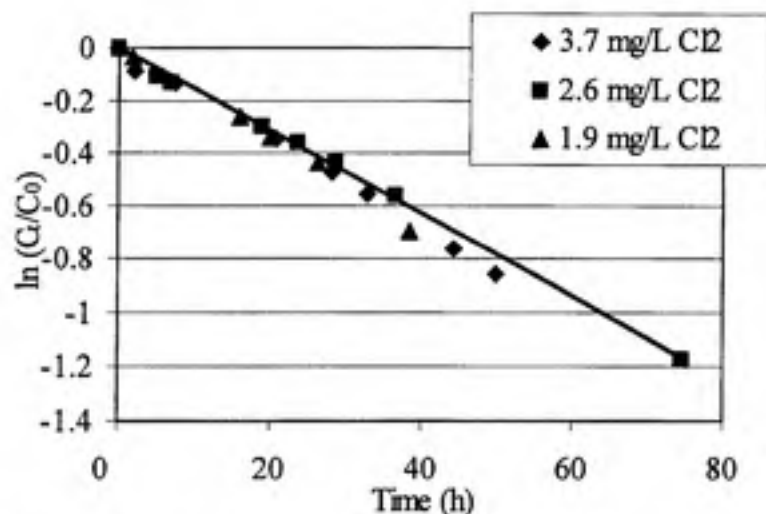


Figure 33 Test of first-order rate model of chloramine decay in PSR with DIP section

Table 15 First-order rate constants for chloramine decay in the presence of DIP

Initial Concentration (mg/L as Cl ₂)	$k_{obs,1}$ (h ⁻¹)	R ²
3.7	1.7×10^{-2}	0.995
2.6	1.6×10^{-2}	0.997
1.9	1.7×10^{-2}	0.996

The second-order rate model was also tested as shown in Figure 34. Lines of best fit were plotted to determine the second-order rate constant for each experiment. The $k_{obs,2}$ values are reported in Table 16 along with the corresponding R² value. The high R² values suggest a good fit. However, there is clearly a systematic deviation from linearity with time that indicates the inappropriateness of the second-order rate model and thus, the superiority of the first-order rate model. Further evidence of the failure of the second order model is the increase in $k_{obs,2}$ with decreasing initial concentration of chloramine concentration; a true second-order model would yield the same $k_{obs,2}$. By comparison, the first-order model (see Table 15) shows almost no variation with initial concentration.

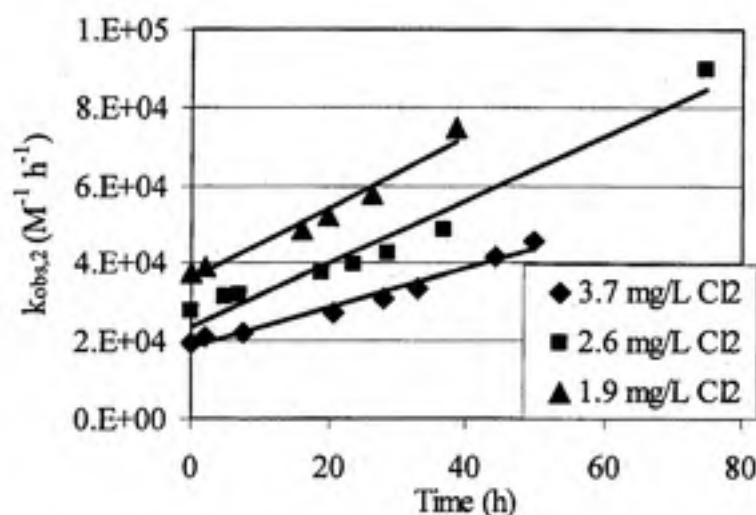


Figure 34 Test of second-order rate model of chloramine decay in PSR with DIP section

Table 16 Second-order rate constants for chloramine decay in the presence of DIP

Initial Concentration (mg/L as Cl ₂)	$k_{obs,2}$ (M ⁻¹ h ⁻¹)	R ²
3.7	500	0.976
2.6	810	0.958
1.9	930	0.971

Unlike the CIP section where highly reactive Fe(II) can be introduced directly through corrosion or dissolution of the tubercle, the cement lining in the DIP prevents significant amounts of iron release. Not surprisingly, the observed first-order rate constants for chloramine decay in the DIP section (Table 15) are an order of magnitude smaller than for decay in CIP (Table 12). However, the rate of chloramine decay in the DIP section is still two orders of magnitude larger than the bulk decay rate constant. Interactions between chloramines and the cement lining of the DIP significantly accelerate the rate of chloramine decay. Account must be taken of the mass transfer effect in order to explore the intrinsic reaction rate of chloramines at the DIP wall.

Effect of Velocity on Observed Chloramine Decay Rate on DIP

Analogous PSR experiments to those wherein CI was the wall material were performed at four velocity settings. For each of these experiments the initial DO was in excess of 8.2 mg/L, the average temperature for each experiment was between 23.2 and 24.4°C and water batches were 10^{-3} M phosphate buffered to pH 8. The first-order rate model was successfully applied to the results from each experiment as presented in Figure 35. Unlike the CIP experiments (see Figure 24), the rate of chloramine decay in all of these experiments is nearly indistinguishable despite the wide range of velocity settings. The rate of chloramine decay does not increase with water velocity as had been observed when the pipe material was CI.

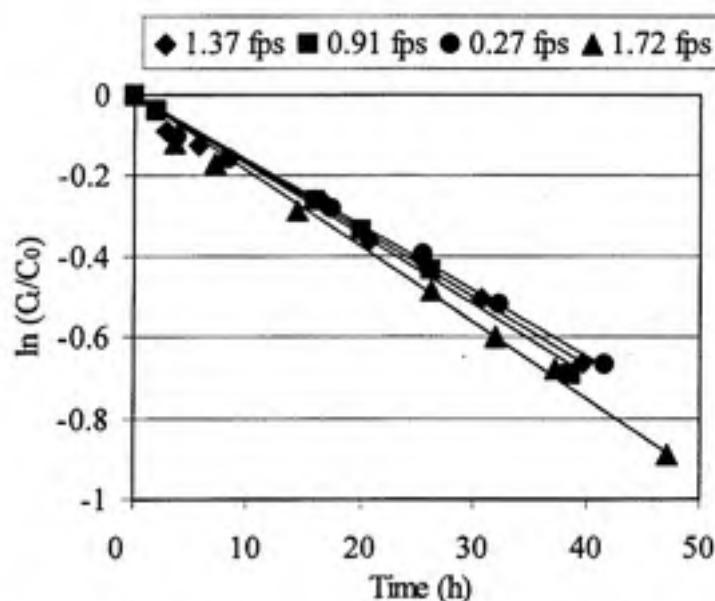


Figure 35 Application of first-order rate model of chloramine decay at four simulated velocities in DIP section at pH 8, 23.8°C

The same set of experiments was repeated twice to confirm that the observed rate constant for chloramine decay was independent of velocity. Summary statistics of the

resulting observed rate constants from all twelve experiments are plotted against the simulated water velocity in Figure 36. Initial DO in all experiments exceeded 8.0 mg/L, the average temperature for each experiment was between 24.2 and 25.1°C and water batches were buffered to pH 8 with 10^{-3} M phosphate. The data point for each velocity setting is the average $k_{obs,1}$ of three experiments and the vertical bars show the 95 percent confidence intervals at 2 degrees of freedom. There is no trend to suggest that $k_{obs,1}$ increases with water velocity.

