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MODELING FREE CHLORINE AND CHLORAMINE DECAY IN A PILOT DISTRIBUTION SYSTEM

by

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ABSTRACT

The purpose of this study was to identify the effect that water quality, pipe material, pipe size, flow conditions and the use of corrosion inhibitors would have on the rate of free chlorine and chloramine decay in distribution systems. Empirical models were developed to predict the disinfectant residual concentration with time based on the parameters that affected it. Different water treatment processes were used to treat groundwater and surface water to obtain 7 types of finished waters with a wide range of water quality characteristics. The groundwater was treated either by conventional treatment by aeration (G1) or softening (G2) or high pressure reverse osmosis (RO) and the surface water was treated either by enhanced coagulation, ozonation and GAC filtration (CSF-O_3-GAC or S1) or an integrated membrane system (CSF-NF or S2). The remaining two water types were obtained by treating a blend of G1, S1 and RO by softening (S2) and nanofiltration (G4).

A pilot distribution systems (PDS) consisting of eighteen (18) lines was built using old pipes obtained from existing distribution system. The pipe materials used were polyvinyl chloride (PVC), lined cast iron (LCI), unlined cast iron (UCI) and galvanized steel (G). During the first stage of the study, the 7 types of water were blended and fed to the PDS to study the effect of feed water quality changes on PDS effluent water quality, and specifically disinfectant residual. Both free chlorine and chloramines were used as disinfectant and the PDSs were operated at hydraulic retention times (HRT) of 2 and 5 days. The PDSs were

periodically tested for free and combined chlorine, organic content, temperature, pH, turbidity and color.

The data obtained were used to develop separate models for free chlorine and chloramines. The best fit model was a first-order kinetic model with respect to initial disinfectant concentration that is dependent on the pipe material, pipe diameter and the organic content and temperature of the water. Turbidity, color and pH were found to be not significant for the range of values observed. The models contain two decay constants, the first constant (K_B) accounts for the decay due to reaction in the bulk liquid and is affected by the organics and temperature while the second constant, K_W, represents the reactions at the pipe wall and is affected by the temperature of the water and the pipe material and diameter. The rate of free chlorine and chloramine decay was found to be highly affected by the pipe material, the decay was faster in unlined metallic pipes (UCI and G) and slower in the synthetic (PVC) and lined pipes (LCI). The models showed that the rate of disinfectant residual loss increases with the increase of temperature or the organics in the water irrespective of pipe material.

During the second part of the study, corrosion control inhibitors were added to a blend of S1, G1 and RO that fed all the hybrid PDSs. The inhibitors used were: orthophosphate, blended ortho-polyphosphate, zinc orthophosphate and sodium silicate. Three PDSs were used for each inhibitor type, for a total of 12 PDSs, to study the effect of low, medium and high dose on water quality. Two PDSs were used as control, fed with the blend without any inhibitor addition. The control PDSs were used to observe the effect of pH control on water quality and compare to the inhibitor use. One of the control PDSs (called PDS 13) had the pH adjusted to be equal to the saturation pH in relation to calcium carbonate precipitation (pH_s) while the pH of the other control PDS (PDS 14) was adjusted to be 0.3 pH units above the pH_s. The disinfectant used for this part of the study was chloramine and the flow rates were set to obtain a HRT of 2 days.

The chloramine demand was the same for PDS 14 and all the PDSs receiving inhibitors. PDS 13 had a chloramine demand greater than any other PDS. The lowest chloramine demand was observed in PDS 12, which received silicate inhibitor at a dose of 12 mg/L, and presented the highest pH. The elevation of pH of the water seems to reduce the rate of decay of chloramines while the use of corrosion inhibitors did not have any effect. on the rate of chloramine decay. The PDS were monitored for chloramine residual, temperature, pH, phosphate, reactive silica, and organic content.

Empirical models were developed for the dissipation of chloramine in the pilot distribution systems as a function of time, pipe material, pipe diameter and water quality. Terms accounting for the effect of pH and the type and dose of corrosion inhibitor were included in the model. The use of phosphate-based or silica-based corrosion inhibitors was found to have no effect on the rate of chloramine dissipation in any of the pipe materials. Only the increase of pH was found to decrease the rate of chloramine decay. The model to best describe the decay of chloramine in the pilot distribution systems was a first-order kinetic model containing separate rate constants for the bulk reactions, pH effect and the pipe wall reactions. The rate of chloramine decay was dependent on the material and diameter of the pipe, and the temperature, pH and organic content of the water. The rate of chloramine decay was low for PVC and LCI, and more elevated in UCI and G pipes. Small diameter pipes and higher temperatures increase the rate of chlorine decay irrespective of pipe material.

Additional experiments were conducted to evaluate the effect of flow velocity on chloramine decay in a pilot distribution system (PDS) for different pipe materials and water qualities. The experiments were done using the single material lines and the flow velocity of the water was varied to obtain Reynolds' numbers from 50 to 8000. A subset of experiments included the addition of blended orthophosphate corrosion inhibitor (BOP) at a dose of 1.0 mg/L as P to evaluate the effect of the inhibitor on chloramine decay. The effect of Reynolds' number on the overall chloramine decay rate (K) and the wall decay rate constant (W) was assessed for PVC, LCI, UCI, and G pipes.

PVC and LCI showed no change on the rate of chloramine decay at any flow velocity. UCI and G pipes showed a rapid increase on the wall decay rate under laminar conditions ($Re < 500$) followed by a more gradual increase under fully turbulent flow conditions ($Re > 2000$). The use of the BOP inhibitor did not have an effect on the rate of chloramine decay for any of the pipe materials studied. Linear correlations were developed to adjust the rate of chloramine decay at the pipe wall for UCI and G depending on the Reynolds' number.

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θ:	Temperature Correction Factor
A:	Temperature correction coefficient
Alk:	Alkalinity
ANOVA:	Analysis of Variance
AOB:	Ammonia Oxidizing Bacteria
ASWT:	Advanced surface water treatment
Avg:	Average
AWWA:	American Water Works Association
AwwaRF:	American Water Works Association Research Foundation
B:	Blend (GW/SW/RO)
B	Wall decay material coefficient for Reynolds number (in/hr)
BAC:	Biologically Activated Carbon
BOP:	Blended Ortho-Phosphate
Br:	Bromides
C:	Chlorine concentration in the bulk
C	Wall decay material constant (in/hr)
C_0:	Initial concentration
^{o}C:	Degrees Celsius
Ca:	Calcium

C_B: Chlorine concentration in the bulk liquid

C_f: Final concentration

Cfu: Coliform forming units

C/GW: Conventional treatment of groundwater

Cl: Chlorides

CL: Confidence Level

Cl_2: Chlorine

cm: Centimeter

cm^3: Cubic centimeter (10^{-3} Liter)

cm^{-1}: Reciprocal cm / per centimeter (UV254 unit)

cpu: Cobalt-platinum color units

CSF: Coagulation, sedimentation, filtration treatment

CT: Concentration (mg/L) times contact time (min)

C_W: Chlorine concentration at the pipe wall

D: Diameter

d: molecular diffusivity of chlorine in water

D/DBP: Disinfection/Disinfection By-Products

DBPs: Disinfection by-products

DI: Distilled

DO: Dissolved Oxygen

DPD: N,N-diethyl-p-phenylenediamine

DV: Dummy Variable

Ea: Activation energy

EPA:	Environmental Protection Agency
ESEI:	Environmental Systems Engineering Institute
F:	Fluoride
Fe(II), Fe^{2+}:	Ferrous iron
Fe(III) , Fe^{3+}:	Ferric iron
fps:	Feet per second
ft:	foot, feet
ft^2:	Square feet
g:	grams
G:	Galvanized Steel
G1:	Conventionally treated Groundwater
G2:	Softened Groundwater
G3:	Softened Blend
G4:	Nanofiltered Blend
GAC:	Granular activated carbon
gpm:	Gallons per minute
GW:	Groundwater
h:	Hours
$[H^+]$:	Hydrogen ions concentration
HAA:	Halo-acetic acids
HPC:	Heterotrophic plate counts
HRT:	Hydraulic residence Time
^oK:	Degrees Kelvin (absolute temperature)

I:	Iodine
ICP:	Inductively- (or Ion-) Coupled Plasma spectroscopy
IMS:	Integrated membrane system
in/h:	Inch per hour
k:	Rate Constant
K:	Overall decay constant
K_{20}:	Rate constant at 20 ^{o}C
K_{B}:	Bulk liquid decay constat
K_{F}:	Mass transfer coeffcient
K_{H}:	pH dependent decay constant
K_{H}:	Coefficient for H^+ term
K_{T}:	Rate constant at temperature T
K_{W}:	Overall wall decay constant
K_{W1}:	Wall reaction rate constant
L:	Length
L:	Liter
LCI:	Lined cast iron
LI:	Langelier Index
LS:	Lime softening
LSI:	Langelier Saturation Index
m^2:	Square meter
m^3/d:	Cubic meter per day
m/h:	Meter per hour

Max:	Maximum
meq/L:	Milli-Equivalents per Liter (10^{-3} equivalents/Liter)
MG:	Member Government
mg/L:	Milligrams per Liter (10^{-3} g/L)
MGD:	Million gallons per day
Min:	Minimum
min:	Minute
mL:	Milli-Liter (10^{-3} Liter)
MWDSC:	Metropolitan Water District of Southern California
NA or N/A:	Not Applicable
NF:	Nanofiltration
NOM:	Natural organic matter
NTU:	Nephelometric turbidity unit
P:	Phophorus
PDS:	Pilot distribution system
pH:	Potential Hydrogen
pH_s:	Saturation pH
PO_4:	Phosphates
ppb:	Parts per billion
ppm:	Parts per million
psi:	Pounds per square inch
PVC:	Poly vinyl chloride
QA:	Quality Assurance

QAP:	Quality Assurance Plan
QA/QC:	Quality Assurance/Quality Control
QC:	Quality Control
Re:	Reynolds' number
Rh:	Hydraulic Radius
RO:	Reverse osmosis filtration
S1:	Ozonated treated Surface Water
S2:	Nanofiltered surface water (IMS)
Sc:	Schmidt number
SDWA:	Safe Drinking Water Act
Sh:	Sherwood's number
Si:	Silica based inhibitor
SM:	Standard Methods
Spec:	Spectroscopy or spectrophotometer
SW:	Surface Water
SWTR:	Surface water treatment rule
T, Temp:	Temperature
T_a:	Absolute temperature
TBW:	Tampa Bay Water Authority
TBWI:	Tampa Bay Water project I
TBWII:	Tampa Bay Water project II
TCP:	Tailored Collaboration Project
TDS:	Total Dissolved solids

THMs:	Trihalomethanes
Titr’n:	Titration
TOC:	Total organic carbon
TP:	Total Phosphorus
u:	Flow velocity in pipe (L/T)
UCF:	University of Central Florida
UCI:	Unlined Cast Iron
μg:	microgram (10^{-6} gram)
UHP:	Ultra High Purity
US:	United States
USEPA:	United States Environmental Protection Agency
UV:	Ultra Violet
UV-254:	Ultra-Violet absorption at 254nm (standard wavelength)
ν:	Kinematic viscosity of water
V/A:	Ratio of volume to wetted area (in a pipe or channel)
W:	Overall wall decay constant
W_{Lam}:	Overall wall decay rate under laminar conditions (in/h)
W_{Turb}:	Overall wall decay rate under turbulent conditions (in/h)
ZOP:	Zinc Ortho-Phosphate

1 INTRODUCTION

Tampa Bay Water is a regional water authority that supplies drinking water to six member governments (MGs) on the west coast of central Florida: the cities of New Port Richey, St. Petersburg, and Tampa, and Hillsborough, Pasco, and Pinellas counties. Historically, the main source of water has been groundwater. For years, TBW has used groundwater from the Floridian Aquifer as the almost exclusive source of water. In 2000, TBW started to reduce the use of groundwater by developing surface water and desalinated water sources. The finished waters from this three sources is being blended and distributed to the MGs. The use of the blended water with characteristics different than the historically used groundwater might have negative effects on the regional distribution system water quality.

TBW sought UCF to conduct two tailored collaboration projects (TCP) “Effects of blending on distribution water quality” and “Control of distribution system water quality in a changing water quality environment using inhibitors” that were sponsored by Tampa Bay Water and the MGs through American Water Works Association Research Foundation (AwwaRF). The projects involved (1) the assessment of the effects that blending of water from different sources can have on distribution system water quality and (2) the use of corrosion inhibitors to minimize adverse effects due to water quality changes.

The data collected allowed the development of empirical models to predict the concentration of free and combined chlorine in a distribution system as a function of time, pipe size and material, temperature and organic content of the water. The use of corrosion control techniques, such as pH control, phosphate and silicate based inhibitors, on chloramine residual was also evaluated. Additional studies to determine the effect of flow velocity on the rate of chloramine residual decay were performed under laminar and turbulent flow conditions.

This dissertation is presented as a partial requirements to obtain a Doctor of Philosophy degree in Environmental Engineering from the University of Central Florida. The content of this dissertation was developed with data obtained during the aforementioned TCPs. This document is composed by a general introduction, a review of pertinent literature, general description of methods and materials and a results section. The results section contains four articles that will be submitted for peer-reviewed journal publication.

1.1 Objectives

The objectives of the proposed research are:

- Determination of the effects of pipe material, hydraulics, water quality and time on free chlorine and chloramine residual dissipation in a drinking water distribution system.
- Development of mathematical models that accurately describe of the effects of pipe material, hydraulics, water quality and time on free chlorine and chloramine residual dissipation in a drinking water distribution system.
- Isolation and comparison of the effects of pipe material, hydraulics, water quality and time on drinking water quality in distribution systems.

- Determination and associated modeling of the effect of corrosion inhibitors on chloramine residual decay.
- Determination and modeling of the effect of flow velocity on chloramine residual decay.

2 LITERATURE REVIEW

Free chlorine and chloramine are used in drinking water to provide primary disinfection (free chlorine only) and residual maintenance (free chorine and chloramine) in drinking water distribution systems. Historically, free chlorine has been used more commonly than chloramine because it is a stronger oxidant and provides multiple benefits such as rapid microbial inactivation as well as color and odor oxidation. The use of chloramine has been increasing recently due to more stringent regulations for disinfection by-products (DBPs). Chloramine is used in waters with elevated concentration of organics where the addition of free chlorine will produce unacceptable levels of DBPs.

2.1 Basic Chlorine Chemistry

Usually, free chlorine is added to the water as chlorine gas, liquid sodium hypochlorite or solid calcium or sodium hypochlorite. Liquid sodium hypochlorite is normally added at a concentration of 10 to 15% by weight. Chlorine gas is more cost-effective but for safety reasons, sodium hypochlorite is sometimes preferred. Regardless of the form of free chlorine used, when it contacts the water, HOCl or OCl^- is formed and is the active form of chlorine.

Hypochlorous acid is a weak acid that has a constant of dissociation, Ka, of $10^{-7.5}$ at $25^{o}C$ (Snoeyink and Jenkins 1980). In water, hypochlorous acid dissociates forming hydrogen and hypochlorite ions (OCl^-) as shown in Equation 2.1.

$$HOCl \leftrightarrow OCl^- + H^+$$ **Equation 2.1**

Free chlorine reacts rapidly with compounds in the water. When dissolved organic matter is present, disinfection by-products (DBP) are formed. The reactions of chlorine with natural organic matter (NOM), especially humic substances, result in the formation of trihalomethanes (THM) and haloacetic acids (HAA). The reaction rate and the compounds formed are dependent on contact time, temperature, pH, chlorine dose and the nature of the organic compound. DBPs are alleged carcinogens and have been found to affect the reproductive or developmental process on animal and are closely regulated by USEPA. DBP regulations have forced many utilities using waters with high concentration of organics to seek alternate disinfectants for primary disinfection and/or residual maintenance. The most commonly used forms of disinfection are ozone, UV light and monochloramine. Ozone and UV are only used for primary disinfection since they are unable to provide a residual for secondary disinfection drinking water distribution systems. The elevated cost of UV light and ozone has limited their use. For cost considerations and ease of use, monochloramine has become the disinfectant of choice for most utilities for distribution system residual.

Chloramines are formed in drinking water by the combination of free chlorine and ammonia. In the treatment plant, free chlorine is added initially to meet primary disinfection regulations and oxidize most of the organics responsible for taste and odor problems, iron and manganese compounds, and inactivate bacteria in the water. The ammonia is added to combine with the remaining free chlorine in the water.

Depending on the ratio of free chlorine to ammonia, the reaction can produce three different compounds: monochloramine (NH_2Cl), dichloramine ($NHCl_2$), and trichloramine (NCl_3) in a stepwise reaction as shown by Equation 2.2, Equation 2.3, and Equation 2.4 (Haas 1999).

$NH_3 + HOCl \leftrightarrow NH_2Cl + H_2O$ **Equation 2.2**

$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O$ **Equation 2.3**

$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$ **Equation 2.4**

The sum of the concentrations of the three species is called combined chlorine. The chloramine species formed depends mainly on the chlorine to ammonia ratio but is also dependent on pH, temperature, and contact time. Monochloramines are the most stable of the chloramines. Monochloramines are formed at a 1:1 chlorine to ammonia molar ratio or 5:1 Cl_2 to NH_3 ratio, by weight, and at a pH of 7.6 to 8.0. When the chlorine to ammonia ratio is higher and the pH is lower, the other two species are obtained. Dichloramines and trichloramines are relatively unstable and quickly decompose at pH values above 7.0 (Montgomery 1985). The excessive addition of free chlorine to a water containing ammonia at a mass ratio of about 7.5:1 will completely oxidize ammonia to nitrogen gas as shown in Equation 2.5. the same effect is obtained at lower ratios when the water contains monochloramines.

$3Cl_2 + 2NH_3 \leftrightarrow N_{2(g)} + 6HCl$ **Equation 2.5**

Free chlorine and chloramine in solution is usually referred as chlorine residual, which dissipates with time due to reactions in water or the pipe wall in drinking water distribution systems. Free chlorine is a stronger oxidant agent than monochloramines and reacts quickly. Monochloramines have a slower rate of decay in drinking water. This property allows monochloramines to protect drinking water for longer periods of time.

Chlorine residuals provide some degree of protection from contamination in the distribution system, which can come from outside or inside the distribution system. When added to water, free chlorine and chloramines can inactivate microorganisms. Chlorine kills bacteria by attacking the cell wall and disturbs respiratory, transport, and nucleic acid activity. Free chlorine attacks viruses by destroying the viral nucleic acid or the protein coat. In general, the rate of inactivation of microorganisms is affected by the pH and temperature of the water. Bacteria and viruses are more sensitive to chlorine with an increase of pH or temperature (Montgomery 1985).

Chemical deposits and biological films form with time on the interior of pipes in distribution systems during the transmission of drinking water. The concentration of organics in these deposits is higher in stagnant or dead zones in distribution systems (Gauthier et al. 1999). These deposits can enter the bulk water because of changes in distribution system water quality and when that happens, it will exert an additional chlorine demand on the distribution system chlorine residual. Studies suggest that at least 0.5 mg/L of either free chlorine or chloramine is needed to reduce biofilm HPCs to approximately 10^3 CFU/cm^3 (Ollos et al. 1998).

2.2 Recent Literature

The concentration of free chlorine and chloramines in water is reduced by reactions with organic and inorganic compounds present in the water. Free chlorine attacks the double bond between carbon elements on long-chain NOM molecules. The more fragmented the organic matter is, the simpler the structure of the by-products. THMs are methane molecules in which halogen atoms (F, Cl, Br, or I) have taken the place of three of the hydrogens.

Monochloramines are more stable than free chlorine but still decay in water. Monochloramine residuals decay due to auto decomposition (Valentine and Jafvert 1988, Duirk et al. 2002) and direct reactions with natural organic matter (Vikesland, Ozekin, and Valentine 1998; Duirk et al. 2005). A comprehensive mechanistic model was developed by Duirk et al. (2002) to predict the loss of monochloramines due to reactions with NOM. According to the model, the auto decomposition of monochloramines in absence of NOM started with hydrolysis reactions that produced free chlorine and ammonia. The molecules of free chlorine then reacted to form dichloramines, which rapidly dissociated into chlorides and ammonia. Monochloramine have been found to be more stable when pH increases and slower rates of decay have been observed at high pH (Duirk et al. 2002 and 2005). Vikesland, Ozekin, and Valentine (2001) found that dichloramines formation increases at lower pH and that increases the rate of monochloramine decay.

Chlorine reacts with inorganic compounds such as iron, manganese, nitrites and sulfates. Iron is usually present in solution in groundwater in its reduced form: ferrous iron Fe (II). Free chlorine reacts very rapidly with ferrous iron as shown in Equation 2.6.

$$2Fe^{2+} + HOCl + H^{+} \rightarrow 2Fe^{3+} + Cl^{-} + H_2O$$ **Equation 2.6**

The reaction between chloramines and ferrous ions (Fe^{++}) is shown in Equation 2.7 (Vikesland and Valentine 2002). The authors found the reaction to be first-order with respect to monochloramine and soluble ferrous iron. The reaction was also dependent on the pH of the water as the overall reaction rate increased with increases in pH.

$$2Fe^{2+} + NH_2Cl + H^+ \rightarrow 2Fe^{3+} + Cl^- + NH_3$$ **Equation 2.7**

In the distribution system, the reactions of free chlorine and chloramines with iron are important since a large percentage of the old pipes are iron-based. Kiéné, Lu and Lévi (1998) found that chlorine was consumed more rapidly in unlined old cast iron and steel than in synthetic material pipes. The rate of chlorine decay was shown to be directly dependent on iron corrosion in field scale investigations. Frateur et al. (1999) found chemical reactions between chlorine and ferrous ions in solution was responsible for most of the free chlorine loss and electrochemical reactions at the metal surface were of little relevance.

Manganese oxidation in water is responsible for formation of colored deposits and stains during laundering operations. Free chlorine is used to oxidize manganese to manganese dioxide before releasing the water to the distribution system. The reaction of free chlorine and manganese is shown in Equation 2.8, the reaction is very rapid and no residual is observed until all manganese is eliminated.

$$Mn^{2+} + HOCl + H^+ \rightarrow Mn^{4+} + Cl^- + H_2O$$ **Equation 2.8**

Nitrites react with free chlorine and chloramines to form nitrates (Vikesland, Ozekin and Valentine 2001). The reaction is shown in Equation 2.9.

$$NO_2^- + NH_2Cl + H_2O \rightarrow NO_3^- + Cl^- + NH_4^+$$ **Equation 2.9**

The reaction of nitrites and chloramines is important because nitrites are an intermediate product of nitrification and the reaction produces free ammonia that is used by the nitrifying bacteria as food source. Vikesland, Ozekin and Valentine (2001) found that a concentration of nitrite as low as 0.5 mg/L as nitrogen had a significant effect on monochloramine decay. Based on the stoichiometric relation, each mg/L of NO_2-N will consume as much as 5 mg/L as Cl_2 of residual. Both free Chlorine and chloramines are very strong oxidizing agents for metallic and organic species present in water.

2.2.1 Chlorine Decay Modeling

The loss of disinfectant residual in drinking water distribution systems is a major concern for water utilities. Disinfectant residual decay in distribution systems is caused by reactions of chlorine with compounds present in the bulk liquid as well as reactions with the pipe surface, iron corrosion products and biofilms on the pipe wall (Biswas, Lu and Clark 1993; Rossman, Clark and Grayman 1994).