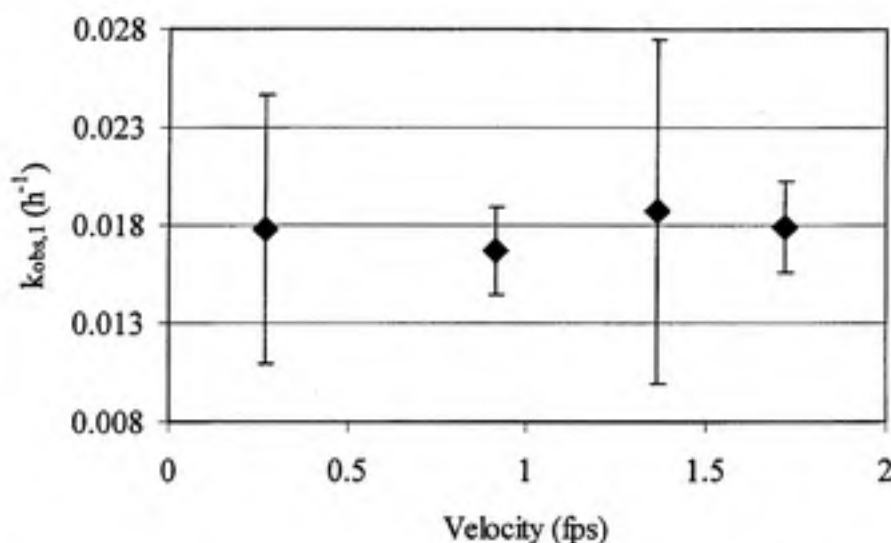


Figure 36 Effect of water velocity on the observed first-order decay rate in DIP at pH 8, 24.6°C

Because $k_{obs,1}$ does not depend on water velocity, mass transfer is not rate limiting for DIP. Thus, the conclusion is that the rate of chloramine transfer to the wall is faster than the intrinsic rate of reaction at the wall. The absence of a mass transfer limitation allows direct determination of the intrinsic rate of reaction at the wall from the experimental rate data. The assumptions are that the bulk and wall reactions are both

first-order and occur in parallel. Equation 45 is then used to calculate the wall reaction rate, K_w , by subtracting the bulk decay constant, k_b , from the observed decay rate; K_w is given by k_w/r_h where r_h is the hydraulic radius of the pipe. DiGiano and Zhang (2005) used the same formulation to calculate k_w for free chlorine decay on DIP.

The k_{obs} values given in Figure 36 were used to calculate the average and standard deviation of k_w by first calculating K_w from Equation 45 (with k_b set equal to $2.9 \times 10^{-4} \text{ h}^{-1}$) and then k_w from Equation 46. The calculation gave an average and standard deviation of k_w (based on 12 measurements) of $6.6 \times 10^{-4} \text{ m/h} \pm 8.1 \times 10^{-5} \text{ m/h}$. Given that k_f at the lowest water velocity (0.27 fps) is $2.2 \times 10^{-2} \text{ m/h}$, k_w is two orders of magnitude smaller thereby confirming quantitatively that the intrinsic rate of reaction at the DIP wall governs the rate of chloramine decay. The mass transfer rate would only affect the observed decay rate at velocities much lower than 0.27 fps.

The effect of pipe material on k_w can be seen by comparing values obtained for CIP and DIP at the same pH (pH 8) and temperature (24.5°C). The k_w on CIP was two orders of magnitude higher than on DIP ($2.4 \times 10^{-2} \text{ m/h}$ vs. $6.6 \times 10^{-4} \text{ m/h}$). A slower rate of decay at the DIP wall is consistent with the absence of oxidizable iron as is present at the CIP wall. However, the observed rate of decay is still much larger than expected for bulk decay alone. DiGiano and Zhang (2005) gave the fraction of observed decay attributable to the wall reaction as:

$$F = \frac{k_{obs,l} - k_{b,l}}{k_{obs,l}} \quad (71)$$

Using the same equation for the chloramine decay results gives $F = 0.998$ for DIP, i.e., 99.8% of chloramine decay is attributable to interactions with the DIP wall.

The fact that significant chloramine decay occurs due to reaction on cement-lined DIP where iron is not presumed to be present demands further explanation. One possibility is direct reaction of chloramine with aluminosilicates, the primary component of cement linings. While no information was found in the literature specifically for chloramine reactions, aluminosilicates have been suggested as a catalyst for chloramine decay (Woolschlager et al. 2001). Aluminosilicate surfaces have a wide range of sites in terms of associated acidity (Campbell 1988). These sites have partially bonded, labile protons that may be transferred to monochloramine. In the process of acidic hydrogen transfer, the monochloramine molecule becomes the cationic monochlorammonium molecule, NH_3Cl^+ , and is held strongly to the aluminosilicate surface by electrostatic forces. The formation of this intermediate (NH_3Cl^+) is the first step in monochloramine autodecomposition by disproportionation as was shown by Equations 16 and 17. Therefore, monochloramine autodecomposition could be catalyzed by acidified aluminosilicate surfaces. This catalytic pathway would be pH dependent.

Effect of pH on Observed Chloramine Decay Rate on DIP

The effect of pH was investigated by conducting PSR experiments with cement lined DIP at pH 7, 8 and 9. In each of these experiments, the simulated water velocity was 0.91 fps, the temperature was 24.5°C and the initial DO was in excess of 8.2 mg/L. The first-order rate model fit all of the data as shown in Figure 37. The $k_{obs,i}$ values are plotted against pH in Figure 38. As expected from the acid catalysis mechanism presented above, the rate of chloramine decay on DIP increased with decreasing pH.

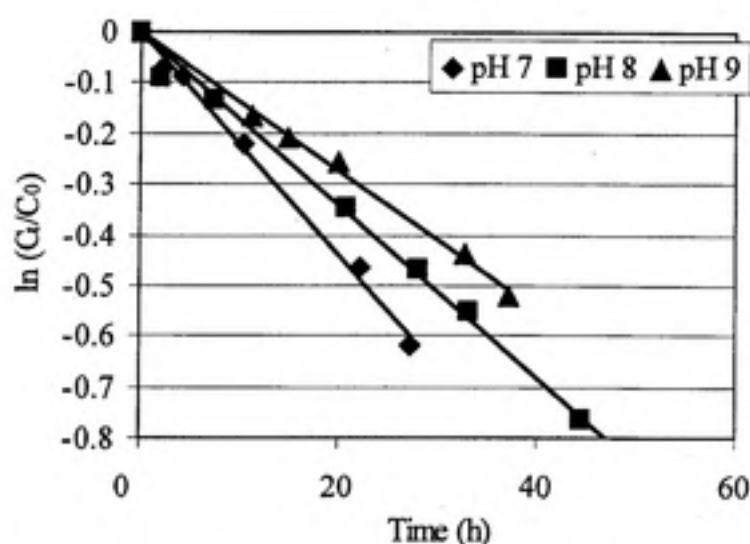


Figure 37 Test of first-order model of decay at three pH values within the DIP section at pH 8 and 0.91 fps

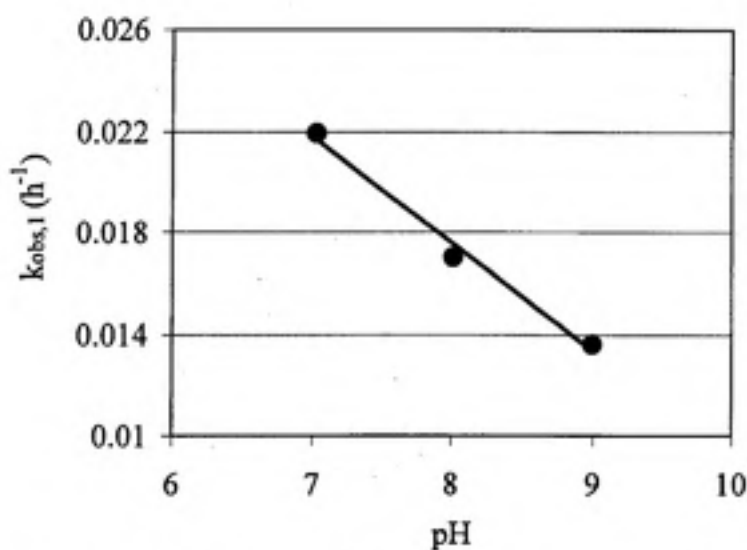


Figure 38 Effect of pH on observed first-order decay coefficient in DIP section at 1.36 fps and 23.5°C

Further investigation was conducted to explore the relationship between pH of the bulk fluid and protonation of the aluminosilicate wall. Todorović and Milonjić (2004) reported the following intrinsic equilibrium constants at the alumina-electrolyte interface:

$pK_{int,a1} = 4.4$, $pK_{int,a2} = 9.6$ and $pH_{PZC} = 7.2$. The $K_{int,a1}$ is for acid dissociation of $>AlOH_2^+$ and $K_{int,a2}$ is for acid dissociation of $>AlOH$. The surface will become increasingly protonated as solution pH decreases from 9 to 7. Thus, it would appear that an increase in the rate of chloramine decay at the wall should be observed by the acid catalysis mechanism.

Assuming as in earlier DIP experiments that mass transfer is not rate controlling, k_w was calculated from $k_{obs,1}$ using Equations 45 and 46. As depicted in Figure 35, k_w decreases linearly with increasing pH and the best fit line ($R^2 = 0.99$) is given by:

$$k_w = -1.58 \times 10^{-4} (pH) + 1.92 \times 10^{-3} \quad (72)$$

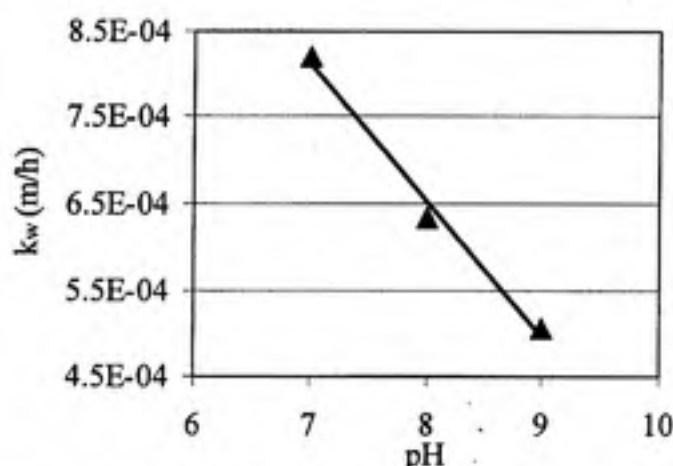


Figure 39 Effect of pH on the intrinsic wall reaction rate in DIP at 24.5°C

No direct comparison between the bulk decay rate constant (h^{-1}) and the intrinsic wall reaction rate constant (m/h) can be made because the dimensions are not the same. However, the effect of pH on both may be compared using available data for rate constants at pH 8 and 9 (k_b was not measured at pH 7). This comparison shows that k_w increases 130 percent while k_b increases 160 percent when pH decreases from pH 9 to pH

8 (at 24.5°C). Both k_w and k_b have similar dependency on pH suggesting the same mechanism of acid catalyzed disproportionation.

Effect of Temperature on Observed Chloramine Decay Rate in DIP

Experiments were conducted at temperatures of 29.1, 24.5 and 13.7°C to determine the extent to which the observed rate of chloramine decay in the DIP section varies with temperature. The first-order model fit the data from each PSR rate experiment as shown in Figure 40. The simulated water velocity was 0.91 fps, pH was buffered at 8 with 10^{-3} M phosphate and initial DO was in excess of 8.0 mg/L for these experiments. As expected, the observed rate of chloramine decay increased with temperature.

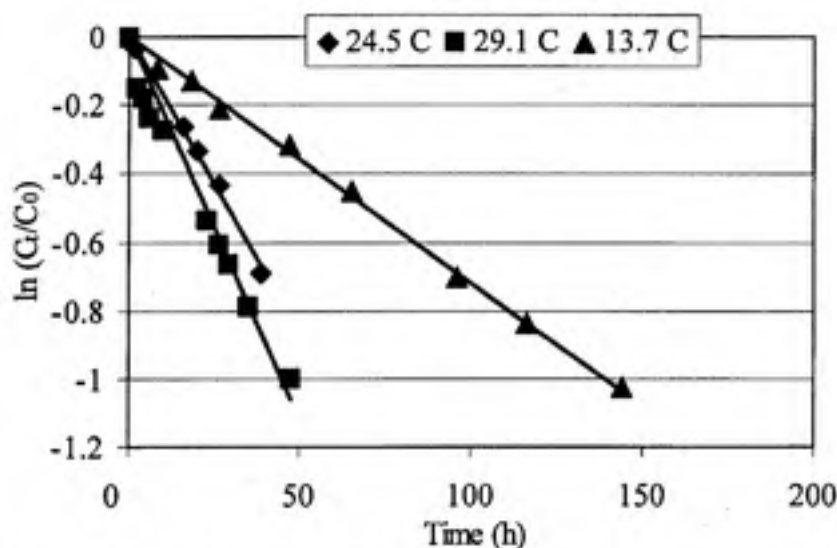


Figure 40 Test of first-order model of decay at three temperatures within the DIP section at pH 8 and 0.91 fps

The k_{obs} values obtained from Figure 40 were used to calculate the corresponding k_w values using Equations 45 and 46. The logarithm of k_w is plotted against the inverse of

temperature according to the Arrhenius form (Equation 58) in Figure 41. The activation energy, which is calculated from the slope of the line, is 56 kJ/mol ($R^2 = 0.997$). By comparison, the activation energy of decay in the finished water sample at pH 9 was 58 kJ/mol (see Figure 11). It is possible that the two E_a values are similar because they share a major chloramine decay pathway: acid catalyzed disproportionation. However, there is not enough information to defend this claim rigorously. For example, the extent to which acid catalysis at the aluminosilicate surface lowers E_a is unknown. If acid catalysis in solution and on aluminosilicate surfaces are energetically similar, it is possible that this similarity is reflected in the two E_a values.