Vasconcelos et al. (1997) found that first-order kinetics could be used for bulk reactions and either zero-order or first-order kinetics could be used for pipe wall reactions. The overall chlorine decay expression postulated for water flowing through a distribution system is shown in Equation 2.10.

$$\left(\frac{dC}{dt}\right)_{Total} = \left(\frac{dC}{dt}\right)_{Bulk} + \left(\frac{dC}{dt}\right)_{Wall}$$ **Equation 2.10**

2.2.1.1 Bulk Decay

Chlorine decay in the bulk liquid has been found to be best described using a first-order kinetics model with respect to initial chlorine concentration. However, this approach has been found to be site specific and do not explain the discrepancies between kinetic constants observed for different waters (Powell et al. 2000b). Some studies have found the kinetic constants for reactions in the bulk liquid to be dependent on the water quality parameters such as temperature and organic content of the water (Kiéné, Lu and Lévi 1998, Hua et al. 1999). Kiéné, Lu and Lévi (1998) used a first-order model with respect to chlorine dose to model bulk chlorine decay with a rate constant (K_b) that is dependent on total organic content (TOC) and temperature. The expression for bulk chlorine decay is presented in Equation 2.11 and the expression for the bulk decay constant is shown in Equation 2.12. The expression for temperature effect has the same form as the Arrhenius equation.

$$\left(\frac{dC}{dt}\right)_{Bulk} = -K_b \times C$$

Equation 2.11

$$K_b = a \times [TOC] \times e^{\left(\frac{-b}{T}\right)}$$

Equation 2.12

where K_b = bulk decay constant
C = chlorine concentration in the bulk
a = 1.8 x 106 L/mg-h
b = 6050 ^{o}K
T = temperature in ^{o}K

A second-order kinetic approach has also been studied by Powell et al. (2000b) as shown in Equation 2.13. In this case, chlorine decay is first order with respect to the chlorine concentration, C, and first order with respect to H, the concentration of compounds reacting with chlorine.

$$\left(\frac{dC}{dt}\right)_{bulk} = -K_b \times C \times H \qquad \textbf{Equation 2.13}$$

Monochloramine dissipation kinetics has also been studied, Maier et al. (2000) has adapted existing free chlorine models to explain chloramines decay. The authors used a first-order kinetic approach for bulk decay as shown by the Equation 2.14. K was evaluated as a single decay coefficient that was maintained constant and also using different coefficients for the bulk and wall reactions. Uncertainty in the chlorine data prevented Maier et al. to reach any definite conclusion regarding the dissipation kinetics of chloramine residual.

$$C(x,t) = [C(0,t_0) - C_\infty] \times \exp^{-Kt} + C_\infty \qquad \textbf{Equation 2.14}$$

where: C_∞ = non-reactive fraction of total chlorine

Monochloramines are relatively unstable and decay with or without the presence of humic materials. Monochloramine decays following two distinct pathways, auto decomposition and direct reaction with the NOM. To provide a basis for DBPs formation models, Duirk et al. (2002) developed a model to predict monochloramine decay due to reactions with NOM. The authors modeled the auto decomposition of monochloramine in absence of NOM starting with hydrolysis reactions that produce free chlorine and ammonia. The molecules of free chlorine that form, then react with another molecule of monochloramines to form dichloramines, which dissociate rapidly into chlorides and ammonia. Monochloramines were also modeled as reacting directly with the humic material and the reactions was assumed to be characterized as an elementary stoichiometric reaction (Duirk et al. 2002). Based on the chloramine decay model, Duirk et al. were able to adequately predict dichloroacetic acid (DCAA) formation by modeling the monochloramine demand of the humic material in solution.

A model to describe monochloramines decay in the presence of phosphates and sulfates has also been studied (Valentine and Jafvert 1988). A general acid catalysis disproportionation of monochloramines was found to produce dichloramines, which quickly decompose into chlorides and ammonia. The rate of chloramine decay was found to be dependent on the concentration of hydrogen, sulfates and phosphates ions in the water. Carbonate and silicate were also suggested as a factor that could significantly increase chloramine dissipation rate in an acid-catalyzed disproportionation reaction.

The effect of bromides and nitrites reactions was included in the development of a model for monochloramine decay (Vikesland, Ozekin, and Valentine 2001). Bromides, up to a concentration of 0.1 mg/L Br, were found to have little effect on monochloramine decay. Nitrites are an intermediate product of incomplete bacterial nitrification of ammonia. Monochloramine reacts with nitrite present in water to produce nitrate as shown in Equation 2.15:

$$NH_2Cl + NO_2^- + H_2O \rightarrow NO_3^- + NH_4^+ + Cl^- \qquad \textbf{Equation 2.15}$$

The stoichiometry indicates that every mole of nitrite would react with a mole of monochloramine, thus reducing the residual concentration. The reduction of monochloramine residual observed during the study was significant, however it was lower than expected by stoichiometry. The demand observed by Vikesland, Ozekin, and Valentine was only 50% of the stoichiometric calculations and the difference was assumed to be consequence of the short duration of the experiment.

2.2.1.2 Wall Decay

The pipes normally used in distribution systems can be classified in two groups: synthetic pipes and metallic pipes. The chemical and biological characteristics and reactions on the interior pipe walls vary significantly by group. Previous studies have reported that synthetic materials such as PVC, medium and high-density polyethylene, cement lined iron and polypropylene have a very low chlorine demand (Kiéné et al. 1998, Hallam et al. 2002). Metallic pipes have high chlorine demand and chlorine decays as chlorine reacts with the elemental metal or the associated corrosion products on the pipe wall, especially in unlined cast iron pipes. Free chlorine reacts chemically with the walls of cast iron pipes and the total chlorine consumption rate could be calculated based on the corrosion current density (Frateur et al. 1999).

Vikesland and Valentine (2002) showed that combined chlorine is depleted due to reactions with iron in the aqueous-phase and at the pipe surface. Monochloramine reacted with Fe^{+2} to form Fe^{+3} and ammonia. The study found that the reaction rate expressions were first-order with respect to both aqueous ferrous ion and monochloramine concentrations, and were also pH dependent. The elevated consumption of chlorine in metallic pipes can also be explained by the higher microbiological activity at the pipe wall. Bacteria have been shown to accumulate in tubercles created in corroded iron pipe or imperfections in the pipe material (Hallam et al. 2001).

Disinfection loss due to reactions at the pipe wall must take into consideration the rate of reactions at the pipe wall, mass transfer limitations of the disinfectants from the bulk liquid to the wall and the available wetted surface area to volume geometry (Frateur et al. 1999; Vikesland, Ozekin and Valentine 2001; Vikesland and Valentine 2002; Hallam et al. 2002). The expression for the wall reaction rate as stated by Rossman, Clark and Grayman (1994) is shown in Equation 2.16.

$$\left(\frac{dC}{dt}\right)_{Wall} = -\left(\frac{A}{V}\right) \times K_{W1} \times C_W$$ **Equation 2.16**

where K_{W1} = Wall reaction rate constant (L/T)
A = Surface area (L^2)
V = Pipe volume (L^3)

For a pipe fulfilled with water, the hydraulic radius reduces to the pipe diameter divided by 4. Equation 2.16 can be written as Equation 2.17:

$$\left(\frac{dC}{dt}\right)_{Wall} = -\frac{4}{D_p} \times K_{W1} \times C_W$$ **Equation 2.17**

where Dp = pipe diameter
C_W = chlorine concentration at the pipe wall

Chlorine concentration at the pipe wall, C_W, is difficult to measure and a expression based on the residual concentration in the bulk liquid, C, should be used instead. K_{W1} must be adjusted for mass transfer limitations that are dependant on the flow regime within the pipe segment. A film resistance model was developed by Rossman, Clark and Grayman (1994), which shows the mass transfer of chlorine towards the pipe wall is proportional to the difference of chlorine concentration between the bulk liquid and the pipe wall as presented in

Equation 2.18. The coefficient K_F is the mass transfer coefficient and has to be determined for the flow conditions.

$$\left(\frac{dC}{dt}\right)_{Mass\ transfer} = -\frac{4}{D_p} \times K_F \times (C - C_W) \qquad \textbf{Equation 2.18}$$

where K_F = mass transfer coefficient
D_p = pipe diameter
C = chlorine concentration in the bulk
C_W = chlorine concentration at the pipe wall

If it is assumed that chlorine reacts as it reaches the pipe wall and there is no accumulation (Rossman, Clark and Grayman 1994), the rate of mass transfer of the disinfectant would be equal to the rate of chlorine decay at the pipe wall as shown in Equation 2.19.

$$\left(\frac{dC}{dt}\right)_{Wall} = \left(\frac{dC}{dt}\right)_{Mass\ transfer} \qquad \textbf{Equation 2.19}$$

Replacement of Equation 2.17 and Equation 2.18 into Equation 2.19 and further manipulation yields Equation 2.20.

$$K_{W1} \times C_W = K_F \times (C - C_W) \qquad \textbf{Equation 2.20}$$

A first order differential equation for chlorine dissipation at the pipe wall can be developed by solving Equation 2.20 for C_W and substituting in Equation 2.17. The resulting model is shown in Equation 2.21. K_W is an overall wall decay constant that combines the mass transfer constant, K_F and the wall reaction constant, K_{W1}.

$$\left(\frac{dC}{dt}\right)_{Wall} = -\frac{4}{D_p} \times \frac{K_{W1}K_F}{(K_{W1}+K_F)} \times C = -\frac{K_W}{D_p} \times C$$ **Equation 2.21**

where K_F = mass transfer coefficient
K_{W1} = wall reaction rate constant
K_W = overall wall decay constant
Dp = pipe diameter
C = chlorine concentration in the bulk

2.2.1.3 Temperature Effects

The rate constants can be adjusted for temperature variations using the van't Hoff – Arrhenius equation shown in Equation 2.22. Based on this equation, the rate constant at operation temperature, K_T, can be calculated from the rate constant defined at a base temperature, in this case 20 ^{o}C, using Equation 2.23.

$$K_T = A \times \exp^{\left(-\frac{E_a}{RT}\right)}$$ **Equation 2.22**

$$K_T = K_{20} \times \theta^{(T-20)}$$ **Equation 2.23**

where E_a = activation energy
R = ideal gas law constant
T = temperature
K_T = dissipation constant at temperature T
K_{20} = dissipation constant at 20 ^{o}C
θ = temperature correction factor
A = constant

2.2.2 Comparison of Free Chlorine and Chloramine

The use of monochloramine for residual maintenance is increasing throughout the United States due to more stringent drinking water regulations. The D/DBP rule (USEPA 1998) specifies maximum level for THMs and HAAs of 80 µg/L and 60 µg/L. Chloramines are the preferred solution when the use of free chlorine leads to excessive production of DBPs (Vikesland, Ozekin and Valentine 2001). In 1990, 22% of the 438 surveyed utilities were using chloramines for residual maintenance (Wilczak et al. 1996). Chloramines are generally accepted to be less reactive in the bulk aqueous stream than free chlorine. Some advantages of the use of chloramines are a more stable residual, less chlorine odor and taste, lower HPC count when free chlorine is not present (Neden et al. 1992) and less production of regulated disinfection by-products.

Even though chloramines have several advantages in light of the new regulations; there are some disadvantages. Chloramines require high CTs (concentration times contact time) to comply with regulations for pathogen inactivation, which severely limits its use as primary disinfectant (USEPA 1990). Monochloramines decompose to ammonia increasing the availability of free ammonia in the distribution system, which promotes biological instability and nitrification in distribution systems. Two thirds of medium and large US distribution systems using chloramines have experienced nitrification with twenty-five percent of the responding utilities reporting moderate to severe nitrification (Wiczak et al. 1996).

Once an episode of nitrification has begun, chloramine concentration is quickly reduced. Therefore, to maintain good water quality, both ammonia oxidizing bacteria (AOB) inactivation and AOB regrowth prevention strategies must be considered. Odell et al. (1996) showed a marked difference in AOB regrowth potential for different chloramine residuals in Metropolitan Water District of Southern California (MWDSC). At 1.7 mg/L as Cl_2, AOB regrowth occurred in 77% of the samples; at 2.0 mg/L as Cl_2, AOB regrowth appeared in 67

% of the samples tested; and with a combined residual of 2.5 mg/L as Cl_2, AOB regrowth appeared in 26% of the samples.

Survival of AOB at different chloramine residuals has been reported. A study conducted in California (Wolfe et al. 1990) indicated that nitrifiers were 13 times more resistant to monochloramine than to free chlorine and chloramine residuals at or below 1.5 mg/L as Cl_2 may not control the growth of these organisms in the distribution system. Odell et al. (1996) showed that AOB survive and grow at 1.2-1.5 mg/L as Cl_2 in MWDSC waters, while Skadsen (1993) reported nitrification occurrence in the distribution system at 5-6 mg/L as Cl_2. AOB seem to have significant resistance to chloramine deactivation.

Lipponen, Suutari and Martikainen (2002) compared the occurrence of nitrification and the number of nitrifying bacteria in different drinking water distribution systems in Finland. The study found that the numbers of ammonia-oxidizing bacteria, nitrite oxidizing bacteria and their oxidation potentials were higher in distribution systems delivering chloraminated water when compared with networks carrying chlorinated waters. An observed increase in turbidity was associated with detachment of sediment with high concentration of nitrifiers from the pipe surface. A positive correlation was found between the occurrence of nitrifying bacteria and the numbers of heterotrophic bacteria and turbidity of the water. Also, accelerated rates of monochloramine decay have been associated with elevated numbers of nitrifiers (Cunliffe 1991).

Distribution system monitoring is necessary to maintain drinking water quality. Several parameters such as nitrite, nitrate, chloramines dose and residual, ammonia, pH, HPC, and DO can be used as indicators of nitrifying bacteria activity in a distribution system (Wilczak et al. 1996, Odell et al. 1996).

2.2.3 Effect of Corrosion Inhibitors on Chloramine Residual Decay

The literature available relating chloramine decay and the use of corrosion inhibitors is limited. The most commonly used corrosion inhibitors in drinking water are phosphate-based and silica-based inhibitors. Phosphate-based inhibitors can be used in the form of orthophosphates, polyphosphates or blends of the two types. Silica-based inhibitors are usually solutions of sodium silicate salts. Phosphorus is one of the nutrients needed for bacterial growth. Chloramines have been shown to decay due to reactions with ferrous iron, Fe(II), a corrosion product (Vikesland and Valentine 2000). Chloramine decay in the presence of phosphate-based inhibitors could either increase due to biofilm growth resulting from the introduction of the phosphate or decrease due to the reduced rate of corrosion. Batté et al. (2003) showed that the addition of phosphate inhibitors to drinking water doubled the phosphate concentration in the biofilm, but did not affect the biofilm densities or its composition. Volk et al. (2000) used two annular reactors made of cast iron to compare control water (plant conditions) with the same water dosed with ZOP at 0.7 mg/L as PO4. No significant difference was observed in the biofilm density, bulk HPC or the effluent chloramine residual between the control and the test reactor. Butterfield et al. conducted a study in 2002 and found that the use of phosphate-based inhibitors reduced free chlorine demand by 10% in the presence of iron corrosion products but had no effect when glass beads coated with iron oxide were used. Phosphates have also been shown to catalyze the disproportionation of monochloramines under certain conditions (Valentine and Jafvert 1988).

2.2.4 Effect of Flow Velocity on Chloramine Decay Rates

The decay of disinfectant residuals in distribution systems have been correlated to the flow velocity inside the pipes (Rossman, Clark, and Grayman 1994; Vasconcelos et al. 1997; Hallam et al. 2002; Doshi, Grayman, and Guastella 2003; Clark and Haught 2005; Mutoti et al. 2007).

Some authors use a mass-transfer limited approach which limits the rate of chlorine decay at the pipe wall to the transfer of chlorine from the bulk liquid to the pipe wall as shown in Equation 2.21 (Rossman, Clark, and Grayman 1994; Vasconcelos et al. 1997; Hallam et al. 2002). The rate at which chlorine moves towards the pipe wall is dependent on the flow conditions. Rossman, Clark and Grayman (1994) provided a relationship between the mass transfer constant, K_F and the dimensionless Sherwood number, Sh, as shown in Equation 2.24.

$$K_F = Sh \times \frac{d}{D_p} \qquad \textbf{Equation 2.24}$$

where d = molecular diffusivity of the species being transported (L^2/T)
Dp = pipe diameter (L)

The Sherwood number has been defined as shown in Equation 2.25 and Equation 2.26 for laminar and turbulent flow (Rossman 2000), respectively.

$$Sh = 3.65 + \frac{0.0668 \times \left({}^{Dp}\!/_{L} \right) \times \left(\mathrm{Re} \times Sc \right)}{1 + 0.04 \times \left[\left({}^{Dp}\!/_{L} \right) \times \left(\mathrm{Re} \times Sc \right) \right]^{0.67}} \quad \text{for Re} < 2{,}300 \qquad \textbf{Equation 2.25}$$

$$Sh = 0.0149 \times \mathrm{Re}^{0.88} \times Sc^{0.333} \quad \text{for Re} > 2{,}300 \qquad \textbf{Equation 2.26}$$

$$Re = \frac{u \times Dp}{\nu}$$ **Equation 2.27**

$$Sc = \frac{\nu}{d}$$ **Equation 2.28**

where Sh = Sherwood number
Dp = pipe diameter (L)
L = pipe length (L)
Re = Reynolds' number
Sc = Schmidt number
u = flow velocity in pipe (L/T)
ν = kinematic viscosity of water
d = molecular diffusivity of chlorine in water

Based on Equation 2.21, Equation 2.24, Equation 2.25 and Equation 2.26, as the flow velocity increases, Reynolds' number, Sherwood's number and the mass transfer rate of chlorine towards the pipe wall increase resulting on a higher wall decay rate, K_W. Clark and Haught (2005) showed that K_W would approach a limiting value at high flow velocities (Re > 7,500).

Recent studies show that the rate of decay is directly dependent on the Reynolds number and specifically the flow velocity for free chlorine (Doshi, Grayman, and Guastella 2003; Clark and Haught 2005) and chloramines (Mutoti et al. 2007). However, contrary to Rossman, Clark and Grayman (1994), the recent studies have found that K_W does not reach a fixed value and instead keeps increasing with the Reynolds' number (Doshi, Grayman, and Guastella 2003; Clark and Haught 2005; Mutoti et al. 2007). Doshi, Grayman, and Guastella (2003) found the half-life of chlorine at the higher flow rates to be in the order of just several minutes. Some overall wall decay constant, K_W, were so high that they were higher than the mass transfer coefficient, K_F, resulting on negative values for the wall reaction rate constant, K_{W1}. Mutoti et al. (2007) observed the same behavior and assumed it was due to an increase in surface area associated with the release of particulate corrosion products from the pipe wall at elevated velocities. It was speculated that chloramines react with the additional iron in the particulate form thus increasing the rate of decay. The additional decay in the metallic pipes resulted in an increased wall reaction rate constant, which they called kw.

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3 METHODS AND MATERIALS

3.1 Pilot Distribution System Description

A pilot distribution system (PDS) was designed and constructed to mimic water quality changes resulting from blending of significantly different source waters in old distribution pipe systems. The PDSs were constructed with pipes obtained from existing distribution systems. The internal chemical and physical structures were maintained during excavation, transport, storage and construction of the PDSs. The existing distribution systems traditionally received conventionally treated groundwater. Once assembled, the pipes were allowed to equilibrate with TBW (Tampa Bay Water) conventionally treated groundwater over a period of 4 months. After equilibrium was established, different blends were introduced into the PDS. The blends are representative of the types of water experienced by distribution systems in the Tampa Bay area of the state of Florida.

The PDSs are composed of 18 different distribution lines that were numbered sequentially as PDS 1 to PDS 18. PDS 1 to 14 are identical hybrid lines that have four different materials connected in series: PVC, unlined cast iron (UCI), lined cast iron (LCI), and galvanized steel (G) pipes. The other 4 lines (PDS 15 to 18) were constructed one for each of the individual pipe material. Each hybrid PDS is composed by: 19 feet of 6-inch PVC, 18 feet of 6-inch lined cast iron, 12 feet of 6-inch unlined cast iron, and 40-feet of 2-inch galvanized steel. The principal characteristics of the PDSs are presented in Table 3.1.

Table 3.1 Characteristics of Hybrid and Single Material Lines

PDS #	Length (ft)	Diameter (inches)	Material
1-14	19-18-12-40	6-6-6-2	Unlined CI, Lined CI, PVC, Galvanized Steel
15	97	6	Unlined cast iron
16	87	6	Lined ductile iron
17	95	6	PVC
18	163	2	Galvanized steel

All pilot distribution systems were provided with a sampling port after each pipe reach to allow an assessment of water quality changes associated with each pipe reach. A picture of the PDSs is shown in Figure 3.1.

Figure 3.1 Pilot Distribution System

The pilot distribution lines were operated to maintain either a five-day or two-day hydraulic residence time (HRT). Standpipes were located at the beginning and end of each PDS to ensure the presence of water inside of the lines at all times. The standpipes were made from translucent plastic pipe that were 60 inches long and had a 4 inches diameter. The standpipes as well as the peristaltic pumps used to control the flow rate can be seen in Figure 3.2.

Figure 3.2 Pilot Distribution System Headwork

3.2 Water Treatment Processes

The sources of the waters used in this study were surface water and groundwater. The source waters were submitted to water treatment processes to obtain seven different finished waters. The finished waters were selected to represent the output of the water treatment plants currently in operation or in construction in the Tampa Bay area. Table 3.2

shows the principal characteristics of the pilot water treatment processes. All the water storage tanks were tested daily for free and total chlorine as well as free ammonia. Free chlorine additions were made to the tanks, as required, to maintain the combined chlorine residual at the desired level.

Table 3.2 PDS Source Waters Description

Symbol	System Description
GW	Ground water source. Treatment by aeration, disinfection by free chlorine with a residual of 4 mg/L after a 5 minute contact time, 4.0 mg/L chloramine residual.
G2	Ground water source. Treatment by lime softening to total hardness of 120 mg/L $CaCO_3$ disinfection by free chlorine with a residual of 4.0 mg/L after a 5 minute contact time, , 4.0 mg/L chloramine residual.
G3	Blend of finished G1, S1 and RO water source. Treatment by lime softening to total hardness of 120 mg/L $CaCO_3$ or alkalinity of not less than 50 mg/, 4.0 mg/L chloramine residual
G4	Blend of finished G1, S1 and RO water source. Treatment by membrane nanofiltration aeration, 4.0 mg/L chloramine residual.
SW	Surface water source. Treatment by ferric sulfate coagulation flocculation settling filtration disinfection by ozonation biologically activated carbon filtration, 4.0 mg/L chloramine residual.
S2	Surface water pretreated by ferric sulfate coagulation, flocculation and sedimentation, followed by nanofiltration, aeration and disinfection by free chlorine with a residual of 4 mg/L after a 5 minute contact time, 4.0 mg/L chloramine residual.
RO	Ground water source. Treatment by membrane reverse osmosis aeration disinfection by free chlorine with a residual of 4 mg/L after a 5 minute contact time , 4.0 mg/L chloramine residual.