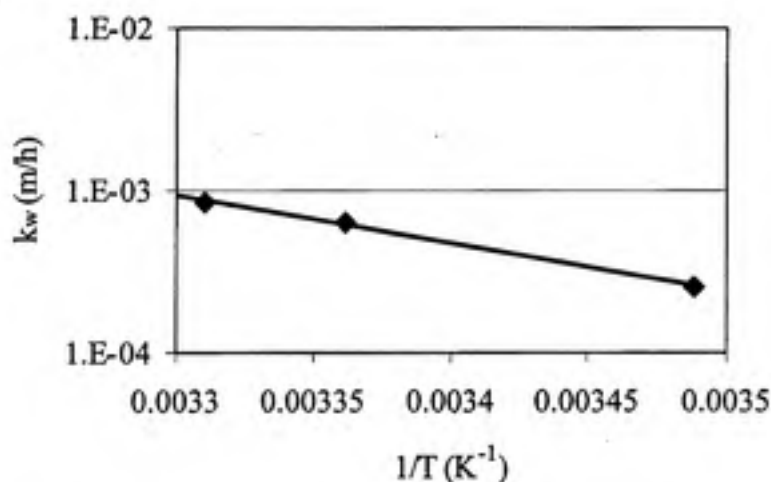


Figure 41 Effect of temperature on intrinsic wall reaction rate in DIP section: determination of activation energies at pH 8

As discussed earlier, a convenient calculation for the effect of temperature on reaction rates in environmental engineering is to relate rate constants to a reference temperature, e.g., 20°C (see Equation 55) where $k_{w,20} = 4.3 \times 10^{-4}$ m/h and $\theta = 1.08$.

Predicting Observed Rate of Decay in DIP

Table 17 is analogous to Table 14 which provided equations to calculate $k_{obs,l}$ for CIP. Equations are given from which the rate data collected in the PSR experiments with DIP can be used to predict $k_{obs,l}$ as a function of k_b , k_f and k_w wherein the effects of pH temperature and water velocity are included. The equation given for $k_{obs,l}$ includes the mass transfer coefficient, k_f , even though mass transfer was not rate controlling at water velocities as low as 0.27 fps in the PSR experiments. Thus, calculations of $k_{obs,l}$ are possible at lower velocities where k_f may become rate controlling. In Table 17, the reference values for the equations to calculate k_w as a function of pH and temperature are pH 8 and $T = 25^\circ\text{C}$, respectively.

Some comments are appropriate concerning k_b . The bulk decay rate, k_b , can be estimated from the rate of decay observed in the DS samples either at pH 6 or at pH 9. The value given in Table 17 for pH 9 is valid when the finished water pH > 7.0 ; however, carbonic acid speciation at lower pH in the DS could accelerate monochloramine autodecomposition. The bulk decay rate may be adjusted for temperature by the Arrhenius relationship (Equation 57). However, in the typical DS temperature range, from 10 to 30°C , the bulk decay constant would vary little ($1.4 \times 10^{-4} \text{ h}^{-1}$ to $3.4 \times 10^{-4} \text{ h}^{-1}$). As shown in Equation 71 the bulk decay accounts for only 0.2 percent of the observed rate of decay in cement-lined DIP at pH 8 and 24.5°C . Thus, regardless of the possible effect of pH on k_b , the $k_{obs,l}$ value is dominated by k_w such that accurate determination of k_b is not important.

Table 17 Equations for Predicting Observed Rate of Decay in DIP

Parameter	Variable Dependency	Equation(s)	Units
k_b	pH, Temp.	$\approx 4.3 \times 10^{-3} \text{ h}^{-1} \text{ (pH 6)}; \approx 2.9 \times 10^{-4} \text{ h}^{-1} \text{ (pH 9)}$ $= 0.121 [v(m/s)]^{0.83} [d(m)]^{-0.17}$	h^{-1}
k_f	Velocity, Temperature	where: $\text{Sh} = 0.023 \text{ Re}^{0.83} \text{ Sc}^{0.33}$; $\text{Re} = \frac{\rho V d}{\mu}$ $\text{Sc}^* = 481$; $D^* = 1.87 \times 10^{-9} \text{ m}^2/\text{s}$	m/h
k_w	pH	$= -1.58 \times 10^{-4} (\text{pH}) + 1.92 \times 10^{-3}$	m/h
	Temperature	$= 4.33 \times 10^{-4} (1.08^{(T-20)})^\dagger$	m/h
k_{obs}	pH, Vel., Temp.	$= k_b + \frac{k_w k_f}{r_h (k_w + k_f)}^\ddagger$ $= \frac{k_w}{r_h} + k_b$	h^{-1}

* Sc , D are given at 25°C and should be recalculated if temperature varies more than $\pm 10^\circ\text{C}$

† Temperature should be input as degrees Celsius

‡ Use if water velocity $< 0.27 \text{ fps}$

Practical Implications of Results for Rate of Chloramine Decay

The rate of chloramine decay in bulk water was two-orders of magnitude slower than reported values of free chlorine. While not explored in detail, k_b was higher in water samples taken from points within the DS compared to finished water, suggesting a possible effect of pH and/or in-situ generation of reactants that accelerate the decay rate. Rate experiments with pH and temperature as master variables showed that k_b increased with decreasing pH and increasing temperature.

The rate of chloramine decay in a simulated DS (the PSR) was considerably faster in DIP than in bulk water and much faster still in tuberculated CIP due to chloramine interactions with pipe wall materials. First-order rate constants for decay in the presence of CIP, in the presence of DIP and in bulk water (at pH 8, 25°C and water velocity of 0.26 fps) are shown graphically in Figure 42. The fact that chloramine decay is over 18

times faster in the presence of CIP than DIP suggests that routine monitoring of chloramine residuals in the DS should include many sampling sites in areas serviced by CIP.

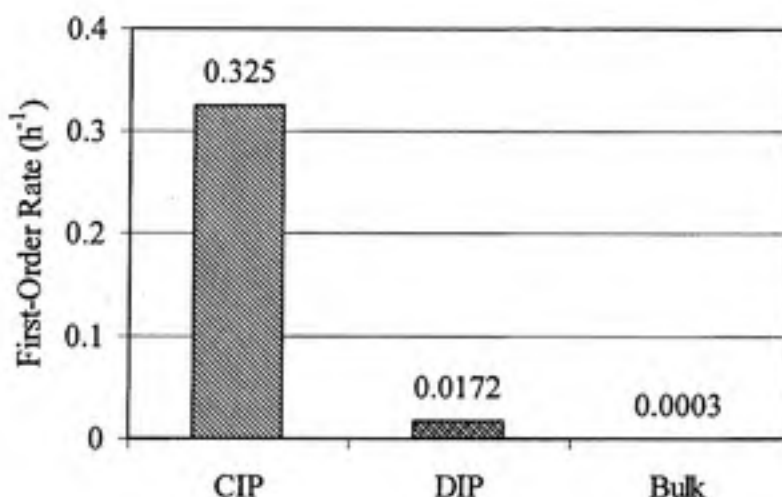


Figure 42 Predicted first-order decay rates in bulk fluid, DIP and CIP at pH 8, 25°C and 0.26 fps simulated water velocity

The acceleration of chloramine decay by an increase in water velocity appears to be important for CIP but not for DIP unless the water velocity is far lower than about 0.3 fps. Thus, water quality models that are applied to a DS with significant lengths of CIP should include the equation given from this research to predict k_{obs} as a function of water velocity. For all intents and purposes, the first-order rate model for k_{obs} as proposed in this research is quite adequate.

Practical implications of proper pH control are apparent from this research as well. As discussed by Valentine et al. (1998), monochloramine autodecomposition is accelerated at lower pH by way of the acid catalyzed disproportionation reaction (Equation 6) and in the presence of lower free ammonia concentrations, by way of the

hydrolysis pathway (Equations 4 and 2). Consequently, chloramine residuals will be more chemically stable if the finished water pH is higher and if the Cl:N dosing ratio is lower. One drawback of a low Cl:N ratio, however, is increased nitrification potential in the DS. These considerations should be weighed.

Regardless of pH control at the water treatment plant, pH will change within the DS especially if there is nitrification. For instance, DiGiano et al. (2000) observed that pH decreased from pH 8.4 to pH 6.9 at one of their sampling stations. Such changes in pH can greatly accelerate the rate of chloramine decay in the presence of CIP and DIP as was shown in the PSR experiments. The pH should be known throughout the DS in order to provide the proper value of k_{obs} from Table 14 for CIP or from Table 17 for DIP in a DS water quality model for Raleigh.

The effect of seasonal temperature change on chloramine decay is also important. As an example, studies of the Raleigh DS (DiGiano et al. 2000 and DiGiano et al. 2002) showed that water temperatures ranged from about 8°C in winter to about 28°C in summer, a 20°C difference. Based on the Arrhenius-derived equations for k_w in Tables 14 and 17, k_{obs} would increase 177 percent for CIP and 432 percent for DIP for a temperature rise of 20°C.

The decay rate of chloramine in the presence of pipe material was compared with that of free chlorine from previous work (DiGiano and Zhang 2005) using the same PSR experiments. In DIP at similar pH (7.9 vs. 8.0 in this study), temperature (21°C vs. 24.5°C in this study) and water velocity (0.53 fps vs. 0.53 fps in this study), the k_{obs} for free chlorine was ten times greater than for chloramine in this work (0.16 vs. 0.013 h⁻¹). Moreover, chloramine decay was independent of water velocity whereas the previous

work showed that free chlorine decay increased with water velocity. This may be a result of the different decay mechanism of each disinfectant.

The acceleration of k_{obs} by CIP was similar for both chloramine decay in this study and free chlorine decay in the study by DiGiano et al. (2004). As an example, at pH 8.2 and with a simulated water velocity 2.03 fps, DiGiano et al. observed that free chlorine decreased from 2.1 to 0.3 mg/L as Cl_2 in 130 minutes. Starting with the same initial concentration of chloramine, the residual would decrease to 0.6 mg/L as Cl_2 over the same period of time (based on using the k_{obs} for chloramine at the same pH and water velocity).

The difference in rate models to describe chloramine and free chlorine decay is important as well. DiGiano et al. (2004) showed conclusively that free chlorine decay in the presence of CIP was described by a zero-order rate model whereas a first-order rate model was far more appropriate in this study to describe chloramine decay in the presence of CIP. The primary reason for this difference is that the rate of free chlorine reaction with corrosion products was fast relative to the rate of corrosion product generation making free chlorine decay dependent on iron release. On the other hand, this research showed that the rate of monochloramine reaction with iron was slower than the rate of iron release; thus, iron was no longer limiting. The need for zero-order expression for free chlorine vs. a first-order rate expression for chloramine decay can easily be accommodated in DS water quality models such as EPANET.

CONCLUSIONS

The pipe-section reactor (PSR), which had been used by DiGiano and Zhang (2005) to investigate the effect of pipe surfaces on the rate of free chlorine decay, was successfully adopted for analogous investigation of the rate of chloramine decay. This reactor design allowed measurement of the effect of water velocity on the rate of chloramine decay at the pipe wall. It was also convenient for quantifying the effects of pH and temperature on the wall reaction rate.

The rate at which chloramine decays in bulk water in the absence of pipe material was investigated in separate batch tests using samples from the finished water and the distribution system in Raleigh, N.C. The following observations were made:

- The rate was described best by pseudo-first or pseudo-second order kinetics;
- As expected from the literature and the relative oxidation-reduction potential, the rate was much slower than that of free chlorine: $2.9 \times 10^{-4} \text{ h}^{-1}$ for chloramine versus $3.3 \times 10^{-2} \text{ h}^{-1}$ for free chlorine from DiGiano and Zhang (2005);
- The pseudo-first order rate constant increased by more than an order of magnitude as pH was reduced from 9 to 6; acid catalyzed disproportionation is the most likely explanation for this observation;
- The rate was somewhat faster in samples taken from the DS than from the finished water, as reactants or catalysts may be generated within the DS;
- The activation energy for the decay in the DS sample at pH 9 was found experimentally to be 44 kJ/mol and this agrees with the E_a for monochloramine autodecomposition found by Valentine et al. (1998) under similar conditions: 41

kJ/mol. In practical terms, this activation energy leads to a 1.8-fold increase in rate for a temperature increase of 10°C.