3.3 Pilot Distribution System Operation

The PDSs were used for the two tailored collaboration projects (TCP), TBWI and TBWII, mentioned in the Introduction. During TBWI, the PDSs were fed with different blends of seven finished waters to determine the effect that changing influent water quality would have on distribution system water quality. During TBWII, all the PDSs were fed with the same blend of groundwater, surface water and desalinated water that was dosed with different types of corrosion inhibitors.

3.3.1 PDS Operation During TBWI

The TBWI project had a duration of 18 months and was divided in 6 phases of 3-month duration each (Taylor et al. 2005). During four (4) of the mentioned phases, seven of the PDSs received 100% of each of the seven finished waters while the other 11 pipes received different blends to obtain a wide range of water quality characteristics. The different blends of the finished waters were produced at the influent standpipes of each PDS by individually regulating the flow of each type of water being delivered using the peristaltic pumps shown in Figure 3.2. The single material lines received water with the same characteristics at all times, a blend of groundwater, surface water and desalinated seawater (reverse osmosis). The PDS were operated at a 5-day hydraulic retention time (HRT) initially (Phase I to III, 12/8/01 to 8/30/02) to simulate dead end conditions in distribution systems. The HRT was changed to 2 days for the rest of the project to allow better maintenance of chloramine residual.

The type of water fed to the PDSs was changed for phases II and IV. The blends composition were not changed, just changed to a different PDS. The blend that each PDS received during phases III and IV were identical to the blend received during phases I and II. The reason to repeat the blend was to evaluate the effect of seasonal changes (winter vs summer and spring vs fall) on water quality. The source waters for phases I to IV for each PDS by phase are summarized in Table 3.3.

Table 3.3 Blends Used by PDS During TBWI Study

PDS – Material	Phase I (12/08/01 to 03/15/02) and Phase III (06/15/02 to 09/13/02)	Phase II (03/16/02 to 06/14/02) and Phase IV (09/14/02 to 12/13/02)
01 – Hybrid	GW (100)	G2 (100)
02 – Hybrid	G2 (100)	GW (100)
03 – Hybrid	SW (100)	S2 (100)
04 – Hybrid	G4 (100)	G3 (100)
05 – Hybrid	RO (100)	SW (100)
06 – Hybrid	GW (55) SW (45)	GW (68) RO (32)
07 – Hybrid	GW (68) RO (32)	GW (55) SW (45)
08 – Hybrid	GW (23) SW (45) RO (32)	GW (60) S2 (30) RO (10)
09 – Hybrid	GW (60) S2 (30) RO (10)	GW (23) SW (45) RO (32)
10 – Hybrid	G2 (50) SW (50)	G2 (62) SW (24) RO (14)
11 – Hybrid	G2 (62) SW (24) RO (14)	G2 (50) SW (50)
12 – Hybrid	G3 (100)	G4 (100)
13 – Hybrid	S2 (100)	RO (100)
14 – Hybrid	GW (62) SW (27) RO (11)	GW (62) SW (27) RO (11)
15 – Unlined Cast Iron	GW (23) SW (45) RO (32)	GW (60) SW (30) RO (10)
16 – Lined Cast Iron	GW (23) SW (45) RO (32)	GW (60) SW (30) RO (10)
17 – PVC	GW (23) SW (45) RO (32)	GW (60) SW (30) RO (10)
18 – Galvanized Iron	GW (23) SW (45) RO (32)	GW (60) SW (30) RO (10)

Note: Values in ( ) indicate the percentage of the source water in blend

Free chlorine and chloramine residual were studied in parallel using PDS 1 through 8. The three principal water sources, GW, SW, and RO, were produced in both a free chlorine and chloramine version. Conventional finished waters (GW, SW, and RO) and a GW/SW/RO blend with a free chlorine residual of 4 mg/L were fed to PDS 1 to 4, respectively, and conventional finished waters (GW, SW, and RO) and a GW/SW/RO blend with a chloramine residual of 4 mg/L fed PDS 5 to 8, respectively. An HRT of two days was used during the study. The type of water and respective percentage fed to each PDS during the disinfectant comparison study is presented in Table 3.4.

Table 3.4 Water Sources by PDS for Free Chlorine Versus Chloramine Study

	PDS							
Water type	1	2	3	4	5	6	7	8
GW Free	100%			62%				
SW Free		100%		27%				
RO Free			100%	11%				
GW Comb					100%			62%
SW Comb						100%		27%
RO Comb							100%	11%

3.3.2 PDS Operation During TBWII

The TBWII project had a duration of 12 months and was divided in 4 phases of 3-month duration each (Taylor et al. 2007). During TBWII, all the PDS were fed a blend of GW, SW and RO. The composition of the blend was changed for each of the phases except for Phase III, which was identical to Phase I to evaluate seasonal effects. Table 3.5 shows the composition of the blend for each of the project phases.

Table 3.5 Blend Ratios of GW, SW, and RO Waters Used During TBWII Project

Phase	Time Period	% GW	%SW	%RO
I	Feb-May 2006	62	27	11
II	May-Aug 2006	27	62	11
III	Aug-Nov 2006	62	27	11
IV	Nov 2006-Feb 2007	40	40	20

GW and RO waters were produced following the respective process shown in Table 3.2 while the SW was transported weekly from the TBW regional surface water treatment plant. The three water types were blended at the ratios shown in Table 3.5 in an individual tank that served as the feed to thirteen (13) of PDS. The other PDS received the same blend; however, its pH was adjusted to the pH_s using hydrochloric acid.

The fourteen hybrid PDS were used for the inhibitor study while the other four, the single material lines, were only used to study the effect of flow velocity (Reynolds' number) on chloramine decay. For the corrosion inhibitor study, four different corrosion inhibitors were selected, blended ortho-phosphate (BOP), ortho-phosphate (OP), zinc ortho-phosphate (ZOP), and silicate. Each inhibitor was dosed at three dose levels, which were low, medium and high. For the phosphate-based inhibitor the doses were 0.5, 1.0, and 2.0 mg/L as total phosphorus. The doses for the silicate inhibitor were 3, 6, and 12 mg/L as SiO_2. The remaining two PDS were used as control lines and received the blend (PDS 14) and the blend adjusted to pH_s (PDS13). A delivery system was constructed that included a common blend tank for each inhibitor and separate pumps to feed each PDS. Figure 3.3 shows the tanks containing the BOP and OP inhibitors and the pumps (next to the tanks) used to feed them to the PDS.

The stock solutions of the corrosion inhibitors were maintained in refrigeration to avoid degradation and diluted solutions were used to feed the PDSs. The dilutions were prepared in 55-gallon (0.21 m^3) tanks, twice a week, and the feed rates of the diluted inhibitor solution were calibrated to obtain the desired inhibitor target concentration. The diluted inhibitor tanks were cleaned every week and maintained with a free chlorine residual enough to minimize bacteriological growth.

Figure 3.3 Corrosion Inhibitor Feeding System

Additionally, a series of experiments were completed to investigate the effect of flow velocity on chloramine residual decay for varying water quality, with and without inhibitors for different pipe materials. The single material PDSs (PDS 15 to PDS 18) were used for experiments in which Reynolds number was varied from 50 to 200 using two types of water quality, GW and RO. To evaluate the effect of BOP inhibitor on chloramine decay, a set of the experiments included the addition of 1.0 mg/L as P.

3.4 PDS Flushing

The PDS lines were flushed every two weeks at a flow velocity of 1 ft/s (0.3 m/s) for several minutes. This duration was selected to allow a minimum of three pipe volumes of flush water to pass through the PDS lines. The nominal length of the hybrid lines is only 100 feet (30.5 m), thus the operation velocities are very small during normal operation. The objective of the flushing was periodic removal of excessive films that may otherwise accumulate on the pipe interior during the nearly stagnant conditions associated with the 2-day HRT. During TBWI, the flush water was prepared following the same blend composition that was being fed to the respective PDS. During TBWII, the blend water was dosed with the corresponding corrosion inhibitor in the flush tank and mixed before flushing. Also during TBWII, the influent and effluent standpipes were cleaned at the same frequency of the flushing to remove biological growths. Flushing and standpipe cleaning operations were concluded at the end of the week (Thursday or Friday).

3.5 Water Quality Sampling

All PDS were provided with a sampling port after each pipe reach to allow an assessment of water quality changes associated with each pipe reach. Monitoring and analyses of many physical, chemical and biological water quality parameters was carried out on the influent, effluent and internal sample ports of the PDS. Samples were usually taken weekly and analyzed on-site for free and total chlorine, temperature, turbidity, UV254 (organic content), apparent color, DO, conductivity and pH. Analytical procedures as stated in the 19th Edition of Standard Methods (APHA, AWWA, and WEF 1999) were utilized, as shown in Table 3.6.

Table 3.6 Analytical Procedures Utilized and Ranges/Reporting Limits

Parameter	Method	Method Reference	Approximate Range
Chlorine, free	DPD colorimetric	Hach 8021	0.1 - 2 ppm
Chlorine, total	DPD colorimetric	Hach 8167	0.1 - 2 ppm
UV-254	UV spectrometry	SM 5910 A	0-0.5200 cm^{-1}
Temperature	Direct reading		0 - 100 deg C
Oxygen, Dissolved (DO)	Membrane probe	SM 4500-O G	0.1 - 20 mg/L
Turbidity	Nephelometric	SM 2130 B	0.02 - 200 ntu
Color, apparent	Spectrometer	SM 2120 B	1 - 50 cpu
pH	Electrometric Method	SM 4500-H+ B	1 – 14 pH units
Total Iron	Electrothermal Atomic Absorption	SM 3113	Reporting limit: 0.01 mg/L
	Direct Air/Acetylene Flame AAS	SM 3111B	Reporting limit: 0.3 mg/L

*All techniques designated with "SM" referenced in Standard Methods are from the 20th Edition (1999).

PDS samples were usually taken at the beginning of the week. The samples were collected at least 60 hours after a flushing event to allow the desired two-day HRT prior to sample collection. When the HRT was 5-days, the samples were taken immediately before the flushing event.

3.5.1 Quality Assurance and Quality Control

Quality assurance and quality control of both the laboratory and field determinations of water quality parameters was established by measuring the precision and accuracy of the analyses. Precision was assessed by duplicating analyses of at least 10% of the samples with at least one duplicate pair being analyzed anytime a sample was collected. Where appropriate standards were available, at least 10% of the samples were spiked with known concentrations of the parameter being analyzed and the recovery measured. To determine the accuracy of measurements, blind duplicates and spikes were also utilized. Dynamic control charts (Shewart charts) were updated monthly and used to determine whether the results were acceptable. Accuracy and precision were maintained within limits defined in the Quality Assurance Plan and approved by the AwwaRF project advisory committee.

3.6 Model Development

Models for free and combined chlorine dissipation were developed using the water quality data obtained for the different PDS. All the parameters were evaluated to determine their effect on the rate of chlorine decay. The modeling was based in water quality variation and not on water treatment process so it could be used for systems with water quality characteristics different from the waters used in this study.

The empirical models were obtained by least square non-linear regression using the SigmaStat 3.5® computer program and the best fit was determined by statistical analysis and visual inspection. Zero-, first-, and second-order kinetic relations were evaluated with different combinations of the analytical parameters measured for the waters. The models were verified with independent data to the 95% confidence interval. The independent data were obtained from the same pilot distribution system, however, these independent data were not used for model development.

3.7 References

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4 EFFECT OF WATER QUALITY ON FREE AND COMBINED CHLORINE RESIDUAL DECAY IN A DRINKING WATER PILOT DISTRIBUTION SYSTEM: UNLINED CAST IRON PIPES

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4.1 Abstract

The influence of water quality on chlorine dissipation in unlined cast iron pipes was investigated in a large scale pilot distribution system. Finished ground, surface and saline waters were blended to produce a wide range of water quality and distributed to 18 different pilot distribution systems (PDS) with 2 and 5-day HRT. Free chlorine and chloramines were used in separate studies, which allowed development of residual dissipation models for free and combined chlorine as a function of dose, pipe geometry, water quality, temperature and time.

A first-order kinetic model best described free and combined chlorine decay in the unlined cast iron pipes of the pilot distribution systems. The model includes separate decay constants for bulk and pipe wall reactions. In this model, the bulk decay constant is affected by the organic content and temperature of the water, while the pipe wall constant varies with temperature. In general, the results indicate that the rate of chlorine dissipation increases with an increase of either temperature or organic content and decreases with an increase of

the pipe diameter. pH was not a factor for either free or combined chlorine because approximately 80% of the data was in the range of 7.8 to 8.1.

Keywords: chloramines, cast iron pipes, pilot distribution system, free chlorine decay, chlorine modeling, water quality.

4.2 Introduction

Disinfection of drinking water is basic to all water treatment facilities. Typically, a disinfection process is controlled by CT (concentration-time disinfection factor) and residual regulations specified in the surface water treatment rule, SWTR (Malcolm Pirnie and HDR Engineering 1991). Chlorine residuals are required at several points of testing throughout the distribution system, desirable at the tap and protects from contamination due to infiltration and bacterial regrowth. Free chlorine reacts with microorganisms, taste and odor compounds, natural organic compounds and inorganic compounds in the bulk and on the surface of the pipe wall, which depletes residual. This work quantifies the depletion of free chlorine and chloramine residuals throughout the distribution system.

Several efforts have been made to develop models to predict chlorine concentration in relation with time. Reactions within the bulk liquid phase and reactions with materials associated with the pipe wall such as pipe surface, corrosion products, biofilm, and deposits have been found to affect chlorine residual decay in distribution systems (Biswas et al. 1993; Rossman et al. 1994). Vasconcelos et al. in 1997 found that bulk reaction chlorine decay models could be based on first-order kinetics while wall reaction can be represented using either zero-order or first-order kinetics. The overall rate constant, K_T can be expressed as Equation 4.1.

$$K_T = K_W + K_B$$ **Equation 4.1**

Where K_W is the decay constant associated with the wall reactions and K_B is the rate constant for the bulk decay.

Usually chlorine decay in the bulk liquid has been modeled using first-order kinetics with respect to chlorine concentration (Jadas-Hécart et al. 1992), but this approach was site specific and failed to explain the discrepancies between the values for the kinetic constant for different waters. The kinetic constant for reactions in the bulk liquid have been found to be dependant on the water quality, specifically on temperature and organic content of the water (Kiéné et al. 1998, Hua et al. 1999).

Kiéné (1998), described bulk chlorine decay using a first-order kinetic rate with respect to chlorine shown in Equation 4.2.

$$[Cl_2]_t = [Cl_2]_0 \exp(-K * t)$$ **Equation 4.2**

Where the constant K is related with total organic compounds (TOC) and temperature following the empirical relationship shown in Equation 4.3

$$K = a * [TOC] * \exp(-E_a/RT)$$ **Equation 4.3**

where: K = 1/min
a = 1.8×10^6 L/mg-min
T = temperature in ^oK
$\exp(-E_a/RT)$ = Arrhenius temperature correction factor

A second-order kinetic approach has also been studied (Powell et al. 2000a), in which chlorine decay is function of the chlorine concentration, C, and the concentration of the different compounds with which chlorine reacts, H (Equation 4.4). In this approach, H does not remain constant as it is consumed in reactions with chlorine.

$$\left(\frac{dC}{dt}\right)_{bulk} = -K_e * C * H \qquad \textbf{Equation 4.4}$$

Various studies found that nth order or parallel first-order kinetics usually provided a more accurate prediction of residual than simple first-order kinetic models, but that the gain in accuracy was not justified by the more complicated models (Vasconcelos et al. 1996, Powell et al. 2000b).

Modeling of monochloramine dissipation is now desirable because of the popularity of its use as secondary disinfectant for distribution systems. Although monochloramines are considered to be more stable than free chlorine, they decay in distribution systems due to auto-decomposition and direct reaction with natural organic matter or NOM (Valentine and Jafvert, 1988). The auto-decomposition of monochloramine starts with hydrolysis reactions that produce free chlorine and ammonia. The molecules of free chlorine then react to form dichloramines, which dissociate rapidly into chlorides and ammonia. Experimental results show that monochloramine disproportionation is catalyzed by the presence of a proton donor (Valentine and Jafvert. 1988). General acid catalysis of monochloramine was studied in the presence of phosphate and sulfate and the rate of chloramines decay was measured under different pH conditions and related to the concentration of hydrogen ion, sulfates and phosphates. In another study, it was found that monochloramines react directly with the humic material and could be characterized as an elementary stoichiometric reaction (Duirk et al. 2002). A semi-mechanistic model was developed to predict the loss of monochloramine due to reactions with NOM as well as provide a basis for disinfection by-products (DBP) formation modeling. Vikesland, Ozekin and Valentine (1998) compared waters with different concentrations of NOM against laboratory grade water. The study showed that monochloramine loss increases with the addition of NOM to the water.

In this study, surface water and groundwater were treated, blended and distributed to a pilot distribution system to determine the effect of blending on distribution water quality. The purpose of this study is to determine the different parameters that affect the rate of chlorine dissipation in unlined cast iron pipes and develop a model that can be used to predict the chlorine residual in a distribution system. Two methods of disinfection were used: free and combined chlorine. Separate models for each species were calculated using nonlinear regression. Free and total chlorine, temperature, pH, color, turbidity and organic content were analyzed to determine their influence on chlorine decay. Adequate statistical tools and visual inspection were used to determine the best model for each case. The models were verified using data collected from the same pilot distribution system that was not used in the regression analysis.

4.3 Methods and Materials

4.3.1 Pilot Distribution System

A pilot distribution system (PDS) was built at the Tampa Bay Water Cypress Creek Wellfield in Land O' Lakes, Florida with pipes taken from existing distribution system. The distribution system is composed of 18 parallel lines. 14 of the PDS were identical, 90-ft long lines made from links of 20 ft (6.1 m) of 6" (0.15 m) diameter PVC, 18 ft (5.5 m) of 6" (0.15 m) diameter lined cast iron or LCI, 12 ft (3.66 m) of 6" (0.15 m) diameter unlined cast iron or

UCI and 40 ft (12.2 m) of 2” (0.05 m) diameter galvanized steel pipes. All pipes were from 10 to 40 years old and taken from actual distribution systems. The other 4 PDS were single material lines, one for each of the previously mentioned pipe materials. The single material unlined cast iron (UCI) PDS is composed of eight (8) reaches with a length of 12 ft (3.66 m) each for a total of 96 ft (29.3 m). Sample ports were located in each line after each pipe section to facilitate sampling. A picture of the PDSs is shown in Figure 4.1.

Figure 4.1 Pilot Distribution System

The flow conditions in the PDS were set as a one-pass flow-through in which the water was fed to the PDS only once and then discarded. The flow rate in the PDSs was calibrated to obtain either a 5-day or a 2-day hydraulic residence time (HRT) to simulate dead end or dead spots in distribution systems. The flow velocity was 11.2 ft/day and 28 ft/day in the UCI portion of the hybrid lines and 19 ft/day and 47 ft/day in the single material

UCI PDS for HRTs of two and five days. The PDSs were flushed weekly at 1 ft/s to avoid excessive accumulation of particles in the PDSs,

4.3.2 Pilot Water Treatment Processes

During the initial phase of the project, the PDSs were fed for 90 days with conventionally treated groundwater carrying free chlorine residual. After this period, different treatment processes were utilized to produce seven types of finished waters. The sources of the waters used in this study were surface water transported weekly from the Hillsborough River and groundwater taken directly from the wells at the Cypress Creek Wellfield. Table 4.1 shows the principal characteristics of the water treatment processes.

Table 4.1 Water Processes Utilized

Process	Source	Treatment	Treatment/Source Abbreviation
RO	Groundwater (GW)	High pressure reverse osmosis (RO), aeration, solids addition	RO/GW
S1	Surface water	Coagulation-sedimentation-filtration (CSF), ozonation, BAC filtration	ASWT(advanced surface water treatment)/SW
S2	Surface water	CSF, nanofiltration (NF), aeration	IMS(integrated membrane system)
G1	Groundwater	Aeration	C/GW(conventional treatment of groundwater)
G2	Groundwater	Lime softening to hardness of 120, filtration	LS/GW(lime softening of groundwater)
G3	Blend of S1, G1 and RO	Lime softening to hardness of 120, filtration	LS/B(lime softening of a blend)
G4	Blend of S1, G1 and RO	Nanofiltration, aeration	NF/B(lime softening of a blend)

The conventionally treated groundwater (G1) was prepared by aeration of raw groundwater followed by disinfection with free chlorine to a minimum chlorine residual of 4 mg/L as Cl_2. When the desired disinfectant was monochloramines, free ammonia in the form of ammonium chloride (NH_4Cl) was added after a contact time of five (5) minutes. The Cl_2 to ammonia-N ratio used was 5:1 to avoid excess ammonia in the PDSs. Six thousand (6000) gallons of G1 were prepared every week.

The surface water (S1) was prepared using enhanced coagulation with ferric sulfate, followed by settling for a minimum of 24 hours and filtration through a 1 micron bag filter and a 0.35 micron cartridge filter. After filtration, the coagulated-settled-filtered (CSF) surface water was ozonated with a minimum ozone residual of 0.6 mg/L to obtain a CT of 1.4 mg/L-min. The ozonated water was then passed through a biologically activated carbon filter followed by a 0.35-micron cartridge filter and aerated to eliminate excess dissolved oxygen. The treated surface water was then disinfected in the same way than G1. Five thousand (5000) gallons of S1 were prepared every week.

The RO water was prepared by desalination of raw groundwater by reverse osmosis (RO) membranes. After membrane filtration, the RO water was aerated and dosed with calcium chloride, sodium bicarbonate and sea salt to simulate the water quality of the water produced at the Tampa Bay Water Regional Seawater Desalination Plant. The pH of the RO finished water was adjusted to achieve a LSI greater than 1 using sodium hydroxide. The RO water was disinfected in the same way than G1. Four thousand (4000) gallons of RO were prepared every week.

G2 and G3 were produced by lime softening of raw groundwater and a blend of G1, S1 and RO respectively. Both waters were softened to a total hardness of 120 mg/L as

CaCO3 followed by settling, filtration, aeration and disinfection. Two thousand (2000) gallons of G2 and one thousand (1000) gallons of G3 were prepared weekly.

G4 and S2 waters were produced using NF membranes filtration. G4 was produced by nanofiltration of a blend of G1, S1 and RO and S2 was produced by nanofiltration of CSF surface water. After filtration, G4 and S2 were aerated and disinfected. One thousand (1000) gallons of each water was prepared every week.

Seven of the PDSs received 100% of the seven finished waters shown in Table 4.1 while the other 11 PDSs received blends of these seven finished waters to vary water quality and simulate the Tampa Bay Water member governments' finished waters. The different blends were prepared directly in vertical standpipes located at the beginning of the PDS using chemical addition pumps (Figure 4.2). Each pump was calibrated to deliver the right amount of water to obtain the desired blend. The standpipes provided a vessel for mixing of the blend component as well as served as safety device in case of loss of power.