PSR experiments with a cast iron pipe section increased the chloramine decay rate greatly over that measured in bulk water. The availability of oxidizable Fe(II) is most likely responsible for providing additional reduced species that can be oxidized by chloramine. Previous PSR experiments with free chlorine had clearly shown a zero-order rate of decay (i.e., independence from free chlorine concentration) (DiGiano and Zhang, 2005). A zero-order rate had been justified because free chlorine reacts so rapidly with Fe(II) that the reaction is limited by availability of Fe(II) from the pipe surface and not by the concentration of free chlorine. However, the rate of chloramine decay was first-order in chloramine concentration in this research. A first-order rate suggests that chloramine reacts more slowly than free chlorine such the rate of reaction is controlled by the chloramine concentration rather than the available Fe(II).

The chloramine decay rate was relatively constant below simulated water velocities of 0.69 fps in the PSR fitted with the cast iron pipe section. However, the rate increased by a factor of 2 when water velocity was increased from 0.69 fps to 1.35 fps. An increase of rate with water velocity is indicative of a mass transfer limitation for the reaction of chloramine at the cast iron wall.

A rate model (Equation 68) was used to account for both the mass transfer limitation and the intrinsic rate of reaction at the wall. A Sherwood-Reynolds-Schmidt number correlation from the literature (Equation 38) was used to estimate the mass transfer coefficient thus allowing Equation 68 to be used to calculate a first-order,

intrinsic rate constant for the wall reaction for each PSR experiment in which pH and temperature were master variables. The intrinsic rate constant was found to:

- Increase with decreasing pH perhaps due to an increase in iron release from corrosion deposits given that the solubility of iron minerals also increases;
- Increase by a factor of about 2.6 for a temperature increase of 10°C, corresponding to an activation energy of 67 kJ/mol.

The rate of chloramine decay measured in the PSR that was fitted with a new, cement-lined ductile iron pipe section was first-order with respect to chloramine as was found for the cast iron pipe. While the decay rate was faster than observed in bulk water in the absence of this pipe material, it was much slower than in the presence of cast iron pipe. Even though Fe(II) may not be available for reaction, another possibility is that chloramine autodecomposition is catalyzed by acidified aluminosilicates comprising the cement lining.

In contrast to the cast iron pipe section, the decay rate in the cement lined ductile iron pipe section did not increase with water velocity. The lack of a mass transfer limitation may be explained by the slower rate of chloramine reaction with the cement lined ductile iron pipe as compared to the cast iron pipe. A slower reaction implies that mass transfer may no longer be rate limiting. Therefore, an intrinsic rate of reaction at the wall could be determined without using the Sherwood-Reynolds-Schmidt mass transfer correlation. This first-order intrinsic rate constant was found to:

- Increase with pH perhaps because the aluminosilicate matrix of the cement lining becomes increasingly acidified such as to increase the capacity of the surface to catalyze chloramine autodecomposition;

- Increase by a factor of about 2.2 for a temperature increase of 10°C, corresponding to an activation energy of 56 kJ/mol.

The practical outcome of this work is a series of equations that can be used by the City of Raleigh in their new water quality model for the distribution system that is under development by their consultant, Hazen & Sawyer. Rate constants and their dependence upon pH and temperature are provided to describe chloramine decay in bulk water and at the surface of cast iron and cement lined ductile iron pipes from the data collected in this research. The methodology used in this research can be used to generate these rate constants for any distribution system. Whether the system specifics of water chemistry and pipe material are important determinants of rate constants remains for further study.

Confirmation of the results of this research by application of the rate models to field studies of chloramine decay in the Raleigh DS is needed. Other recommendations for future work include:

- Extension of the methodology used in this research to explore the rate of chloramine decay in the presence of other pipe materials and linings;
- Research into the proposed mechanism of chloramine autodecomposition catalysis on the aluminosilicate surfaces in cement mortar pipes and linings;
- Exploration of the nature of reactants generated in the distribution system which were observed to accelerate the rate of chloramine decay in bulk water.

REFERENCES

- Appenzeller, B.M.R., M. Batté, L. Mathieu, J.C. Block, V. Lahoussine, J. Cavard and D. Gatel. 2001. Effect of Adding Phosphate to Drinking Water on Bacterial Growth in Slightly and Highly Corroded Pipes. *Water Res.*, 35(4): 1100-1105.
- Baribeau H., M. Prévost, R. Desjardins, P. Lafrance. 2001. Changes in Chlorine and DOX Concentrations in Distribution Systems. *Journal AWWA*, 93(12): 102-114.
- Benjamin, M.M., H. Sontheimer and P. Leroy. 1996. Corrosion of Iron and Steel. In *Internal Corrosion of Water Distribution Systems*. Cooperative Research Report, Denver Colo.: *AWWARF*.
- Blenke, H. 1978. Mixing and Dispersing in Loop Reactors. Edited by M. Bruxelmane and S. Lefebvre. C7-1-C7-55. In *Proc. International Symposium on Mixing*. Mons, France: Faculte Poytechnique du Mons.
- Campbell, I.M. 1988. *Catalysis at Surfaces*. New York, N.Y.: Chapman and Hall.
- Camper A.K., K. Brastrup, A. Sandvig, J. Clement, C. Spencer, A.J. Capuzzi. 2003. Effect of Distribution System Materials on Bacterial Regrowth. *Journal AWWA*, 95(7): 107-121.
- Cantor, A.F., J.K. Park and P. Vaiyavatjamai. 2003. Effect of Chlorine on Corrosion in Drinking Water Systems. *Journal AWWA*, 95 (5): 112-123.
- Chang Y.C., K. Jung. 2004. Effect of Distribution System Materials and Water Quality on Heterotrophic Plate Counts and Biofilm Proliferation. *Journal Microb. Biotech.*, 14(6): 1114-1119.
- City of Raleigh EMJWTP. 2004. Finished Water Quality Report.
http://www.raleighnc.gov/publications/Public_Uilities/Finished_Water_Quality_Report-2004.pdf
- Clark R.M. and R.C. Haught. 2005. Characterizing Pipe Wall Demand: Implications for Water Quality Modeling. *Journal Water Res. Plan. Mgmt. - ASCE*, 131(3): 208-217.
- Clark, R.M. and M. Sivaganesan. 1998. Predicting Residuals and Formation of TTHMs in Drinking Water. *Journal Environ. Eng. - ASCE*, 124(12) 1203-1210.

- Clesceri, L.S., Greenburg, A.E. and A.D. Eaton (eds). 1999. *Standard Methods for the Examination of Water and Wastewater* 20th Ed. Washington, D.C. American Public Health Association.
- Cowman, G.A. and P.C. Singer. 1996. Effect of Bromide Ion on Haloacetic Acid Speciation Resulting from Chlorination and Chloramination of Aquatic Humic Substances. *Environ. Sci. Technol.*, 30: 16-24.
- Cunliffe, D.A. 1991. Bacterial Nitrification in Chloraminated Water Supplies. *Applied Environ. Biotech.*, 57(11): 3399-3402.
- Cussler, E.L. 1984. *Diffusion: Mass Transfer in Fluid Systems*. London, U.K.: Cambridge University Press.
- DiGiano, F.A., D.E. Francisco, W. Zhang and L. Todd. 2000. Bacterial Regrowth in Drinking Water Distribution Systems: A Comparison of Durham and Raleigh. *Journal UNC WRRI*, Report No. 326.
- DiGiano, F.A., W. Zhang, A. Travaglia, D.E. Francisco and M. Wood. 2002. Occurrence of Bacterial Regrowth and Nitrification in the Raleigh Distribution System and Development of an EPANET Model for Future Assessments. *Journal UNC WRRI*, Report No. 338.
- DiGiano, F.A. V. Speight and W. Zhang. 2004 Disinfection Decay and Corrosion: Laboratory and Field Studies. *AWWARF and AWWA*.
- DiGiano, F.A. and W. Zhang. 2005. Pipe Section Reactor to Evaluate Chlorine-Wall Reaction. *Journal AWWA*, 97(1): 74-85.
- Doshi, B., W.M. Grayman, D. Guastella and T. Young. 2003. Field Testing the Chlorine Wall Demand in Distribution Systems. In *Proc. of the AWWA Water Annual Conference*, Anaheim, C.A.
- Duirk, S.E., B. Gombert, J. Choi and R. L. Valentine. 2002. Monochloramine Loss in the Presence of Humic Acid. *Journal Environ. Monit.*, 4: 85-89.
- Duirk, S.E., B. Gombert, J.P. Croué and R.L. Valentine. 2005. Modeling Monochloramine Loss in the Presence of Natural Organic Matter. *Water Res.*, 39: 3418-3431.
- Edwards D.K., V.E. Denny and A.F. Mills. 1976. *Transport Processes*. New York, N.Y.: McGraw-Hill.

- Ely, R., M. Hyman, D. Arp, R. Guenther and K. Williamson. 1995. A Cometabolic Kinetics Model Incorporating Enzyme Inhibition, Inactivation and Recovery: II. Trichloroethylene Degradation Experiments. *Biotech. Bioeng.*, 46: 232-235.
- Frateur, I., C. Deslouis, L. Ki  n  , Y. L  vi and B. Tribollet. 1999. Free Chlorine Consumption Induced by Cast Iron Corrosion in Drinking Water Distribution Systems. *Wat. Res.*, 33(8):1781-1790.
- Gauthier, V., B. G  rard, J.M. Portal, J.C. Block and D. Gatel. 1999. Organic Matter as Loose Deposits in a Drinking Water Distribution System. *Water Res.*, 33(4):1014-1026.
- Geankoplis, C.J. 1978. *Transport Processes and Unit Operations*. Boston, Mass.: Allyn and Bacon, Inc.
- Gotoh, K. 1989. Residual Chlorine Concentration Decreasing Rate Coefficients for Various Pipe Materials. *Water Sup.*, 7:164-172.
- Hallam, N.B., J.R. Westa, C.F. Forstera, J.C. Powell and I. Spencer. 2002. The Decay of Chlorine Associated with the Pipe Wall in Water Distribution Systems. *Water Res.*, 36: 3479-3488.
- Hand, V.C. and D.W. Margerum. 1983. Kinetics and Mechanism of the Decomposition of Dichloramine in Aqueous Solution. *Inorg. Chem.*, 22(10):1449-1456.
- Jafvert, C.T. and R.L. Valentine. 1987. Dichloramine Decomposition in the Presence of Excess Ammonia. *Water Res.*, 21(8):967-973.
- Jafvert, C.T. and R.L. Valentine. 1992. A Reaction Scheme for Chlorination of Ammoniacal Water. *Environ. Sci. Technol.*, 26(3): 577-586.
- Jensen, J.N. 1988. Interferences by Chloramines in the Measurement of Free Available Chlorine. Ph.D. diss. University of North Carolina at Chapel Hill.
- Ki  n  , L., W. Lu, and Y. L  vi. 1998. Relative Importance of the Phenomenon Responsible for Chlorine Decay in Drinking Water Distribution Systems. *Water Sci. Technol.*, 38(6):219-227.
- Leao, S.L. 1981. The Kinetics of Combined Residual Chlorination. Ph.D. diss. University of California, Berkeley.
- LeChevallier, M.W., C.D. Lowry, and R.G. Lee. 1990. Disinfection of Biofilms in a Model Distribution System. *Journal AWWA*, 82(7): 87.

- LeChevallier, M.W., C.D. Lowry, R.G. Lee, and D. Gibbon. 1993. Examining the Relationship Between Iron Corrosion and the Disinfection of Biofilm Bacteria. *Journal AWWA-Res. Technol.*, 85 (7): 111-123.
- LeRoy, P., Schock, M. R., Wagner, I. and H. Hultschulte. 1996 Cement-based materials. In *Internal Corrosion of Water Distribution Systems* 2nd Ed. American Water Works Association Research Foundation/TZW. Denver, Colo.
- Lieu N.I., R.L. Wolfe and E.G. Means. 1993. Optimizing Chloramine Disinfection for the Control of Nitrification. *Journal AWWA*, 85(2): 84-90.
- Maier, S.H., R.S. Powell and C.A. Woodward. 2000. Calibration and Comparison of Chlorine Decay Models for a Test Water Distribution System. *Water Res.*, 34(8): 2301-2309.
- Margerum, D.W., E.T. Gray and R.P. Huffman. 1978. Chlorination and the Formation of N-Chloro Compounds in Water Treatment. In *Organometals and Organometalloids: Occurrence and Fate in the Environment*. Edited by F.E. Brinckman and J.M. Bellama. Washington, D.C.: American Chemical Society.
- Margerum, D.W., L.M. Schurter et al. 1994. Water Chlorination Chemistry: Nonmetal Redox Kinetics of Chloramine and Nitrite Ion. *Environ. Sci. Technol.*, 28(2): 331-337.
- Morris, J.C. and R.A. Isaac. 1983. A Critical Review of Kinetic and Thermodynamic Constants for the Aqueous Chlorine-Ammonia System. In *Water Chlorination: Chemistry, Environmental Impact and Health Effects. Volume 4*. Edited by R.L. Jolley et al. Ann Arbor, Mich.: Lewis Publishers, Inc.
- Niquette P., P. Servais and R. Savoir. 2000. Impacts of Pipe Materials on Densities of Fixed Bacterial Biomass in a Drinking Water Distribution System. 34(6): 1952-1956.
- Norton, C.D. and M.W. LeChevallier. 1997. Chloramination: Its Effect on Distribution System Water Quality. *Journal AWWA*. 89(7) 66-77.
- Odell, L.H., G.J. Kirmeyer et al. 1996. Controlling Nitrification in Chloraminated Systems. *Journal AWWA*. 88(7): 86-98.
- Olson, R.M. and S.J. Wright. 1990. *Essentials of Engineering Fluid Mechanics*. New York, N.Y.: Harper and Row.