Figure 4.2 Feed Pumps and Influent Standpipes

Samples taken from the PDSs were analyzed immediately in a properly equipped field laboratory. 1-L borosilicate bottles were used to collect all the samples. Each sample bottle was cleaned previously at the main laboratory. When used in the field, each bottle was pre-rinsed with about 100 mL of distilled water and then about 100 mL of sample to be collected. After these pre-rinses, sample was actually collected. The samples were analyzed for free and total chlorine, organic content (UV-254), temperature, turbidity, apparent color and pH. Analytical procedures as stated in the 20th Edition of Standard Methods (1999) were utilized, as shown in Table 4.2. All listed parameters analyzed immediately on-site using appropriate field methods and no storage was necessary.

Table 4.2 Water Quality Analytical Methods

Parameter	Method	Method Reference	Approximate Range
Free Chlorine	DPD colorimetric	HACH 8021	0 – 2 ppm
Total Chlorine	DPD colorimetric	HACH 8167	0 – 2 ppm
Temperature	Direct reading	SM-2550 B	0 – 100 deg C
UV-254	UV spectrometry	HACH 10054	0 – 0.5200 cm^{-1}
NPDOC	Persulfate/UV oxidation	SM 5310C	0.1 to 20 mg/L
pH	Electrometric	SM-4500-H^+ B	2 - 13
Color, apparent	Visible spectrometry	SM 2120 B	1 – 50 cpu
Turbidity	Nephelometric	SM 2130 B	0.02 – 200 NTU

SM = Standard Methods of Water and Wastewater Analysis, 20th ed (1999)
Hach = DR4000 Spectrometer Method Handbook. USEPA accepted or approved

A Quality Assurance Plan (QAP) covering laboratory and field procedures was maintained and abided by for entire project. Quality control of the analytical procedures was done by measuring the precision and accuracy of the analyses. All parameters in the field were assessed for precision. However, the principle of accuracy based upon recovery of standard addition does not apply to many of the field parameters. Precision was assessed by measuring the reproducibility observed between duplicate analyses. Quality control requirements for the analytical methods required ten percent of all samples be analyzed in duplicate with at least one duplicate pair being analyzed each day sample analyses are performed. Accuracy evaluation encompassed the use of spikes, known reference samples, and control standards. Purchased reference check samples and standards were used to assess analytical accuracy. Ten percent of all samples, with a minimum of one sample per day whenever analyzes are performed, were spiked for all analytes being tested for which it was applicable. Shewart control charts for matrix spikes, check standards, blanks, and precision were maintained throughout the project. Table 4.3 presents the QA/QC matrix for all the parameters analyzed.

Free and total chlorine were measured using the DPD colorimetric method with a range of 0 to 2 ppm, pertinent dilutions were utilized for larger concentrations. Two Barnstead/Thermolyne distillation units provide ultra-pure water for sample dilution and reagent preparation. The temperature and pH of the water was measured directly using a standard mercury thermometer and an electrometric pH meter respectively. UV-254 was used as an indicator of the organic content of the water.

Table 4.3 Quality Control and Quality Assurance Methods Utilized by Parameter

Parameter	Accuracy			Precision - Duplication
	Matrix Spikes	Check standards	Blanks	
Free and Total Chlorine	No (not appl)	Yes	Yes	Yes
UV254	No (not appl)	No (not appl)	Yes	Yes
Temperature	No (not appl)	No (not appl)	No (not app)	Yes
Turbidity	No (not appl)	Yes	Yes	Yes
Apparent Color	No (not appl)	Yes	Yes	Yes
pH	No (not appl)	Yes	Yes	Yes
NPDOC	Yes	Yes	Yes	Yes

Not appl = not applicable

The average organic content and the relationship between UV-254 and NPDOC (non-purgeable dissolved organic carbon) was determined for the waters used in this project, and are presented in Figure 4.3 and Figure 4.4 respectively. As shown in Figure 4.3, the finished water NPDOC varied with the degree of treatment, which indicates that the order of finished water NPDOC by treatment by source was RO/GW< IMS/SW< NF/B< ASWT< LS/B< LS/GW< C/GW.

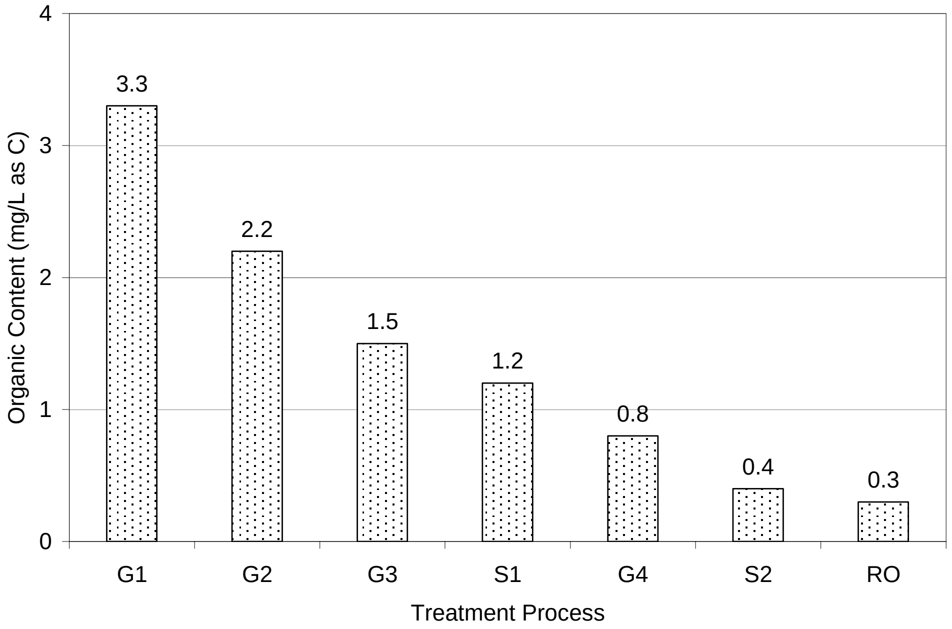

Figure 4.3 Organic Content of Finished Waters by Treatment System

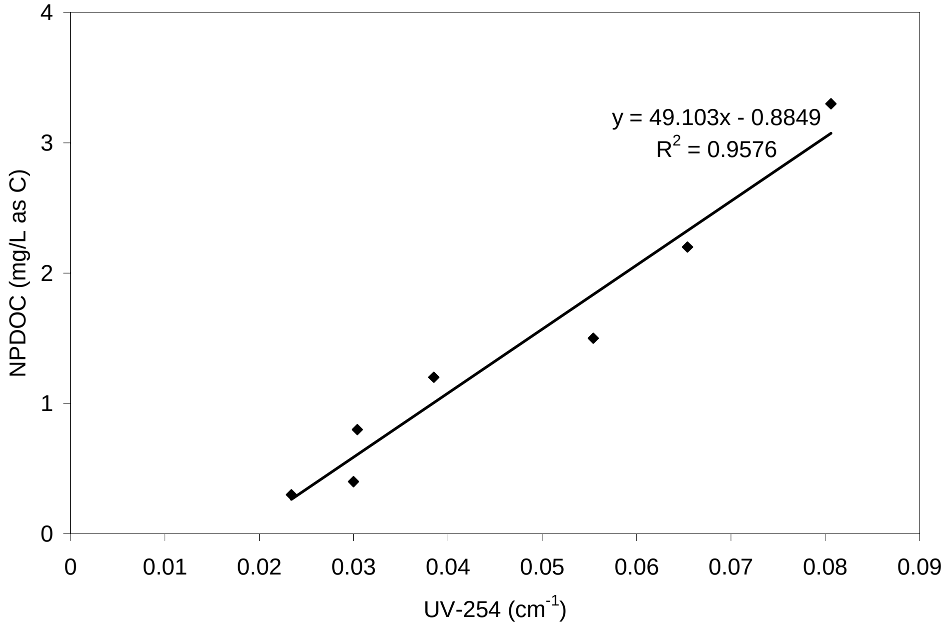

Figure 4.4 Relation Between NPDOC and UV-254

NPDOC correlated well with UV-254, as shown in Figure 4.4 and by the R^2 of 0.96. The linear regression equation used to predict NPDOC using UV254 is shown in Equation 4.5.

$$NPDOC(mg/L) = 49.1 * UV254\left(cm^{-1}\right) - 0.885 \qquad \textbf{Equation 4.5}$$

The project had a duration of 18 months and samples were taken at different times of the year including winter and summer. A total of 165 pairs of data were collected for chloramines and 110 pairs of data were collected for free chlorine.

4.3.3 Model Development

Models for free and combined chlorine dissipation in the cast iron pipes were developed using the water quality data obtained for the different waters. All the parameters were evaluated to determine their effect on the rate of chlorine decay. The modeling was based in water quality variation and not on water treatment process so it could be used for systems with water quality characteristics different from the waters used in this study. The empirical models were obtained using non-linear regression and the best fit was determined by statistical analysis and visual inspection. Zero-, first-, and second-order kinetic relations were evaluated with different combinations of the analytical parameters measured for the waters. The models were verified with independent data obtained from the pilot distribution system which was not used for the model, to the 95% confidence interval. For free chlorine, 78 data pairs were used for the model development and 32 were used for the verification of the model. In the case of combined chlorine or chloramines, 123 data pairs were used for the model and the remaining 42 for model verification.

4.4 Results and Discussion

4.4.1 Free Chlorine Model

During the free chlorine experiments, a total of 110 pairs of data were collected. The ranges of the different water quality parameters analyzed are included in Table 4.4. The average influent free chlorine was 2.9 mg/L was Cl_2 with a maximum of 6.2 mg/L was Cl_2, the temperature varied from 18 to 32 ^{o}C with an average of 23 ^{o}C and the organics ranged from 0 to 1.5 mg/L.

Table 4.4 Range of Water Quality for Free Chlorine Model

Parameter	Average	Maximum	Minimum
Influent Free Chlorine, mg/L as Cl_2	2.9	6.2	0.2
Effluent Free Chlorine, mg/L as Cl_2	2.1	5.8	0.1
UV254, cm^{-1}	0.032	0.048	0.006
Temperature	23.2	32.0	18.0
Turbidity	0.5	1.1	0.1
Apparent Color	4	14	0
pH	8.1	8.5	7.8
NPDOC	2.0	2.9	0.4

Free chlorine residual decayed in unlined cast iron pipes at different rates depending on the organic content of the water and the temperature. Decline of free chlorine residual increased in UCI PDSs as time, UV-254 (organic content) and temperature increased. Figure 4.5 shows the effect of organic content on free chlorine residual decay. All data points shown in Figure 4.5 were collected after the same HRT (7.5 hours) and at the same temperature. The fraction of free chlorine remaining (C_f/C_0) decreases with the increase of the organic content (UV254) from 0.8 to 0.6 as the organics increase from 0.01 to 0.05 cm^{-1}.

Figure 4.6 shows the effect of temperature on free chlorine residual decay with time. The residual is maintained longer at 18 ^{o}C than at 24 ^{o}C. The points in Figure 4.6 correspond to actual data from the PDS and the solid lines are the model predictions.

No relation between pH and the rate of chlorine decay was observed due to the small range of pH values utilized during the study. The range of pH was 7.8 to 8.5 with 74% of the data between 8.0 and 8.1. Color and turbidity were not observed to have an effect on chlorine dissipation rate.

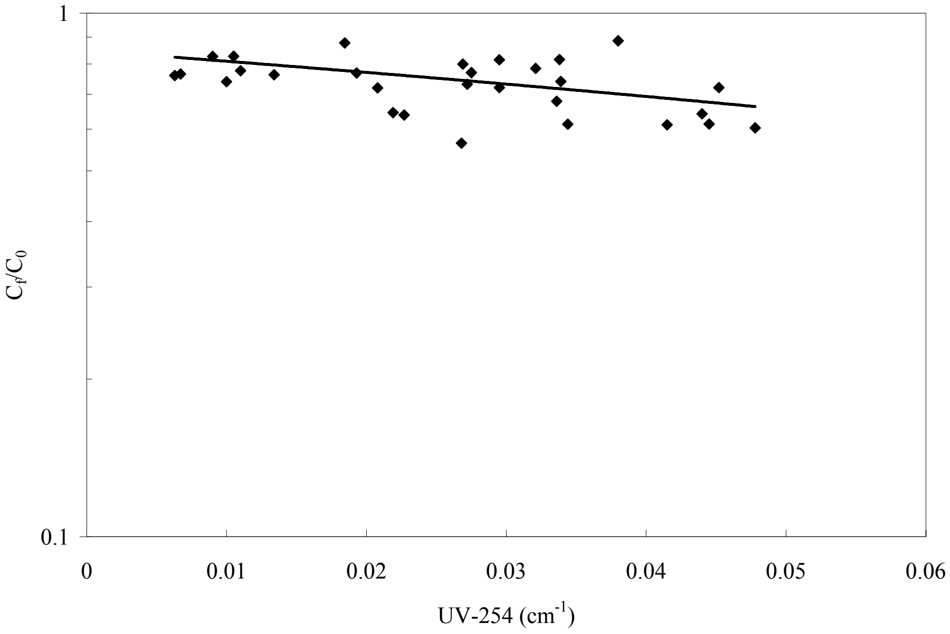

Figure 4.5 Effect of Organic Content on Free Chlorine Residual

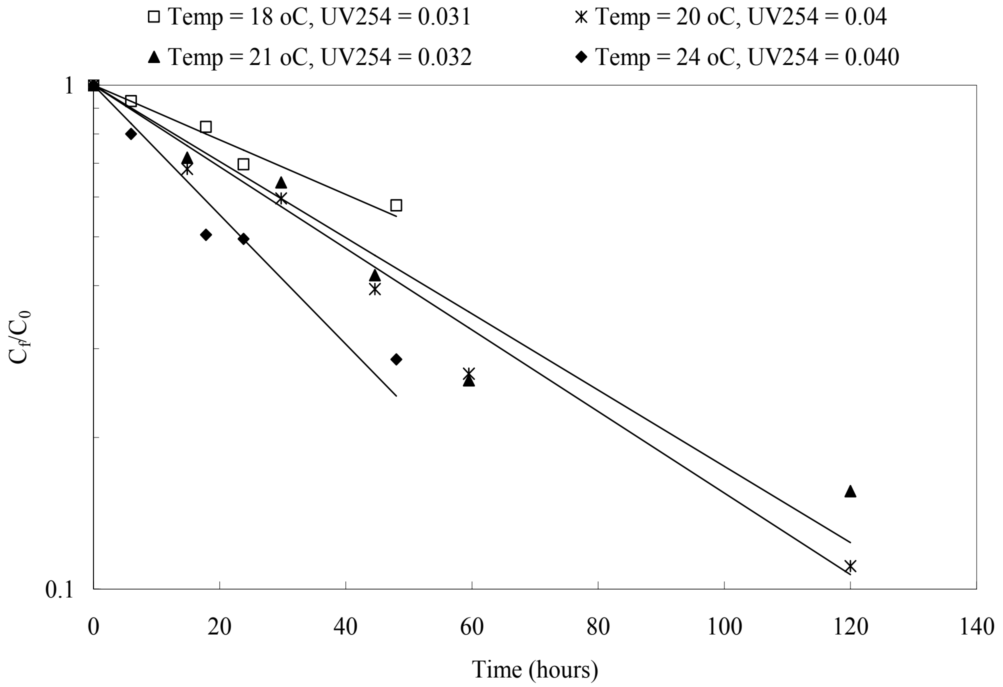

Figure 4.6 Effect of Temperature on Free Chlorine Residual

Free chlorine decay in the UCI PDSs was accurately described by a first-order kinetic model with respect to initial chlorine concentration and time. The general model is shown in Equation 4.6.

$$Cl_{2-t} = Cl_{2-0} * \exp\left(-\left(K_B * UV254 + \frac{K_W}{D}\right) * A^{(T-20)} * time\right) \qquad \textbf{Equation 4.6}$$

where: K_B = bulk decay constant (cm/hr)
K_W = wall decay constant (inches/hr)
Cl_{2-t} = chlorine concentration at time t (mg/L as Cl_2)
Cl_{2-0} = initial chlorine concentration (mg/L as Cl_2)
A = temperature correction coefficient
T = temperature in degrees C
time = time expressed in hours
D = pipe diameter (inches)

In the model, the rate of chlorine decay is expressed using two constants: one for the bulk liquid reactions noted as K_B, and the other for the pipe wall reactions, K_W. The bulk dissipation rate is dependent on UV-254, temperature and time, while the wall dissipation rate is dependent on temperature, pipe diameter, and time. The values of the exponents and A were obtained by non-linear regression:

K_B = 0.172 cm/hour
K_W = 0.063 inches/hour
A = 1.13

A coefficient of determination, R^2, of 0.97 was obtained for the model with a level of significance of 0.001, which indicates that it is a very good fit to the data.

The simulated decay of a 4 mg/L as Cl_2 residual free chlorine residual as a function of time, temperature and UV-254 (NPDOC) of the bulk water is shown in Figure 4.7. Residual is shown to decrease with increasing time, NPDOC and temperature. The upper plane on Figure 4.7 corresponds to predictions for water with a NPDOC of 0.3 mg/L as C running through a 6-inch unlined cast iron pipe and the lower plane corresponds to water with a NPDOC of 3.0 mg/L as C running through the same type of pipe. The white, horizontal plane represents the minimum regulatory free chlorine residual in the distribution system of 0.2 mg/l as Cl_2. Increasing NPDOC an order of magnitude from 0.3 to 3.0 mg/L (which is within common finished water NPDOCs) decreases residual by approximately 0.7 mg/L as Cl_2. At 10 ^{o}C, water with 0.3 mg/L NPDOC would have a residual of 2.4 mg/L after 5 days (120 hours) compared with 1.7 mg/L for water with the same temperature and residence time at 3.0 mg/L NPDOC. Two waters with 0.3 and 3.0 mg/L NPDOC at 30 ^{o}C and 1.25 days residence time would have residuals of 0.3 and 0.9 mg/L as Cl_2. Implications of the model for utilities are distribution system residual can be enhanced by prudent distribution system design or flushing to reduce residence time and reducing NPDOC by source or treatment selection, but have very little control over temperature.

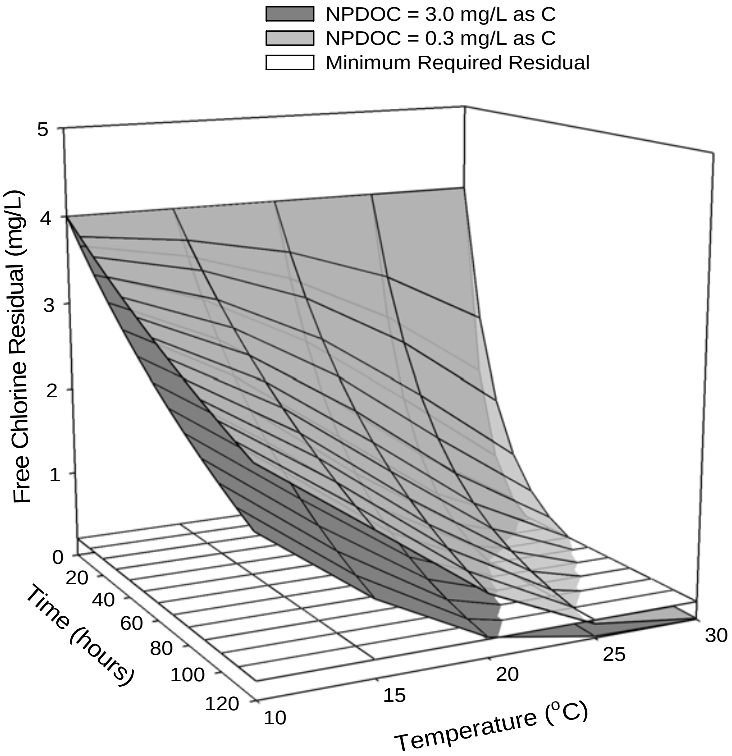

Figure 4.7 Predicted Effect of NPDOC and Temperature on Free Chlorine Decay in Unlined Cast Iron Pipes

The rate of free chlorine dissipation varies with temperature. The value of the temperature correction factor, A, was 1.13, which means that the rate of residual decay doubles for every 5.7 °C increase of the temperature of the bulk water. The effect of temperature can be observed in Figure 4.7, the water with 3.0 mg/L NPDOC maintains a 1.7 mg/L residual at 10 °C after 5 days; however the residual is gone for the same water after 5 days and 1.5 days at 20 °C and 30 °C respectively. A similar scenario is observed for the water with 0.3 mg/L NPDOC.

4.4.2 Combined Chlorine Model

During the combined chlorine experiments, a total of 165 pairs of data were collected. The ranges of the different water quality parameters analyzed are included in Table 4.5. The average influent free chlorine was 2.5 mg/L was Cl_2 with a maximum of 4.6 mg/L as Cl_2, the temperature varied from 13 to 32 ^oC with an average of 26.4 ^oC and the organics ranged from 0 to 3.2 mg/L.

Table 4.5 Range of Water Quality for Combined Chlorine Model

Parameter	Average	Maximum	Minimum
Influent Combined Chlorine, mg/L as Cl_2	2.5	4.6	0.0
Effluent Combined Chlorine, mg/L as Cl_2	1.0	3.1	0.0
UV254, cm^{-1}	0.045	0.083	0.017
Temperature	26.4	32.0	13.0
Turbidity	0.6	5	0.1
Apparent Color	4	11	0
pH	8.1	8.5	7.8
NPDOC	1.3	3.2	0

The rate of combined chlorine decay in UCI PDSs increased as time, UV-254 (organic content) and temperature increased. Figure 4.8 shows how the organic content affect combined chlorine residual decay. All data points shown in Figure 4.8 were collected after the same HRT (7.5 hours) and at the same temperature. The fraction of free chlorine remaining (C_f/C_0) decreases from 0.8-0.9 to around 0.5 with the increase of the organic content (UV254) from 0.03 to 0.07 cm^{-1}. Figure 4.9 shows the effect of temperature on combined chlorine residual decay with time. The residual decay is relatively slow at 16.5 ^oC when compared with the decay at higher temperatures (26 to 29 ^oC). The points in Figure 4.9 correspond to actual data from the PDS and the solid lines are the model predictions.

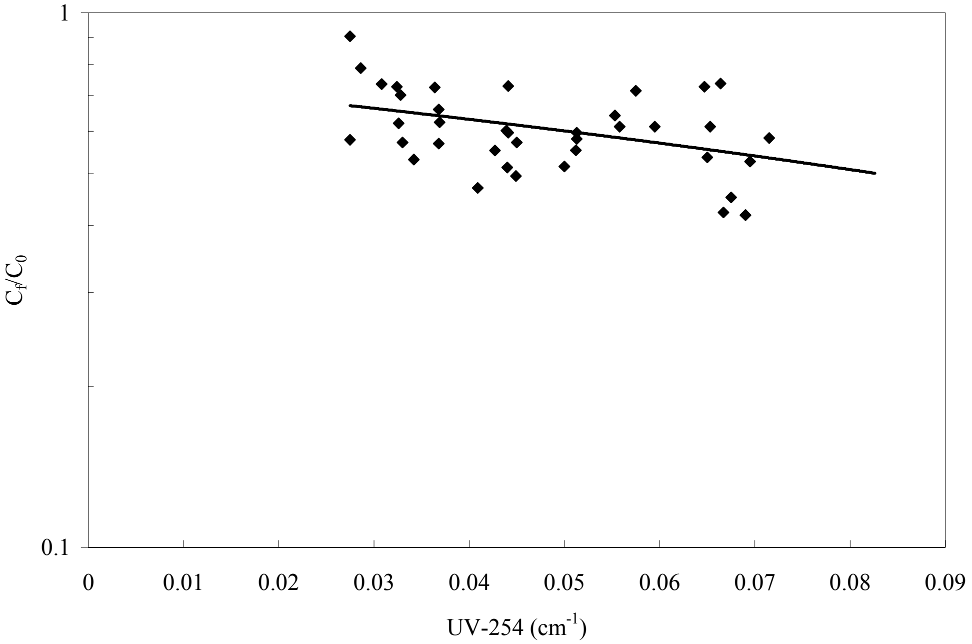

Figure 4.8 Effect of Organic Content on Combined Chlorine Residual

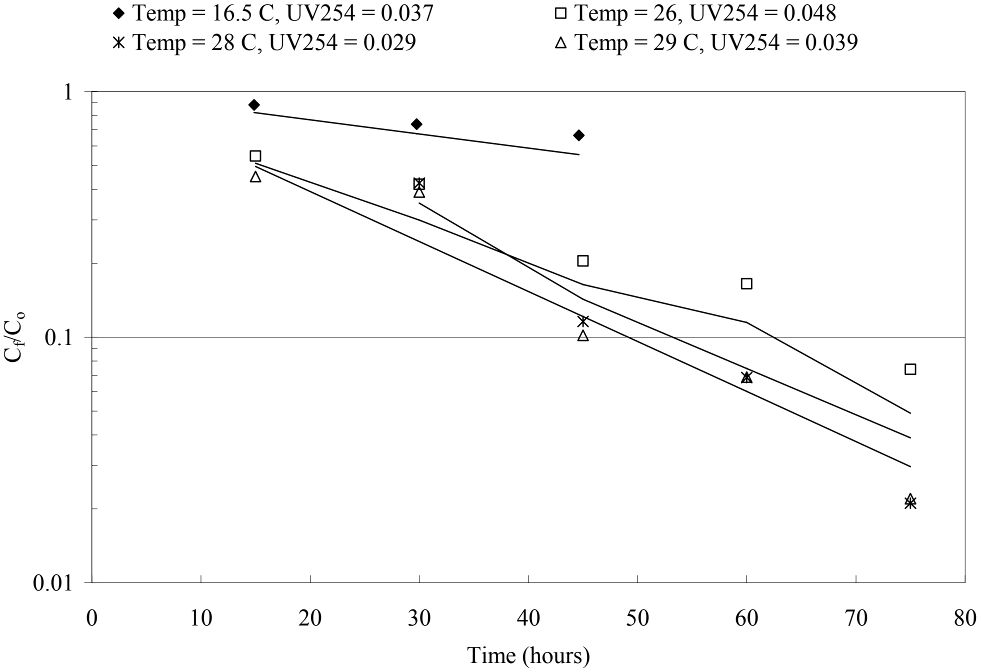

Figure 4.9 Effect of Temperature on Combined Chlorine Residual

The model for combined chlorine (monochloramines) decay in the UCI pipes of the distribution system was also found to follow first-order kinetics with respect to chlorine concentration. The general form of the model is shown in Equation 4.6. As with free chlorine, pH, color and turbidity were not significant in this model. The range of pH was 7.1 to 8.2 with 87% of the data between 7.8 and 8.1. The R^2 obtained for the model was 0.87. The values of the exponents and A were obtained by non-linear regression and are:

K_B = 0.147 cm/hour
K_W = 0.084 inches/hour
A = 1.11

Figure 4.10 shows the effect of organic content and temperature on the rate of combined chlorine decay in UCI pipes. The upper plane on Figure 4.10 corresponds to predictions for chloraminated water with a NPDOC of 0.3 mg/L as C running through a 6-inch unlined cast iron pipe and the lower plane corresponds to water with a NPDOC of 3.0 mg/L as C running through the same type of pipe. The white, horizontal plane represents the minimum regulatory combined chlorine residual in the distribution system of 0.6 mg/l as Cl_2.

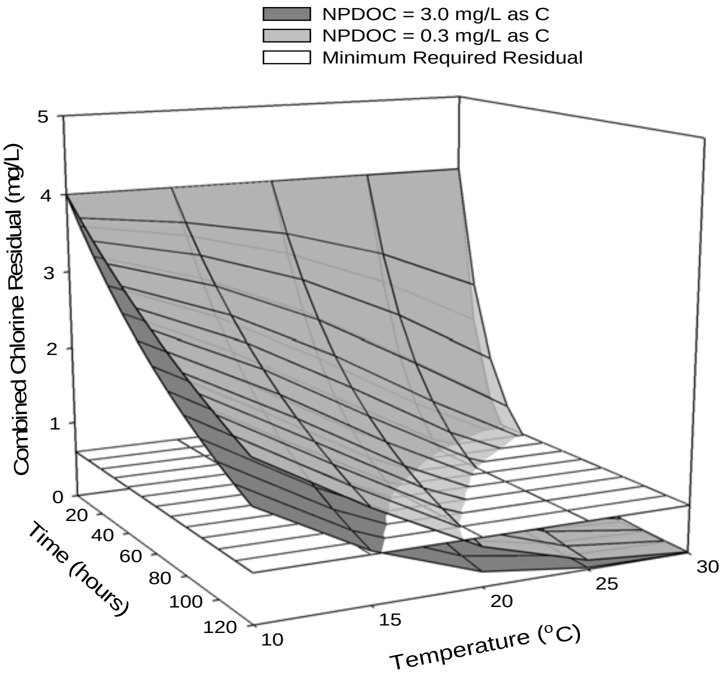

Figure 4.10 Predicted Effect of NPDOC and Temperature on Combined Chlorine Decay in Unlined Cast Iron Pipes

A reduction of the organic content of the water increases the time the combined residual can be maintained in the UCI distribution system. Figure 4.10 shows that the water with 0.3 mg/L NPDOC maintains a residual greater than 0.6 mg/L as Cl_2 for 150% longer than 3.0 mg/L NPDOC water. 0.3 mg/L NPDOC water will maintain the minimum 0.6 mg/L as Cl_2 residual for 108, 64 and 38 hours at 20 ^oC, 25 ^oC and 30 ^oC as compared to 74, 44 and 26 hours a 3.0 mg/L NPDOC water at 20 ^oC, 25 ^oC and 30 ^oC for a 3.0 mg/L water.

As for free chlorine residuals, the rate of chloramine dissipation varies with temperature. The value of the temperature correction factor for the chloramine model is 1.11, which means that the rate of residual decay doubles for every 6.7 ^oC increase in the bulk water temperature. It is not surprising that the effect of temperature on residual dissipation is slightly less for chloramines relative to free chlorine. The effect of temperature can be observed in Figure 4.10. 3.0 mg/L NPDOC water maintains a residual of 1.3 mg/L at 10 °C after 5 days, but only for 3.1 days and 1.1 days at 20 °C and 30 °C respectively.

4.4.3 Model Verification

The models for free chlorine and chloramine residual decay in UCI PDSs were verified using independent data. About 25 % of the data collected from the pilot distribution system was separated and was not used for the development of the model. Figure 4.11 shows actual free chlorine and chloramine residual plotted against predicted free chlorine and chloramine residuals obtained using the respective model.

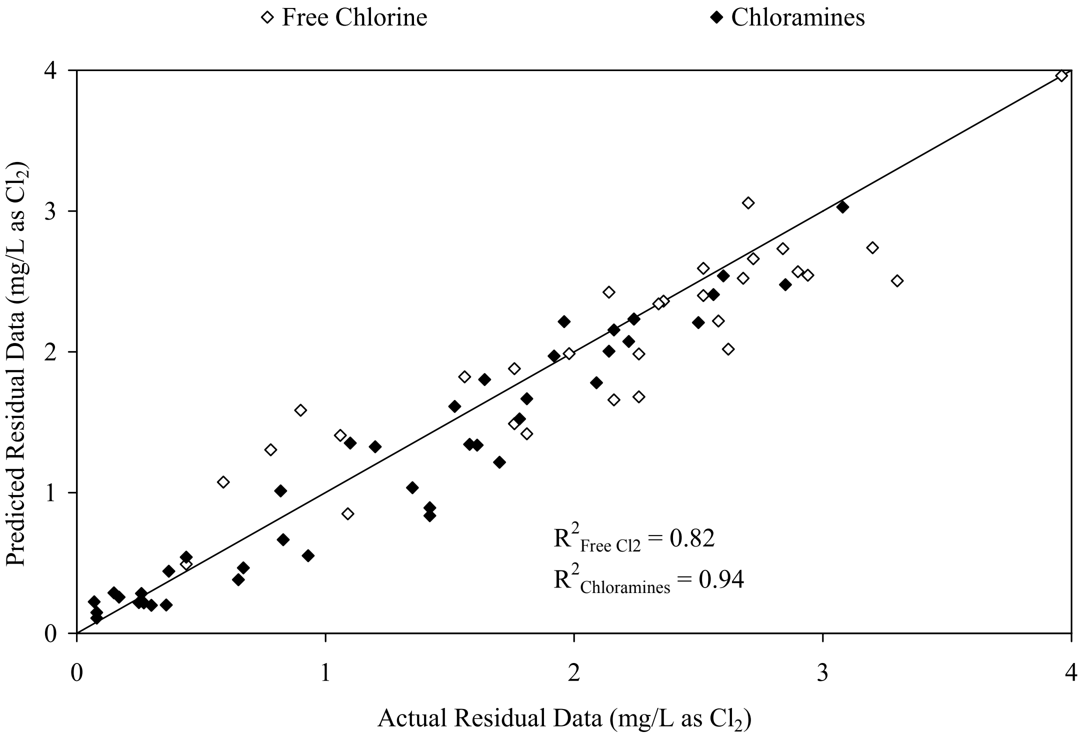

Figure 4.11 Free Chlorine and Chloramine Models Verification

The solid line at 45 degrees represents a good match between predicted and actual values. Most points are close to and evenly distributed around the line of perfect fit, which indicates that the models are useful to predict free chlorine and chloramine residual in UCI distribution systems. R^2 were 0.82 for free chlorine and 0.94 for chloramine models.

4.5 Conclusions

Chlorine decay in unlined cast iron distribution systems can be modeled using first-order kinetics with respect to chlorine concentration. The rate of chlorine dissipation is a function of time, organic content and temperature.

The rate of chlorine dissipation in UCI distribution systems is dependent on aqueous organic concentration. The organic content of the water does not produce an effect of the same magnitude with chloramines as with free chlorine because chloramines are less reactive than free chlorine. A reduction in organics from 3.0 mg/L as C to 0.3 mg/L as C is predicted to increase the duration that water retains a free chlorine residual in UCI pipes by 71% and by 46% for a combined chlorine residual.

The temperature of water in a UCI distribution system affects the rate of chlorine dissipation. The rate of chlorine dissipation in UCI pipes will double for every 5.7 ^{o}C increase on temperature for free chlorine and 6.7 ^{o}C for combined chlorine

The models were verified using independent pilot distribution system data not used in the models development

4.6 Acknowledgements

The University of Central Florida (UCF) and UCF project team wish to express their sincere gratitude to Tampa Bay Water (TBW); Hillsborough County, FL; Pasco County, FL; Pinellas County, FL; City of New Port Richey, FL; City of St. Petersburg, FL; and City of Tampa, FL which are the Member Governments of TBW and the American Water Works Association Research Foundation (AwwaRF) for their support and funding for this project. The TBW project team wishes to recognize Christine Owen-TBW Project Officer, Roy Martinez-AwwaRF Project Officer and to the members of the Project Advisory Committee-Koby Cohen, Jonathan Clement, and Bruce Johnson.

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5 PIPE MATERIAL EFFECT ON FREE AND COMBINED CHLORINE DECAY

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5.1 Abstract

The rates of free and combined chlorine decay in a pilot distribution system were found to be highly dependent on the pipe material. PVC, lined and unlined cast iron and galvanized steel pipes taken from actual distribution systems were assembled to form 18 pilot distribution systems (PDS). The pilot distribution systems were operated at hydraulic retention times of 2 and 5 days. Free chlorine and monochloramines were, at different times, used as disinfectants in the study. The PDSs were monitored for free and total chlorine, temperature, pH, and organic content. Empirical models for chlorine dissipation in drinking water distribution systems were developed as a function of pipe material, pipe diameter and water quality. Separate models for free and total chlorine decay were developed using non-linear regression.

The best model to describe the decay of free and combined chlorine in the pilot distribution systems was a first-order kinetic model containing separate rate constants for the bulk and the pipe wall reactions. The form of the model and the rate constants were obtained by material for free and total chlorine using non-linear regression. The rate constants were dependent on the material and diameter of the pipe as well as the temperature and organic

content of the water. Free and combined chlorine decay was slow and similar in PVC and lined ductile iron pipes, and was significantly faster in the unlined metallic pipes: unlined cast iron and galvanized steel pipes. Small diameter pipes and higher temperatures increase the rate of chlorine decay irrespective of pipe material.

5.2 Introduction

Chlorine decay in distribution systems has been described by first-order kinetics and, in laboratory experiments, the simple first-order model shown in Equation 5.1 has usually provided a good fit to chlorine decay (Jadas-Hécart et al. 1992, Hua et al. 1999, Rossman et al. 1994, Powell et al. 2000a).

$$C = C_0 \exp(-K * time)$$ **Equation 5.1**

In distribution systems, chlorine residual decay is due not only to reactions within the bulk liquid phase but to reactions with materials associated with the pipe wall (Biswas et al. 1993, Rossman et al. 1994). Some recent models separate these effects as shown in Equation 5.2, and express the overall dissipation rate constant as the sum of wall and bulk reactions.

$$K_T = K_B + K_W$$ **Equation 5.2**

Where: K_W = Kinetic constant for the wall reactions
K_B = Kinetic constant for the bulk reactions

Vasconcelos et al. in 1997 postulated that free chlorine decay models could be based on first-order kinetics for bulk reactions, and either zero-order or first-order kinetics for the wall reactions. The bulk kinetic constant has been reported to be influenced by the water quality, especially organic content and temperature (Powell et al. 2000b). Monochloramines decompose with or without the presence of inorganic or organic matter. When NOM is present, it reacts directly with free chlorine or monochloramines or catalyzes the auto decomposition of the monochloramines (Vikesland, Ozekin and Valentine 1998).

In distribution systems, the principal factors that consume free and combined chlorine are deposits, corrosion products, reactions with the pipe material and biofilm growing at the internal pipe walls (Lu et al. 1999, Gauthier et al. 1999). The pipes used in distribution systems can be classified in two groups: synthetic pipes and metallic pipes. While deposits and biofilm growth is common for both groups, corrosion and reactions with the pipe wall material are not. Previous studies reported that synthetic materials such as PVC, medium and high-density polyethylene, cement lined iron and polypropylene have a very low demand of chlorine (Kiéné et al. 1998, Hallam et al. 2002). Metallic pipes, especially unlined iron-based pipes, deplete chlorine rapidly as chlorine reacts with corrosion products and the metal at the pipe wall. Free chlorine reacts chemically with the walls of cast iron pipes and the chlorine consumption rate has been related to the corrosion current density (Frateur et al. 1999). In 2002, Vikesland and Valentine showed that combined chlorine is consumed due to reactions with iron in the aqueous-phase and at the pipe surface. Monochloramine was found to react with Fe(II) to form Fe(III) and ammonia. The study found that the reaction rate expressions were first-order with respect to aqueous ferrous ion and the monochloramine concentration, and were also pH dependent. The elevated consumption of chlorine in metallic pipes could also be explained by the higher microbiological activity at the pipe wall. Bacteria have been shown to accumulate in tubercles created in corroded iron pipe or imperfections in the pipe material (Hallam et al. 2001). Deposits in the pipes have also been found to be a reservoir of carbon and nitrogen that support bacterial growth and reduce chlorine residual (Gauthier et al. 1999).

The reaction rate at the pipe surface is affected by the specific surface area available for reaction and the rate of chlorine transport towards the pipe wall (Rossman et al. 1994, Vasconcelos et al. 1997). A mass transfer approach developed by Rossman (Rossman et al. 1994), indicates that the overall wall decay constant could be obtained by combining the hydraulic radius of the pipe, the mass transfer coefficient from the bulk liquid to the pipe wall, and the wall reaction rate constant and is shown in Equation 5.3.

$$K_W = \frac{K_{W1} * K_F}{R_h(K_{W1} + K_F)} = \frac{K'}{R_h}$$ **Equation 5.3**

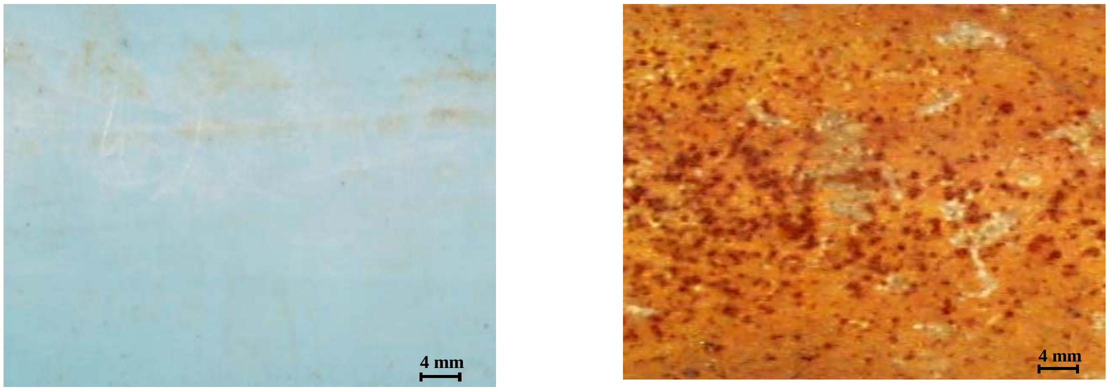
Where: K_{W1} = wall reactions kinetic constant (ft/hr)
K_F = mass transfer coefficient (ft/hr)
K' = overall wall decay kinetic constant (ft/hr)
R_h = hydraulic radius (ft)

The purpose of this study was to quantitatively describe chlorine and chloramine dissipation as a function of pipe material and water quality in a distribution system. Different pipe materials were used, which were relatively inert PVC and lined cast iron and more reactive galvanized steel and unlined cast iron. Models were determined by pipe material and disinfectant.

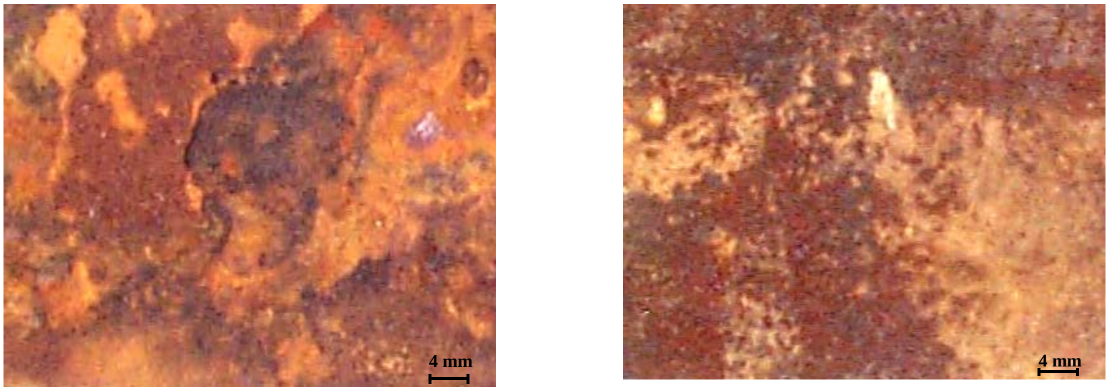
5.3 Materials and Methods

5.3.1 Pilot Distribution System (PDS)

A pilot distribution system composed of 18 parallel lines was built using poly-vinyl chloride (PVC), lined and unlined cast iron (LCI and UCI) and galvanized steel (G) pipes that had been in operation for longer than 20 years. The pipes were taken from Tampa Bay Water member governments' actual distribution systems and assembled at the pilot site at the Cypress Creek Well field in Land O' Lakes, Florida. Figure 5.1 shows close-up pictures of samples of the pipe materials utilized.



(a) PVC (b)LCI



(c) UCI (d) G

Figure 5.1 Pictures of Internal Surfaces of Aged Pipes Utilized

Fourteen (14) of the PDS were hybrid lines, constructed using pieces of each material connected in series. Each hybrid line is composed of 19 feet of 6-inch PVC, 18 feet of 6-inch LCI, 12 feet of 6-inch UCI and 40 feet of 2-inch G pipes. The other four PDS are single material pipes as shown in Table 5.1.

Table 5.1 General PDS Characteristics

PDS #	Length (ft)	Diameter (inches)	Material
15	97	6	Unlined cast iron
16	87	6	Lined ductile iron
17	95	6	PVC
18	163	2	Galvanized steel
1 – 14	100 (19 – 18 – 12 – 40)	6 – 6 – 6 – 2	PVC – LCI – UCI – G

To facilitate the monitoring of the PDS, sample ports were located after each type of pipe in the hybrid lines and at regular intervals in the single material lines. A picture of the PDSs is shown in Figure 5.2. The water was pass through the PDS once and then discarded. The hydraulic residence time (HRT) in the PDS was regulated to five (5) days during the first seven months of the project and changed to two (2) days afterwards to ensure the presence of a disinfectant residual throughout the PDS during the warm months of the year. The flow velocities through the PDS were small ranging from 11.2 ft/day to 47 ft/day. The flow conditions represent worse case condition in a full scale distribution system (dead or near dead end conditions). To avoid excessive accumulation of deposits inside the pipes, the PDS were flushed every two weeks at a velocity of 1 ft/sec using a minimum of 3 pipe volumes of water. Standpipes were located at the beginning and end of each PDS as a safety measure to avoid the drying of the pipes in case of a power failure (Figure 5.3).

Figure 5.2 Picture of Pilot Distribution System

Figure 5.3 Influent Standpipes and Feed Pumps

5.3.2 Chlorine Residual Types

Free chlorine at a target concentration of 4 mg/L as Cl_2 was used as disinfectant for the initial 90 days of the project. Afterwards, combined chlorine (chloramines) was used as disinfectant at the same target concentration. The duration of this part of the project was 12 months. In addition, a complementary study was conducted using eight (8) of the hybrid PDS during three months. Four (4) of the lines were fed with groundwater (G1), surface water (S1), desalinated water (RO) and a blend that used free chlorine as disinfectant and the other four (4) PDS received the matching type of water using chloramines as disinfectant. This part of the study allowed side by side comparison between the two disinfectants.

5.3.3 Waters

During the initial 90 days of project, all the PDSs were fed with conventionally treated groundwater using a free chlorine residual of 4.0 mg/L. After the initial period, seven (7) different treatment processes were utilized to produce finished waters. Surface water from the Hillsborough River and groundwater taken directly from the wells at the Cypress Creek Wellfield were the water sources utilized. The waters were named based on the water source: G1, G2, G3, and G4 for groundwater and S1 and S2 for surface water or the treatment used (RO). The treatment processes were selected based on treatment plants in existence in the member governments systems.