- Perdue, E.M. and N.L. Wolfe. 1982. Modification of Pollutant Hydrolysis Kinetics in the Presence of Humic Substances. *Environ. Sci. Technol.*, 16(12): 847-852.
- Qiang, Z.M. and C.D. Adams. 2004. Determination of Monochloramine Formation Rate Constants with Stopped-Flow Spectrophotometry. *Environ. Sci. Technol.*, 38(5): 1435-1444.
- Qualls, R.G. and J.D. Johnson. 1983. Kinetics of the Short-Term Consumption of Chlorine by Fulvic Acid. *Environ. Sci. Technol.*, 17: 692-698.
- Rompere, A., M. Prevost, P. Brisebois, J. Lavoie. 2000. Impacts of Implementing a Corrosion Control Strategy on Biofilm Growth. *Water Sci. Technol.*, 41(4-5): 287-294.
- Rossman, L.A., P.F. Boulos and T. Altman. 1993. The Discrete Volume Element Method for Network Water Quality Models. *Journal Water Res. Plan. Mgmt.*, 119(5): 505-517.
- Rossman L.A., R.A. Brown, P.C. Singer, J.R. Nuckols. 2001. DBP Formation Kinetics in a Simulated Distribution System. 2001. *Water Res.*, 35(14): 3483-3489.
- Rossman, L.A., R.M. Clark, W.M. Grayman. 1994. Modeling Chlorine Residuals in Drinking Water Distribution Systems. *Journal Environ. Eng.*, 120(4) 803-821.
- Sarin, P., V.L. Snoeyink, J. Bebee, W.M. Kriven and J.A. Clement. 2001. Physico-Chemical Characteristics of Corrosion Scales in Old Iron Pipes. *Water Res.*, 35(12): 2961-2969.
- Sarin, P., V.L. Snoeyink and W.M. Kriven. 2002. Interactions of Corrosion Scales in Old Iron/Steel Drinking Water Distribution Pipes. In *Abstracts of Papers of the American Chem. Soc.*, 223: 141-GEOC Part 1.
- Sarin, P., J.A. Clement, V.L. Snoeyink and W.M. Kriven. 2003. Iron Release from Corroded Cast Iron Pipe. *Journal AWWA*. 95(11) 85-96.
- Sarin, P., J. Bebee, M.A. Beckett, K.K. Jim, D.A. Lytle, J.A. Clement, W.M. Kriven and V.L. Snoeyink. 2004. Mechanism of Release of Iron from Corroded Iron/Steel Pipes in Water Distribution Systems. *Water Res.*, 38(5) 1259-1269.
- Sathasivan, A., I. Fisher and G. Kastl. 2005. Simple Method for Quantifying Microbiologically Assisted Chloramine Decay in Drinking Water. *Environ. Sci. Technol.*, 39: 5407-5413.

- Schock, M.R. 1999. Internal Corrosion and Deposition Control. In *Water Quality and Treatment: A Handbook of Community Water Supplies*. 5th Ed. Edited by R.D. Letterman and AWWA. New York, N.Y.: McGraw-Hill.
- Snoeyink, V. and D. Jenkins. 1980. *Water Chemistry*. New York, N.Y.: John Wiley and Sons, Inc.
- Sontheimer, H., W. Kolle and V.L. Snoeyink. 1981. The Siderite Model of the Formation of Corrosion-Resistant Scales. *Journal AWWA*, 73(11): 572-579.
- Todorović, Z.N. and S.K. Milonjić. 2004. Determination of Intrinsic Equilibrium Constants at an Alumina/Electrolyte Interface. *Journal Serb. Chem. Soc.*, 69 (12): 1063-1072.
- Valentine, R.L. and C.T. Jafvert. 1988. General Acid Catalysis of Monochloramine Disproportionation. *Environ. Sci. Technol.*, 22(6): 691-696.
- Valentine, R.L., Jafvert, C.T. and S.W. Leung. 1988. Evaluation of a Chloramine Decomposition Model Incorporating General Acid Catalysis. *Water Res.*, 22(9):1147-1153.
- Valentine, R.L., K. Ozekin, and P.J. Vikesland. 1998. Chloramine Decomposition in Distribution System and Model Waters. Denver, Colo.: *AWWARF and AWWA*
- Vasconcelos, J.J., L.A. Rossman, W.M. Grayman, P.F. Boulous and R.M. Clark. 1997. Kinetics of Chlorine Decay. *Journal AWWA*, 89(7): 54-65.
- Vikesland, P.J., Ozekin, K. and R.L. Valentine. 1998. Effect of Natural Organic Matter on Monochloramine Decomposition: Pathway Elucidation Through the Use of Mass and Redox Balances. *Environ. Sci. Technol.*, 32(10): 1409-1416.
- Vikesland, P.J., Ozekin, K. and R.L. Valentine. 2001. Monochloramine Decay in Model and Distribution System Waters. *Water Res.*, 21(8):967-973.
- Vikesland, P.J. and R.L. Valentine. 2000. Reaction Pathways Involved in the Reduction of Monochloramine by Ferrous Iron. *Environ. Sci. Technol.*, 34: 83-90.
- Vikesland, P.J. and R.L. Valentine. 2002. Iron Oxide Surface-Catalyzed Oxidation of Ferrous Iron by Monochloramine: Implications of Oxide Type and Carbonate on Reactivity. *Environ. Sci. Technol.*, 36: 512-519.

- Volk, C., Dundore, E., Schiermann, J. and M.W. LeChevallier. 2000. Practical Evaluation of Iron Corrosion Control in a Drinking Water Distribution System. *Water Res.*, 34(6): 1967-1974.
- Walski, T.M. 2000. Water Quality Aspects of Construction and Operations. In *Water Distribution Systems Handbook*. Edited by L.W. Mays. New York, N.Y.: McGraw-Hill.
- Weber, W.J. and F.A. DiGiano. 1996. *Process Dynamics in Environmental Systems*. New York, N.Y.: John Wiley and Sons, Inc.
- Wilczak, A., J.G. Jacangelo, J.P. Marcinko, L.H. Odell, G.J. Kirmeyer and R.L. Wolfe. 1996. Occurrence of Nitrification in Chloraminated Distribution Systems. *Journal AWWA*, 88(7): 74-85.
- Wolfe, R.L., N.I. Lieu, G. Izaguirre, E.G. Means. 1990. Ammonia-Oxidizing Bacteria in a Chloraminated Distribution System – Seasonal Occurrence, Distribution and Disinfection Resistance. *Applied Environ. Microbio.*, 56(2): 451-462.
- Woolschlager, J., B. Rittmann, P. Piriou, L. Ki  n   and B. Schwartz. 2001. Using a Comprehensive Model to Identify the Major Mechanisms of Chloramine Decay in Distribution Systems. *Water Sci. Technol.: Water Sup.*, 1(4):103-110.
- Ysusi, M. 2000. System Design: An Overview. In *Water Distribution Systems Handbook*. Edited by L.W. Mays. New York, N.Y.: McGraw-Hill.