Conventionally treated groundwater (G1) was prepared by aeration of raw groundwater followed by disinfection with free chlorine to a minimum chlorine residual of 4 mg/L as Cl_2. After a contact time of 5 minutes, ammonium chloride (NH_4Cl) was added to form monochloramines. The Cl_2 to ammonia-N ratio used was 5:1 to avoid excess ammonia in the influent to the PDSs. Six thousand (6000) gallons of G1 were prepared every week.

The surface water (S1) was prepared using enhanced coagulation with ferric sulfate, followed by settling for a minimum of 24 hours and filtration through a 1 micron bag filter and a 0.35 micron cartridge filter. After filtration, the coagulated-settled-filtered (CSF) surface water was ozonated with a minimum ozone residual of 0.6 mg/L to obtain a CT of 1.4 mg/L-min. After ozonation, the water was passed through a biologically activated carbon (BAC) filter followed by a 0.35 micron cartridge filter. The excess dissolved oxygen was eliminated by aeration. The treated surface water was then disinfected in the same way than G1. Five thousand (5000) gallons of S1 were prepared every week.

The RO water was prepared by desalination of raw groundwater by reverse osmosis (RO) membranes followed by aeration to remove hydrogen sulfide (H_2S). The RO permeate was then dosed with calcium chloride, sodium bicarbonate and sea salt to simulate the water quality of the water produced at the Tampa Bay Water Regional Seawater Desalination Plant. The pH of the RO finished water was adjusted to reduce corrosiveness to 0.3 pH units above the saturation pH (pH_s). The RO water was disinfected in the same way than G1. Four thousand (4000) gallons of RO were prepared every week.

Two types of softened waters were prepared: G2 and G3. G2 was produced by lime softening of raw groundwater while G3 source water was a blend of G1, S1 and RO. The target of the softening process in both cases was a total hardness of 120 mg/L as $CaCO_3$ and was followed by settling, filtration, aeration and disinfection. Two thousand (2000) gallons of G2 and one thousand (1000) gallons of G3 were prepared weekly.

G4 and S2 waters were produced using nanofiltration (NF) membranes. G4 was produced by nanofiltration of a blend of G1, S1 and RO while S2 was produced by nanofiltration of CSF surface water. After membrane filtration, G4 and S2 were aerated and disinfected. One thousand (1000) gallons of G4 and S2 were prepared every week.

The PDSs were fed using chemical addition pumps that were calibrated to deliver the right quantity of water to the standpipes to obtain the desired blend (Figure 5.3). Seven of the PDSs received 100% of the seven finished waters mentioned before while the other 11 PDSs received different blends of the seven finished waters to obtain a wide range of water quality and simulate the Tampa Bay Water member governments' finished waters.

5.3.4 Sampling

Water quality samples were taken at the influent, effluent and internal ports of the PDSs. Samples were taken and analyzed on-site for free and total chlorine, color, turbidity, temperature, UV-254 (a surrogate for organic content) and pH. The analytical procedures utilized are as stated in the 20th Edition of Standard Methods (1999) and are shown in Table 5.2. Standards and duplicates were analyzed every time samples were collected and used to develop accuracy and precision control limits throughout the project. Duplicates were analyzed for at least ten percent of the samples with a minimum of one duplicate pair being analyzed any time a sample is collected.

Table 5.2 Analytical Procedures Utilized

Parameter	Method	Method Reference	Approximate Range
Free Chlorine	DPD colorimetric	HACH 8021	0 – 2 ppm
Total Chlorine	DPD colorimetric	HACH 8167	0 – 2 ppm
Temperature	Direct reading	SM-2550 B	0 – 100 deg C
UV-254	UV spectrometry	HACH 10054	0 – 0.5200 cm^{-1}
pH	Electrometric	SM-4500-H^+ B	2 - 13
Color, apparent	Visible spectrometry	SM 2120 B	1 – 50 cpu
Turbidity	Nephelometric	SM 2130 B	0.02 – 200 NTU

5.3.5 Model Development

The water quality data obtained for the different PDS during the study was separated by pipe material and analyzed with respect to time using a non-linear regression computer program (SigmaStat 3.5®). Zero-, first and second order kinetic models that contained several combinations of water quality parameters were tested to find the best fit model. The modeling effort was directed at water quality parameters and not at water treatment process to ensure the results could be used for any type of water. The best fit model was determined using statistical evaluations (goodness of fit) and visual inspection. Approximately 25 % of the data collected from the pilot distribution system was separated and was not used for the model development. This independent data was used to verify the model.

5.4 Results and Discussion

5.4.1 Free Chlorine

Free chlorine residual decayed at different rates in the pilot distribution system (PDS) depending on the pipe material as shown in Figure 5.4. The rate of chlorine consumption was lower in PVC and lined cast iron pipes. These materials are fairly inert and do not have high chlorine demand. Chlorine concentration declined rapidly in the iron-based pipes. Figure 5.4 shows the observed profiles of water with an UV-254 of 0.0430 cm^{-1}, a pH of 8.1 and a temperature of 21.5 ^{o}C. PVC and lined cast iron pipes maintained about 80% of the initial concentration after 5 days (120 hours) while UCI pipes lost 80% of the residual in the same amount of time. In the galvanized pipes, the residual went from 5 mg/L to 0.5 mg/L in 32 hours and disappeared after 48 hours.

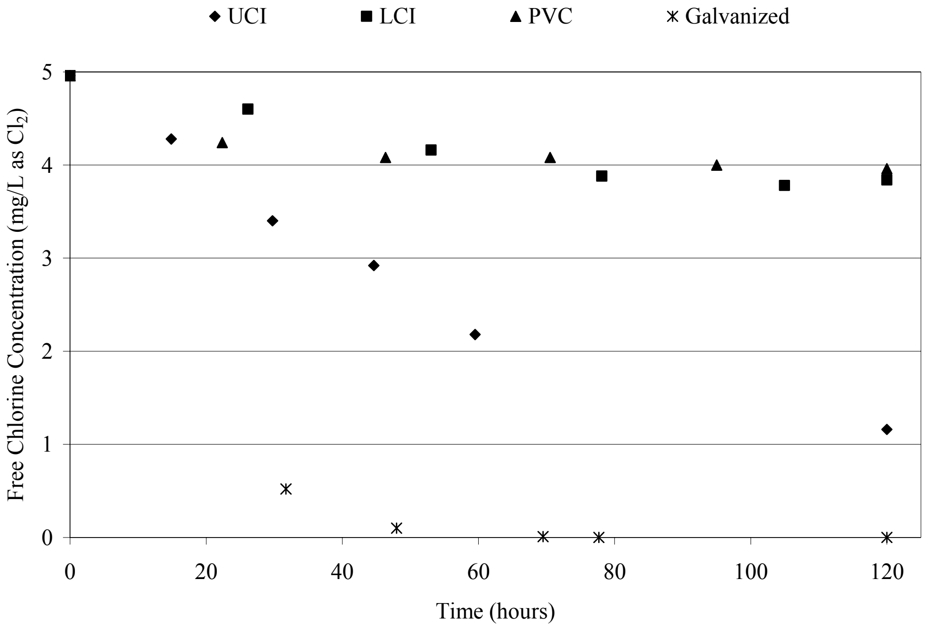


Figure 5.4 Effect of Pipe Material on Free Chlorine Residual in PDS

For all the pipe materials, the rate of decay of chlorine residual increased in PDSs irrespective of material as time, UV-254 (organic content) and temperature increased. Figure 5.5 shows the effect of the change on temperature and organic content of the water had on the fraction of chlorine residual remaining ($Cl_{2\text{-}f}/Cl_{2\text{-}0}$) in the PDS after 5 days.

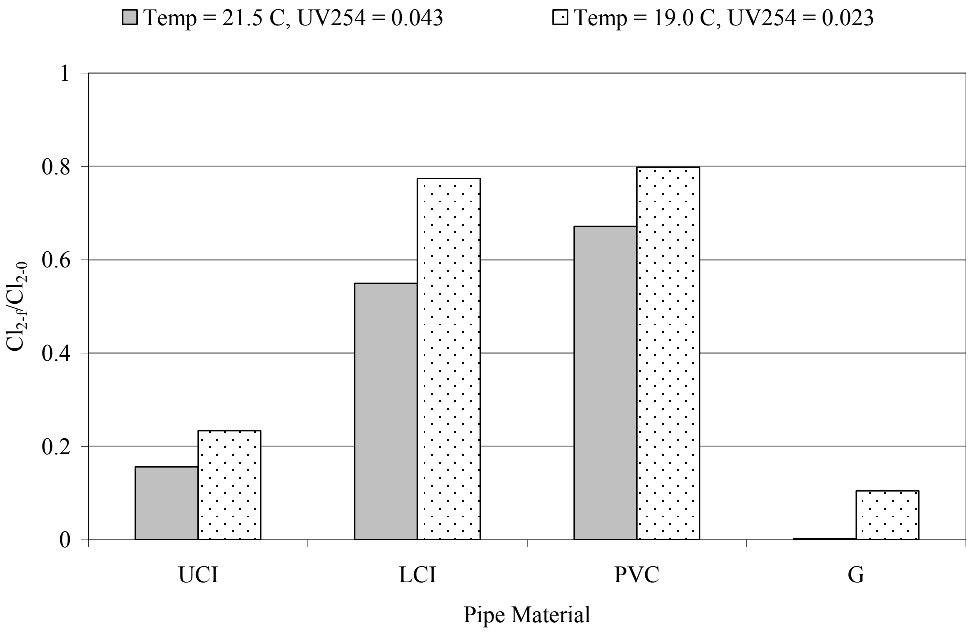


Figure 5.5 Effect of Water Quality Changes on Free Chlorine Decay in PDS

The best model to describe free chlorine decay in the PDSs was a first-order kinetic model with respect to initial chlorine dose and time. The general formula of the model is shown in Equation 5.4.

In the model, the dissipation rate of chlorine in the pilot distribution system is expressed using two constants: K_B for the bulk liquid reactions and K_W for the pipe wall reactions. The bulk dissipation rate is affected by UV-254, temperature and time, while the wall dissipation rate is affected by temperature, pipe diameter, and time. The values of the coefficients and the temperature correction factor (A) were obtained by non-linear regression for each of the pipe materials and are shown in Table 5.3.

$$Cl_{2-t} = Cl_{2-0} * \exp\left(-\left(K_B * UV254 + \frac{K_W}{D} \right) * A^{(T-20)} * time \right) \qquad \textbf{Equation 5.4}$$

Where: K_B = bulk decay constant (cm/hr)
K_W = wall decay constant (inches/hr)
$Cl_{2\text{-}t}$ = chlorine concentration at time t (mg/L as Cl_2)
$Cl_{2\text{-}0}$ = initial chlorine concentration (mg/L as Cl_2)
A = temperature correction coefficient
T = temperature in degrees Celsius
time = time expressed in hours
D = pipe diameter (inches)

Table 5.3 Free Chlorine Models Coefficient Values and R^2

Material	Parameter	Value	R^2
PVC	K_B	0.048	0.97
	K_W	0.007	
	A	1.15	
Lined Cast-Iron	K_B	0.084	0.93
	K_W	0.007	
	A	1.18	
Unlined Cast Iron	K_B	0.172	0.97
	K_W	0.063	
	A	1.13	
Galvanized Steel	K_B	0.614	0.93
	K_W	0.054	
	A	1.04	

The model coefficients show that chlorine decay was highly affected by the pipe material. In general, free chlorine decayed faster in UCI and the rate of chlorine dissipation for PVC and lined iron was slower than that for cast iron and galvanized steel. The value of K_B for PVC and lined-iron are very low (0.048 and 0.084 cm/h), which indicates that there is little effect of these materials on bulk rate decay. K_B for the metallic pipes are larger than K_B

for PVC and LCI, for UCI pipes is 2 and 4 times larger than LCI and PVC and K_B for galvanized steel is 13 and 7 times larger. The larger values of K_B for iron-based pipes may be explained by the reactions of chlorine with iron corrosion products and other materials that dissolved from the pipe walls into the water increasing the chlorine demand of the bulk liquid.

The wall kinetic constant, K_W, for galvanized and UCI pipes are 8 and 9 times larger than K_W for PVC and LCI which may be explained by the reactivity of chlorine with the ferrous material of the pipe or the presence of additional biological activity on the unlined metallic pipes. Surface characterization studies done in pipe coupons showed that the pipe roughness of LCI and galvanized pipes is similar indicating that pipe material and not surface roughness is the main characteristic that affects free chlorine decay in the PDS (Taylor et al. 2007).

The temperature correction factor, A, ranged from 1.04 (for galvanized steel) and 1.18 (for lined cast iron). The rate of free chlorine decay would double for increment of temperature of 17 ^{o}C for galvanized steel pipe and 5 ^{o}C for lined cast iron pipes. The effect of temperature on free chlorine dissipation can make it difficult to maintain a residual in the distribution system in summertime conditions.

Figure 5.6 shows predictions of the effect of pipe material on free chlorine decay on water with an organic content of 1 mg/L as NPDOC and temperatures ranging from 10 to 30 ^{o}C for pipes with a diameter of 6 inches. PVC and LCI pipes are predicted to maintain their free chlorine residuals above the minimal regulatory limit of 0.2 mg/L as Cl_2 for at least 5 days, even when the temperature reaches 30 ^{o}C. UCI pipes are predicted to maintain the residual until the temperature rises above 24 ^{o}C and galvanized steel pipes would not be able to maintain the residual at almost any temperature. The increase in chlorine dissipation rates with an increase in temperature may be due to the increase on the rate of chlorine reaction with water at higher temperatures as well as the increased rate of bacterial growth or other distribution system phenomena at higher temperatures near or at the pipe wall.

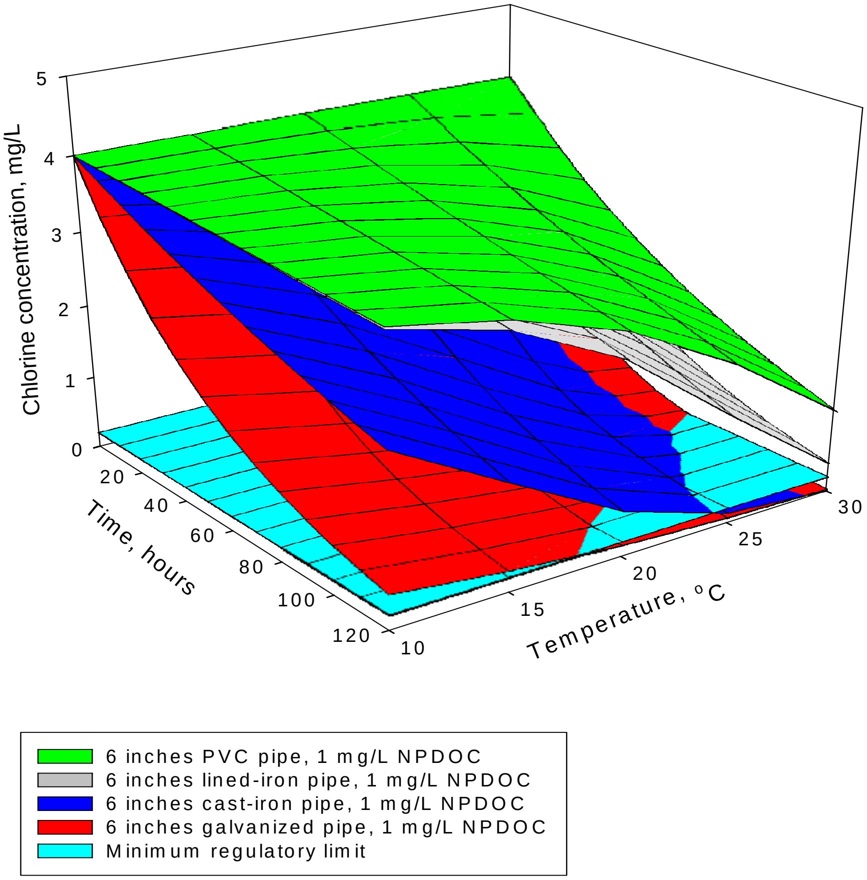


Figure 5.6 Effect of Pipe Material and Temperature on Free Chlorine Decay

As shown in Table 5.3, the models are a good fit to the data, presenting values of R^2 of or above 0.93. About 20 to 25% of the data collected from the pilot distribution system was not used to develop the models and was used as independent data to verify the predictive value of the models. Figure 5.7 shows actual effluent free chlorine residual compared with the predicted value obtained using the model based on the initial free chlorine residual, the water quality and the residence time. Figure 5.7 shows that the predicted chlorine residuals are evenly distributed around the line of perfect fit and the results are acceptable for the range of 0 to 5 mg/L as Cl_2.

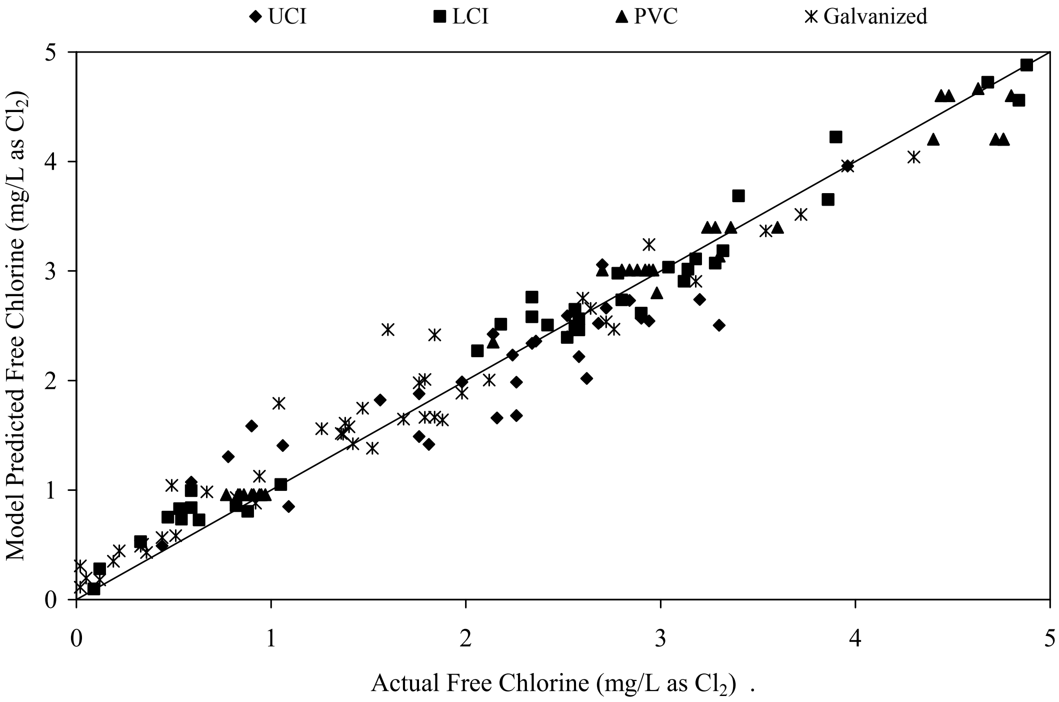


Figure 5.7 Free Chlorine Model Verification

5.4.2 Combined Chlorine

Combined chlorine residual followed the same trend exhibited by free chlorine. Combined chlorine decayed faster in the unlined metallic pipes and was slower in PVC and LCI pipes. Figure 5.8 shows the decay of combined chlorine in the PDS for water with an initial residual of 3.7 to 4.0 mg/L as Cl_2, an UV-254 of 0.044 cm^{-1}, a pH of 8.1 and a temperature of 16^{o}C. The combined chlorine decay in the PVC and LCI pipes was slow and maintained about 90% of the initial concentration after 5 days (120 hours) while UCI pipes lost 80% of the residual in the same amount of time. In the galvanized pipes, the residual went from 4 mg/L to 0.8 mg/L in 34 hours and was completely lost after 50 hours.

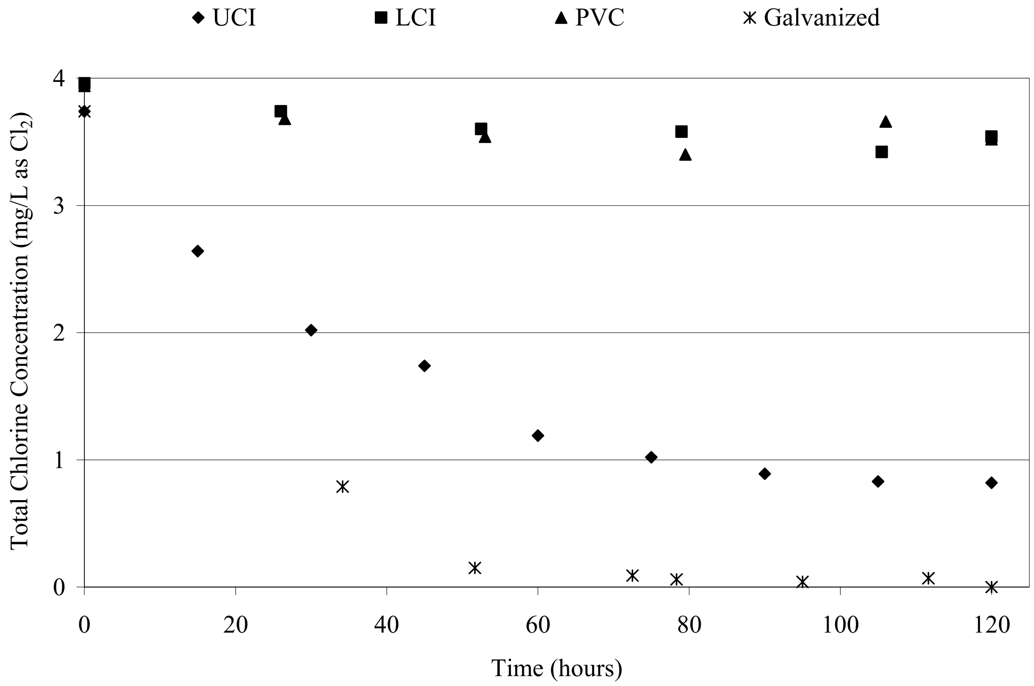


Figure 5.8 Effect of Pipe Material on Combined Chlorine Residual in PDS

The rate of decay of combined chlorine residual increased in the PDS when UV-254 and temperature increased for all pipe materials as shown in Figure 5.9. Figure 5.9 shows the fraction of chlorine residual remaining (Cl_{2-f}/Cl_{2-0}) in the PDS after 5 days for three water quality conditions. The fraction of residual remaining was larger for the water at lower temperature and UV-254 and decreased when either temperature or UV-254 increased. The galvanized pipes completely lost the residual under the conditions presented.

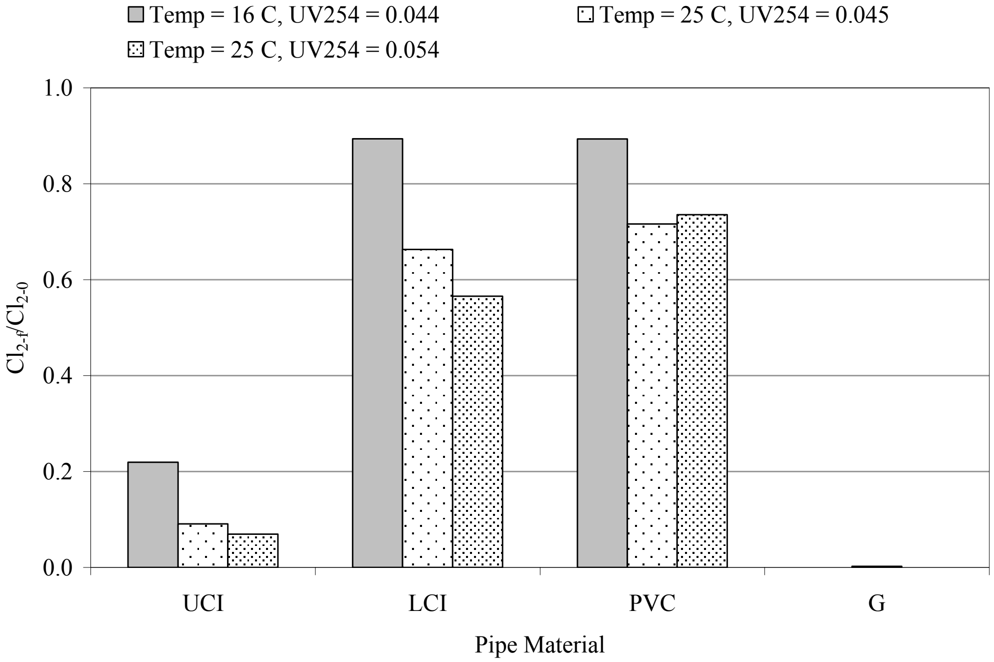


Figure 5.9 Effect of Water Quality Changes on Combined Chlorine Decay

Combined chlorine (monochloramine) decay was found to follow first-order kinetics with respect to chlorine concentration. The general formula of the model is shown in Equation 5.5. As with the free chlorine model, the rate constant was found to be dependent on UV-254, temperature and time. Combined chlorine dissipation increases with increasing UV-254, temperature and time.

$$Cl_{2-t} = Cl_{2-0} * \exp\left(-\left(K_B * UV254 + \frac{K_W}{D} \right) * A^{(T-20)} * time \right) \qquad \textbf{Equation 5.5}$$

Where: K_B = bulk decay constant (cm/hr)
K_W = wall decay constant (inches/hr)
Cl_{2-t} = chlorine concentration at time t (mg/L as Cl_2)
Cl_{2-0} = initial chlorine concentration (mg/L as Cl_2)
A = temperature correction coefficient
T = temperature in degrees Celsius
time = time expressed in hours
D = pipe diameter (inches)

In this model, the rate of chlorine decay is expressed using two constants: one for the bulk liquid reactions, K_B, and another for the pipe wall reactions, K_W. Both kinetic constants were developed by non-linear regression. The model coefficients and R^2 are shown in Table 5.4.

Table 5.4 Combined Chlorine Models Coefficient Values and R^2

Material	Parameter	Value	R^2
PVC	K_B	0.020	0.90
	K_W	0.007	
	A	1.16	
Lined Cast-Iron	K_B	0.017	0.90
	K_W	0.011	
	A	1.16	
Unlined Cast Iron	K_B	0.147	0.87
	K_W	0.084	
	A	1.11	
Galvanized Steel	K_B	0.319	0.87
	K_W	0.073	
	A	1.12	

K_B for PVC and lined-iron are 0.020 and 0.017 cm/h, which indicate that there is little effect of these materials on combined chlorine decay in the bulk liquid. For UCI and galvanized steel pipes the values of K_B are 0.15 and 0.32 cm/h, which is 7 and 9 times and 16 and 19 times larger than the value for PVC and LCI respectively. The difference may be explained by the reactions of chlorine with available corrosion by-products or the presence additional biological activity on the unlined metallic pipes. The corrosion products on unlined cast iron and galvanized pipe provide greater surface area for biological growth that the PVC and lined ductile iron pipes.

K_W is almost identical for PVC and lined-iron pipes, which indicates that both materials react in a similar form with combined chlorine. PVC and lined iron are considered fairly inert materials and have a minimum chlorine demand. UCI and galvanized steel pipes have values of K_W that are 10 and 12 times larger than PVC and LCI this may be explained for the reactivity of chloramines with the ferrous material of the pipe. Previous studies (Vikesland and Valentine 2002) have shown that monochloramine reacts with iron at the pipe wall to form ammonia and chlorides, as presented in Equation 5.6.

$$2Fe(II)_{surf} + NH_2Cl + H^+ \rightarrow 2Fe(III) + NH_3 + Cl^- \qquad \textbf{Equation 5.6}$$

The temperature correction factor obtained for the model range from 1.11 for UCI to 1.16 for PVC and LCI which means that the decay rate will double for every 5 to 7 ^{o}C increment in water temperature. Figure 5.10 shows the predicted effect of the pipe material and temperature on combined chlorine decay. The predictions were calculated for a water with a 1 mg/L of organic content as NPDOC and an initial combined chlorine concentration of 4 mg/L as Cl_2 in pipes with a diameter of 6 inches.

PVC and LCI pipes were predicted to maintain 90% of the initial residual after 5 days at a temperature of 10 ^{o}C, but would lose 75 to 80% of the residual when the temperature increases to 30 ^{o}C. For temperatures above 18 ^{o}C, UCI and galvanized steel pipes will not carry the minimum combined chlorine residual of 0.6 mg/L required by regulations after 5 days.

In the same way than for free chlorine, some of the data was separated, not used for modeling and used to verify the models. Figure 5.11 shows the actual independent combined chlorine residual data versus the prediction using the models based on initial chlorine residual, pipe material, and water temperature and UV-254.

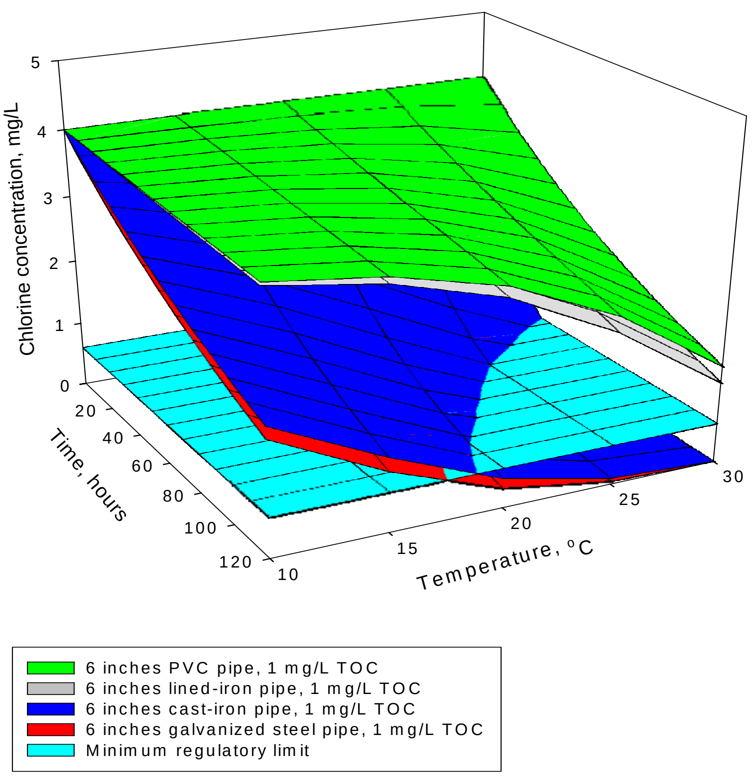


Figure 5.10 Effect of Pipe Material and Temperature on Combined Chlorine Decay

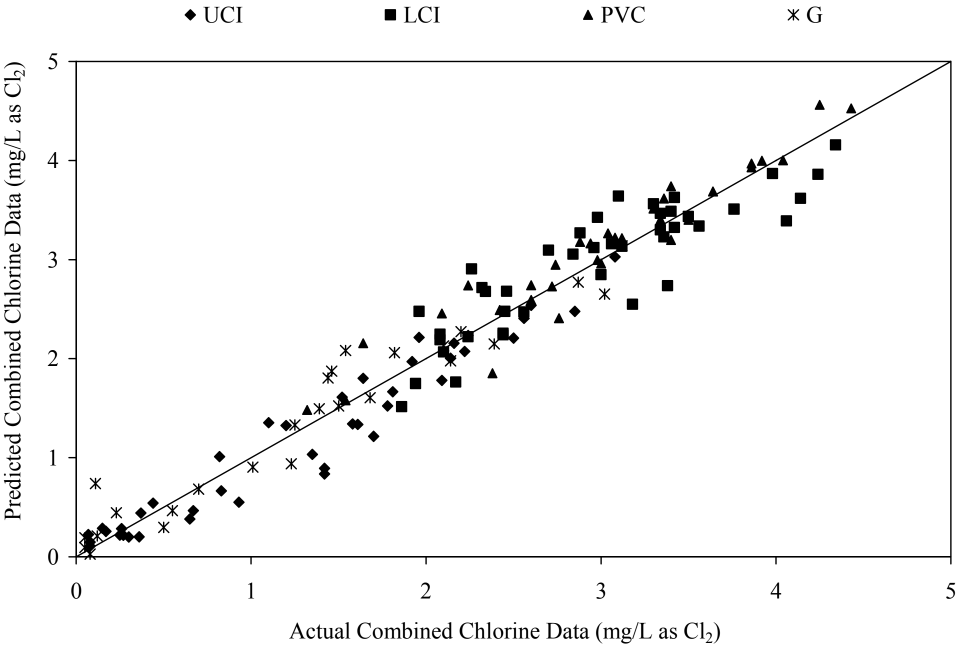


Figure 5.11 Combined Chlorine Models Verification

5.5 Conclusions

Free chlorine and combined chlorine (monochloramines) decay in a pilot distribution system followed first-order kinetics with respect to initial chlorine concentration. The rate of chlorine dissipation was affected by the pipe material, temperature and organic content of the water.

The rate of free and combined chlorine dissipation in a distribution system is highly dependent on the pipe material. Free and combined chlorine decayed faster in iron-based pipes than in inert material pipes such as PVC and lined cast iron. PVC and lined iron pipes have similar low values for the decay constants while cast iron and galvanized steel present greater values due to the reactivity of chlorine with iron based pipes.

The rate of free chlorine dissipation is predicted to double for an increase of temperature between 5 and 17 ^{o}C. The rate of combined chlorine decay would double for an increase of 5 to 7 ^{o}C. Water with low content of organics will maintain the chlorine residual longer than waters with high concentration of NOM in any type of pipe.

Maintenance of combined or free chlorine residuals in unlined metallic pipes for 4 or more days is predicted to be difficult at temperatures above 20 ^{o}C.

5.6 Acknowledgements

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6 MODELING CHLORAMINE DECAY IN DISTRIBUTION SYSTEM IN THE PRESENCE OF CORROSION INHIBITORS

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6.1 Abstract

The rates of chloramine decay in a pilot distribution system (PDS) receiving corrosion inhibitors were evaluated. Phosphate-based inhibitors (blended ortho-poly phosphate, orthophosphate and zinc orthophosphate), silicate based inhibitors and pH control were used in a PDS formed by aged PVC, lined and unlined cast iron and galvanized steel pipes. Fourteen (14) identical PDS lines were used for the study, each inhibitor type was dosed to three PDS at a low, medium and high dose and two additional PDS were maintained at pH_s and pH_s+0.3 for a total of 14 PDSs. The pilot distribution systems were operated for a year at hydraulic retention times of 2 days to mimic dead-end conditions.

The PDS were monitored for chloramine residual, temperature, pH, phosphate, reactive silica, and organic content. An empirical models for the dissipation of chloramine in the pilot drinking water distribution systems was developed as a function of time, pipe material, pipe diameter and water quality. The model to best describe the decay chloramine in the pilot distribution systems was a first-order kinetic model containing separate rate constants for the bulk reactions, pH effect and the pipe wall reactions. The form of the model and the rate constants were obtained by pipe material using non-linear regression. The

rate of decay was dependent on the material and diameter of the pipe as well as the temperature, pH and organic content of the water. The rate of chloramine decay was low for PVC and lined cast-iron pipes, and was greater in the unlined cast iron and galvanized steel pipes. Small diameter pipes and higher temperatures increase the rate of chlorine decay irrespective of pipe material. The use of phosphate-based or silica-based corrosion inhibitors was not found to have an effect on the rate of chloramine dissipation in any of the pipe materials. Only the increase of pH was found to decrease the rate of chloramine decay.

6.2 Introduction

Corrosion of metallic pipes and corrosion products exert a demand on disinfectant residual (Vikesland and Valentine 2002, Frateur et al. 1999), resulting on greater chloramine decay rates been observed in unlined metallic pipes than in PVC and other synthetic pipes (Kiéné, Lu and Lévi 1998, Hallam et al. 2002, Arevalo et al. 2004). Chloramine residual is lost when it reacts with ferrous iron, Fe^{2+}, either at the pipe wall or in solution to form ferric iron, Fe^{3+}, (Vikesland and Valentine 2002) as shown in Equation 6.1. Ferric iron might precipitate back on to the pipe surface or continue through the distribution system to reach the consumer as “red water”.

$$2Fe^{2+} + NH_2Cl + H^+ \rightarrow 2Fe^{3+} + Cl^- + NH_3 \qquad \textbf{Equation 6.1}$$

Corrosion inhibitors are used to control or reduce corrosion in drinking water distribution systems. The most commonly used corrosion control techniques are phosphate and silicate-based inhibitors and pH elevation. Phosphate-based inhibitors create a protective layer on the surface of metallic pipes that protects against corrosion (Benjamin et al. 1990).

Orthophosphates, polyphosphates, blends of poly-ortho as well as zinc orthophosphate have shown to reduce the release of iron and the corrosion rate (Persson, Nilsson, and Sjoberg 1996; Klueh and Robinson 1988; Moriarty 1990; Volk et al. 2000). The silica in sodium silicate inhibitors has a negative charge and monomeric silica $(SiO_3)^{2-}$ has been reported to adsorb at the anodic sites of the electrochemical corrosion cell and form a protective film on the pipe surface preventing corrosion (PQ Bulletin 37-3 2001). pH elevation limits the corrosivity of water based on the Larson index and could promote calcium carbonate precipitation on the pipe surface.

Since corrosion inhibitors reduce iron corrosion it should be expected to reduce the rate of residual decay. LeChevalier et al. (1993) found that high corrosion rates interfered with monochloramine disinfection by preventing the biocide from penetrating the biofilm. LeChevalier, Welch and Smith (1996) found that distribution systems with low percentage of unlined cast iron pipes and that used phosphate-based inhibitors had fewer coliform bacteria. However, the addition of phosphate-based inhibitors could increase biofilm populations since phosphorous is a limiting factor for bacterial growth in some distribution systems. A study found that microbial growth in drinking water in Finland increased with phosphate addition (Miettinen, Vartiainen and Martikainen 1997). Results of a survey of US utilities (McNeill and Edwards 2001) showed that almost 70% of the utilities identified the increase in bacterial growth as a drawback to the use of phosphate inhibitors to control corrosion. Other studies have found no changes on biofilm development due to the use of corrosion inhibitors (Rompré et al. 2000, Batté et al. 2003).

Limited literature is available relating chloramine decay and the use of corrosion inhibitors. Volk et al. (2000) used two annular reactors made of cast iron to compare control water (plant conditions) with the same water dosed with ZOP at 0.7 mg/L as PO_4. The effluent chloramine residual was the same for the test and the control reactors and there was no difference in biofilm density or the bulk HPC. Batté et al. (2003) showed that the addition of phosphate inhibitors to the water doubled the phosphate concentration in the biofilm, but did not affect the biofilm densities or its composition. Butterfield et al. conducted a study in 2002 and found that the use of PO_4 inhibitors reduced free chlorine demand by 10% in the presence of iron corrosion products but had no effect on glass beads coated with iron oxide.

The objective of this study was to determine the effect of corrosion inhibitors on chloramine residual decay in a drinking water distribution system. Orthophosphate, blended ortho-polyphosphate, zinc orthophosphate and silicate inhibitors as well as pH control were used in a pilot distribution system composed of 14 lines operating in parallel. The rates of chloramine decay were calculated for PVC, unlined cast iron, lined cast iron and galvanized steel pipes.

6.3 Methods and Materials

Pipes excavated from actual distribution systems in the Tampa Bay area in Florida and were used to build 14 pilot distribution systems (PDS) shown in Figure 6.1. The PDSs were identical and were composed of 19 ft (5.85 m) of 6-inch PVC pipe followed by 18 feet (5.5 m) of 6-inch lined cast iron (LCI), 12 feet (3.7 m) of 6-inch unlined cast iron (UCI) and 40 feet (12.2 m) of 2-inch galvanized steel pipe.

Figure 6.1 Pilot Distribution Sytem

The PDSs were numbered sequentially PDS 1 to PDS 14, from right to left in Figure 6.1. Standpipes were located at the beginning and end of each PDS as a precautionary measure in case of leaks or pipe failure. The standpipes were approximately 60 inches (1.5 m) long and made from translucent 4-inch (0.1 m) PVC pipe. The flow rate to the PDS was controlled using peristaltic pumps that were set to obtain a 2-day hydraulic retention time (HRT). Sampling ports were located at the influent and effluent of the PDS as well as after each pipe type to monitor water quality changes due to the specific pipe material.

The water fed to the PDS was a blend of conventionally treated groundwater (GW), treated surface water (SW) and water desalinated by reverse osmosis membranes (RO). A description of the treatments that source water were submitted to are shown in Table 6.1.

Table 6.1 PDS Source Waters Description

Symbol	System Description
GW	Ground water source. Treatment by aeration, disinfection by free chlorine with a residual of 4 mg/L after a 5 minute contact time, 4.0 mg/L chloramine residual.
SW	Surface water source. Treatment by ferric sulfate coagulation flocculation settling filtration disinfection by ozonation biologically activated carbon filtration, 4.0 mg/L chloramine residual.
RO	Ground water source. Treatment by membrane reverse osmosis aeration disinfection by free chlorine with a residual of 4 mg/L after a 5 minute contact time, 4.0 mg/L chloramine residual.

The duration of the study was 12 months and was divided in 4 phases of 3 months duration each. The blend that was fed to the PDS was maintained constant for the duration of each phase. However, the blend composition changed from phase to phase, with the exception of Phase III, which was identical to Phase I, to evaluate seasonal effects. Table 6.2 shows the composition of the blend for each phase. The blend was prepared weekly in a single tank and then used to feed all PDS.

Table 6.2 Blend Composition by Phase

Phase	Time Period	% GW	%SW	%RO
I	Feb-May 2006	62	27	11
II	May-Aug 2006	27	62	11
III	Aug-Nov 2006	62	27	11
IV	Nov 2006-Feb 2007	40	40	20

Four different corrosion inhibitors were selected for the study, ortho-phosphate (OP), zinc ortho-phosphate (ZOP), a blend of ortho- and polyphosphates (BOP), and silicate. Each inhibitor was dosed to three PDSs at a low, medium and high dose. The doses selected for the phosphate-based inhibitors were 0.5, 1.0, and 2.0 mg/L as total phosphorus. For the silicate inhibitor the doses were 3, 6, and 12 mg/L as SiO_2. A delivery system was constructed that included a common blend tank for each inhibitor and separate pumps to feed each PDS. Figure 6.2 shows the tanks containing the BOP and OP inhibitors and the pumps (next to the tanks) used to feed them to the PDS. The remaining two PDS were used as control lines and received the blend (PDS 14) and the blend adjusted to pH_s (PDS13).

Figure 6.2 Corrosion Inhibitor Tanks and Feeding System

The nominal length of the PDS was approximately 100 feet and the flow rate was selected to mimic conditions similar to dead end or near dead end locations in distribution systems. The PDS were flushed every two weeks at a flow velocity of 1 ft/s with at least 3 pipe volumes of water. The flushing was designed to avoid excessive accumulation of films inside the PDS. The water used to flush each PDS was the blend with the addition of the corresponding inhibitor at the required dose for the individual PDS. For PDS 13 and 14, the pH of the flush water was adjusted as required.

6.3.1 Water Quality Sampling

Samples were usually taken weekly on the influent and effluent of the PDS and analyzed on-site for free and total chlorine, temperature, turbidity, UV254 (organic content), apparent color, DO, conductivity and pH. Samples from the internal sample ports were taken in 12 sampling events and analyzed for the same parameters. All the samples were taken at least 60 hours after a flushing event to ensure the desired HRT of two days. Analytical procedures used are shown in Table 6.3 and are as stated in the 20th Edition of Standard Methods (APHA, AWWA, and WEF 1999). 1-Liter borosilicate bottles were used to collect all the samples. Each sample bottle was cleaned previously at the UCF main laboratory. In the field, each sample collection bottle was pre-rinsed with distilled water followed for several rinses using the sample to be collected. The sample to be analyzed was collected after these pre-rinses and analyzed immediately in the field laboratory.

Table 6.3 Analytical Procedures and Reporting Limits

Parameter	Method	Method Reference	Approximate Range
Chlorine, free	DPD colorimetric	Hach 8021	0.1 - 2 ppm
Chlorine, total	DPD colorimetric	Hach 8167	0.1 - 2 ppm
UV-254	UV spectrometry	SM 5910 A	0-0.5200 cm^{-1}
Temperature	Direct reading		0 - 100 deg C
Oxygen, Dissolved (DO)	Membrane probe	SM 4500-O G	0.1 - 20 mg/L
Turbidity	Nephelometric	SM 2130 B	0.02 - 200 ntu
Color, apparent	Spectrometer	SM 2120 B	1 - 50 cpu
pH	Electrometric Method	SM 4500-H+ B	0.1 pH units

*All techniques designated with "SM" referenced in Standard Methods are from the 20th Edition (1999).

6.3.2 Quality Assurance and Quality Control

Quality assurance and quality control of all water quality parameters analyzed was established by determining the precision and accuracy of the analyses. At least 10% of the samples were taken as duplicates with at least one duplicate pair being analyzed anytime a sample was collected. Where appropriate standards were available, sample corresponding to at least 10% of the collected samples were spiked with known concentrations of the parameter being analyzed and the recovery measured. Dynamic control charts or Shewart charts, were maintained for each parameter and updated monthly. The control charts were used to determine whether the results were acceptable or corrective measures were needed. Accuracy and precision were maintained at all times within limits defined in the Quality Assurance Plan and approved by the AwwaRF project advisory committee.

6.3.3 Model Development

A model for chloramine decay was developed previously using non-linear regression with data obtained from the same PDSs used during this study (Taylor et al. 2005). The decay of chloramine in a distribution system was found to be best described using a first–order kinetics model with respect to chloramine concentration. The non-linear model showed pipe material, TOC, temperature, pipe geometry and time significantly affected chloramine concentration. The modeling was based in water quality parameters and not on water treatment process so it could be used for waters different from the waters used in the study.

The effect of corrosion control techniques (corrosion inhibitors and pH control) would be quantified and the model developed by Taylor et al. (2005) modified to include such effect. Least square non-linear regression methods were used to modify the empirical models using the SigmaStat 3.5® computer program with the best fit being determined by statistical analysis and visual inspection. The models were verified to the 95% confidence interval using independent data. The data used for model verification was obtained from the same pilot distribution system, however, it was not used during model development.

6.4 Results and Discussion

The PDS were fed blended water from a common tank. In this tank, the chloramine residual was continually monitored and adjusted to maintain a target residual around 5.0 mg/L as Cl_2. The influent and effluent to the PDS were monitored weekly for a year. A one way analysis of variance (ANOVA) was used to verify that the influent residual to all 14 PDSs was the same during the study. The probability value or p-value of the ANOVA test was 0.3, which meant the influent residual for all the PDS was the same. A p-value greater than 0.05 means that there was not a statistically significant difference between the populations being tested.

The results of the ANOVA test are shown in Table 6.4 and shows the total number of samples, the average influent residual and the standard deviation for each of the PDSs. The overall average chloramine residual for all the PDSs was 4.9 mg/L as Cl_2 with the lowest average influent residual being 4.7 mg/L as Cl_2 for PDSs 6, 9 and 13 and the highest average influent residual being 5.1 mg/L as Cl_2 for PDSs 1 and 14.

Table 6.4 Results of ANOVA Test for PDS Influent Residual Concentration

PDS #	# of observations	Average influent NH_2Cl residual (mg/L Cl_2)	Std Dev
1	52	5.1	0.89
2	52	4.9	0.95
3	52	4.8	0.90
4	52	5.0	0.94
5	52	4.9	1.00
6	52	4.7	0.92
7	52	4.9	1.03
8	52	4.8	0.96
9	52	4.7	1.00
10	52	5.0	0.96
11	52	5.0	1.00
12	52	5.0	0.95
13	52	4.7	0.94
14	52	5.1	0.96

6.4.1 Temperature Effect on Chloramine Decay

The rate of decay of chloramine increased as temperature increased. The effect of temperature on chloramine demand in PDS 1 is shown in Figure 6.3. In the cold months of the year, when the average temperature in Florida is around 20 ^{o}C, the chloramine demand was about 2 mg/L as Cl_2. During the hot months of summer, when the average temperature is around 30 ^{o}C, the chloramine demand increased to 3 to 4 mg/L as Cl_2.

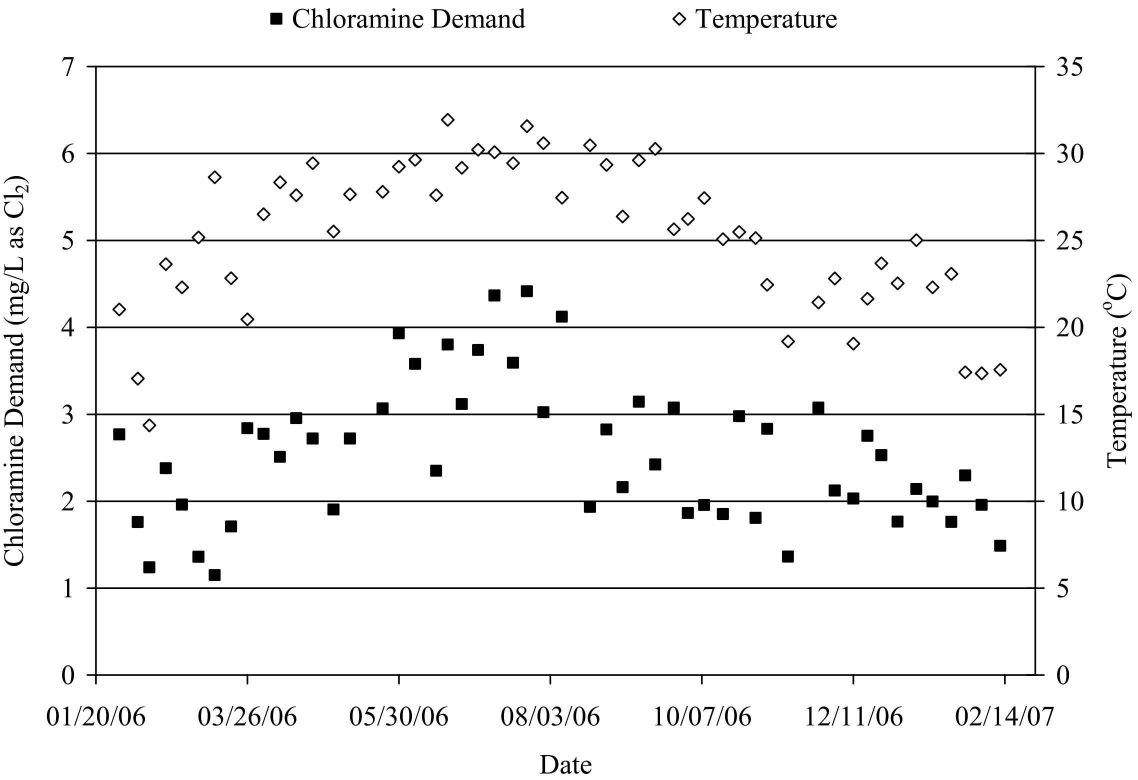

Figure 6.3 Effect of Temperature on Chloramine Demand in PDS 1

The rate of chloramine decay have been shown to increase with temperature (Powell et al. 2000; Kiéne, Lu and Lévi, 1998; Jadas-Hécart et al, 1992). The reaction rate constants can be adjusted for temperature using a relation derived from the Van’t Hoff – Arrhenius equation shown in Equation 6.2. The Arrhenius equation can be manipulated to obtain an expression that allows for calculation of the rate constants at operation temperature, K_{Temp} from a base rate constant defined at a specific temperature, usually 20 ^{o}C (Equation 6.3). An Arrhenius type temperature correction factor was calculated in combination with other parameters by non-linear regression and is discussed later in this section.

$$K_T = A \times \exp^{\left(-\frac{E_a}{RT_a}\right)} \qquad \textbf{Equation 6.2}$$

$$K_T = K_{20} \times \theta^{(T-20)} \qquad \textbf{Equation 6.3}$$

where A = constant
K_{Temp} = dissipation constant at temperature T
K_{20} = dissipation constant at 20 ^{o}C
E_a = activation energy
R = ideal gas constant
T_a = absolute temperature (^{o}K or ^{o}R)
T = temperature (^{o}C)
θ = temperature correction factor

6.4.2 Effect of pH on Chloramine Decay

As mentioned previously, PDS 13 and PDS 14 were used as control lines. The pH of PDS 14 influent was routinely 0.3 pH units higher than the saturation pH (pH_s) for the respective water quality. The water quality of PDS 13 was similar identical to PDS 14 except for pH, which was adjusted to the pH_s. The pH was adjusted using hydrochloric acid (HCl). The pH of the water in the PDSs receiving phosphate-based inhibitors and low concentrations of silica based inhibitors were the same than the pH for PDS 14. The pH of PDS 11 and PDS 12, which received water with silicate inhibitor at doses of 6 and 12 mg/L as SiO_2 were higher than the pH of all other PDSs. The pH of PDS 11, PDS 12, PDS 13 and PDS 14 were 8.2, 8.3, 7.9 and 7.7 respectively.

The chloramine demand for PDS 11, PDS 12, PDS 13 and PDS 14 was calculated for each sampling event and a paired t-test was conducted to determine if there was a difference in demand between the PDSs. The result of the paired t-tests is shown in Table 6.5, p-values lower than 0.05 mean that there is a significant difference between the means. It can be seen in Table 6.5 that PDS 13 had the highest average chloramine demand at 2.9 mg/L as Cl_2, followed by PDS 14 with a demand of 2.6 mg/L as Cl_2, and PDS 12 had the lowest chloramine demand at 2.3 mg/L as Cl_2. The average chloramine demand for PDS 11, PDS 12, PDS 13 and PDS 14 were statistically significant, with the exception of the test between PDS 11 and PDS 14 which showed the difference was not statistically significant. These results indicate that chloramine demand decreases when pH increases.

Table 6.5 Paired t-test for Chloramine Demand in PDS 11 to PDS 14

PDS #	# Obs.	pH	Mean NH_2Cl demand (mg/L Cl_2)	p-value	Significant?
13	52	7.7	2.93	-	
14	52	7.9	2.64	PDS 13 vs 14 = 0.03	Yes
11	52	8.2	2.48	PDS 13 vs 11 = 0.00	Yes
				PDS 14 vs 11 = 0.12	No
12	52	8.3	2.33	PDS 13 vs 12 = 0.00	Yes
				PDS 14 vs 12 = 0.01	Yes

6.4.3 Effect of Pipe Material on Chloramine Decay

Samples were taken on 12 different sampling events from the internal ports of the PDS to assess the effect that each individual pipe material have on chloramine decay. The 12 sampling events were spaced during a 6-month period (9/2006 to 2/2007). The chloramine residual decayed in the pilot distribution system at different rates depending on pipe material. PVC and lined cast iron (LCI) showed lower rates of chloramine decay while chloramine concentration declined more rapidly in the unlined cast iron (UCI) and galvanized steel (G) pipes. An overall first-order rate of chloramine decay (K) was calculated for each PDS and each of the pipe materials within a PDS. Figure 6.4, Figure 6.5, Figure 6.6, and Figure 6.7 show the average K for PVC, LCI, UCI and G pipes by inhibitor type and dose. Error lines are also included for each PDS showing the maximum and minimum K observed.

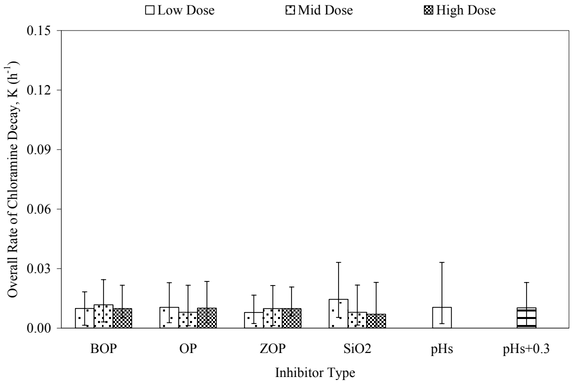

Figure 6.4 Average Overall Rate of Chloramine Decay in PVC Pipes

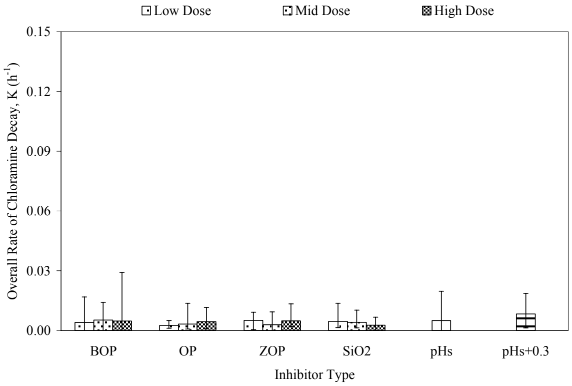

Figure 6.5 Average Overall Rate of Chloramine Decay in LCI Pipes

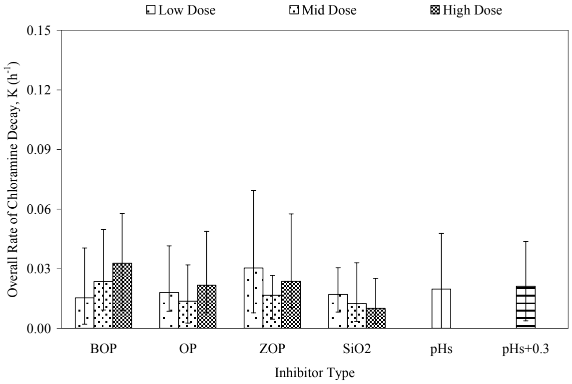

Figure 6.6 Average Overall Rate of Chloramine Decay in UCI Pipes

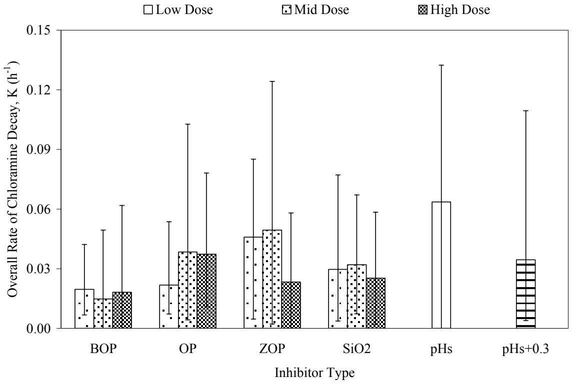

Figure 6.7 Average Overall Rate of Chloramine Decay in G Pipes

The chloramine decay rate in the PVC pipes ranged from 0.007 h^{-1} and 0.015 h^{-1} as shown in Figure 6.4. There is not much difference between the control lines, between the inhibitors and the control lines or within the inhibitors by type or dose. Figure 6.5 shows the rate of chloramine decay in the LCI pipes to be between 0.003 h^{-1} and 0.008 h^{-1}. Similar to the PVC pipes, there seems to be little variations between the PDSs by inhibitor type or dose.

Figure 6.6 shows the rates of decay in the UCI pipes, which range from 0.010 h^{-1} for PDS 12 to 0.033 h^{-1} for PDS 3. However, most of the PDS showed K that were around 0.020 h^{-1}, which was also K for the control lines. The rate of decay in the UCI pipes were approximately twice the K for PVC pipes and 3 to 6 times the K for LCI pipes. For G pipes, K ranges from 0.015 h^{-1} to 0.064 h^{-1} with 10 of the 14 PDS in the range of 0.02 h^{-1} to 0.04 h^{-1} (Figure 6.7). The values of K for G pipes were slightly greater than K for UCI pipes and 4 to 10 times greater than K for PVC and LCI pipes.

6.4.4 Effects of Corrosion Inhibitors on Chloramine Decay

The average chloramine demand for each PDS for the entire year of duration of the study is shown in Figure 6.8. Chloramine concentrations were measured daily in the feed tanks, and samples were taken weekly from the PDS influent and effluent. The samples were collected simultaneously for all 14 PDSs, so that the effects of temperature on chloramine dissipation are considered.

Figure 6.8 shows that PDS 14 (pH_s+0.3) had a lower chloramine demand (2.6 mg/L) than PDS 13 (pH_s) (2.9 mg/L) and that there is no readily apparent difference in chloramine demand between PDS 14 and the PDSs using inhibitors. The average chloramine demand for the twelve inhibitor PDSs had a range from 2.3 to 3.2 mg/L as Cl_2. However, for nine of the twelve PDSs, the range of chloramine loss varied only from 2.5 to 2.7 mg/L as Cl_2. The broader range of chlorine demand is due to the demand observed in PDS 7 (3.2 mg/L as Cl_2), PDS 10 (2.8 mg/L as Cl_2), PDS 12 (2.3 mg/L as Cl_2), and PDS 13 (2.9 mg/L as Cl_2). The chloramine demand for the PDSs receiving BOP and OP inhibitors appears to be equal and possibly increases with inhibitor dose. Likewise, the chloramine demand for the PDSs receiving ZOP and Si inhibitors appears to be practically equal, but decreases with inhibitor dose. In general, the data shown in Figure 6.8 do not provide any obvious relationship between inhibitor use and chloramine demand in the PDSs.

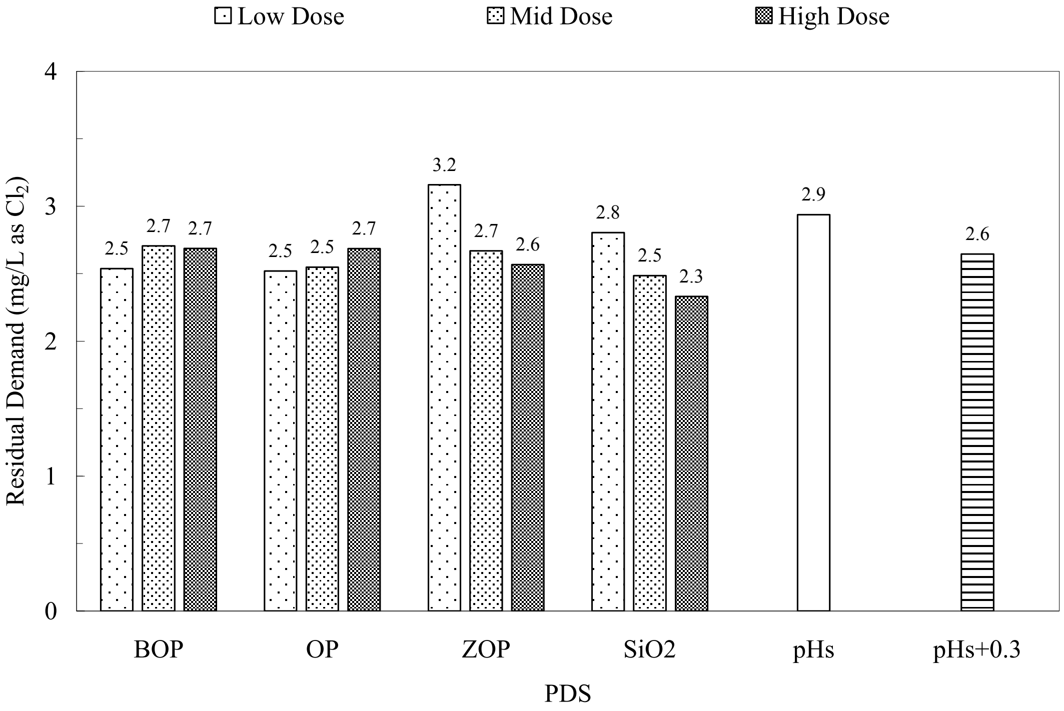

Figure 6.8 Average Chloramine Residual Demand by PDS

To determine if the differences observed in chloramine residual demand were significant, paired t-test for means were conducted between PDS 13 and 14 (the control lines) and the rest of PDS. The results of the t-tests are shown in Table 6.6. PDS with a p-value below 0.05, which corresponds to a 95% confidence level of certainty, were considered as being significantly different than the control PDS.

The comparison of PDS 13 to the rest of the PDSs shows the chloramine demand in PDS 13 was significantly lower than the chloramine demand for PDS 7 and significantly greater than all other PDSs. The comparison to PDS 14 to the rest of the PDSs shows that the chloramine demand was not significantly different for PDS 14 and PDS 1, 2, 3, 4, 5, 6, 8, 9, 10, 11 and 13. The chloramine demand in PDS 14 was greater than PDS 12 demand and lower than PDS 7 demand. As did the global view, this indicates that there was no apparent relationship between inhibitor type or dose and effluent chlorine residual in any of the PDS.

Table 6.6 Results of Paired t-test for Chloramine Demand Between PDS 1 to 12 and PDS 13 and 14

PDS #	Average NH_2Cl Demand (mg/L Cl_2)	Standard Deviation	Comparison to PDS 13		Comparison to PDS 14	
			p-value	Significantly Different?	p-value	Significantly Different?
1	2.54	0.8	0.00	Yes	0.26	No
2	2.71	1.2	0.02	Yes	0.60	No
3	2.69	1.0	0.02	Yes	0.67	No
4	2.52	1.0	0.00	Yes	0.25	No
5	2.55	1.2	0.00	Yes	0.43	No
6	2.69	1.1	0.04	Yes	0.67	No
7	3.16	1.2	0.03	Yes	0.00	Yes
8	2.67	1.1	0.02	Yes	0.80	No
9	2.57	1.2	0.00	Yes	0.48	No
10	2.80	1.0	0.16	Yes	0.07	No
11	2.48	1.1	0.00	Yes	0.12	No
12	2.33	1.1	0.00	Yes	0.01	Yes
13	2.94	1.3	N/A	N/A	0.03	Yes
14	2.65	0.7	0.03	Yes	N/A	N/A

As mentioned before, the pH of the water could explain the differences on chloramine demand between PDS 11, PDS 12, PDS 13 and PDS 14. PDS 12 showed the highest average pH of all the PDS at 8.3 followed by PDS 11 at 8.2, PDS 13 had the lowest at 7.7 while PDS 14 had a pH 7.9 which was similar to all the other PDS. Literature indicates that chloramines are more stable at higher pH (Valentine and Jafvert 1988; Vikesland, Ozekin, and Valentine 2001; Duirk et al. 2002).

6.4.5 Empirical Model for Chloramine Decay

An empirical model to predict the decay of chloramines in the PDSs was developed using the data obtained during this study. Based on previous research (Arevalo et al. 2004), a first-order kinetic approach with respect to initial chloramine residual was used. The general form of the initial model is shown in Equation 6.4. The model includes a constant for decay due to reactions in the bulk liquid (K_B), a constant for wall decay for each pipe material (W) and decay terms to account for effects of corrosion control strategies (pH control, phosphate and silicate corrosion inhibitor) and inhibitor dose. Dummy variables (DV) were used to separate the data by pipe material and corrosion inhibitor measures.

The dummy variables are coefficients that take values of either ones and zeros to indicate the presence or absence of the respective parameter. This allows the model to be adjusted to achieve sensitivity to a specific pipe material and a specific corrosion inhibitor for a constant set of water quality parameters. The dummy variables DV_{PVC}, DV_{LCI}, DV_{UCI} and DV_G are ones when the data corresponds to the respective pipe material and zeros when the data corresponds to any of the other pipe materials. DV_{TP}, DV_{SiO2} and DV_H are the dummy variables for phosphate inhibitors (PDS 1 to PDS 9), silicate inhibitor (PDS 10 to PDS 12) and pH control (PDS 13 and PDS 14) respectively. The use of the variables TP, SiO_2 and H allows the user to determine the effect of the dose of the inhibitors or the pH change.

$$Cl_{2(t)} = Cl_{2(0)} * \exp\left[\left(\begin{array}{l} K_B * UV + K_H * H * DV_H + K_{TP} * TP * DV_{TP} \\ + K_{SiO_2} * SiO_2 * DV_{SiO_2} + \dfrac{W_{PVC} * DV_{PVC}}{D_{PVC}} \\ + \dfrac{W_{LCI} * DV_{LCI}}{D_{LCI}} + \dfrac{W_{UCI} * DV_{UCI}}{D_{UCI}} + \dfrac{W_G * DV_G}{D_G} \end{array}\right) * \theta^{(T-20)} * time\right]$$

Equation 6.4

where $Cl_{2(t)}$ = chlorine concentration at time t (mg/L as Cl_2)
$Cl_{2(0)}$ = initial chlorine concentration (mg/L as Cl_2)
K_B = bulk decay constant (cm/hr)
K_H = coefficient for H^+ term
K_{TP} = coefficient for total phosphorus parameter
K_{SiO2} = coefficient for silica parameter
W_{PVC} = wall decay constant for PVC pipe (in/hr)
W_{LCI} = wall decay constant for LCI pipe (in/hr)
W_{UCI} = wall decay constant for UCI pipe (in/hr)
W_G = wall decay constant for G pipe (in/hr)
UV = UV254 (cm^{-1})
H = molar concentration of H^+ (mol/L)
TP = total phosphorus (mg/L as P)
SiO_2 = Silica (mg/L as SiO_2)
DV_i = dummy variable for parameter i (H^+, TP, SiO_2, PVC, LCI, UCI and G)
D_i = pipe diameter of pipe material i (inches)
θ = temperature correction coefficient
T = temperature in degrees C
time = time expressed in hours

The wall decay rates are specific for each pipe material while the bulk decay constant, $K_{B,}$ was taken as an intrinsic property of the water and is assumed to be the same for all pipe materials. Any additional demand resulting from contaminants entering the bulk from the pipe wall is included in the pipe wall decay rate constant. K_B was set at 0.02 cm/hour based on the K_B obtained for the PVC and LCI pipes in previous study (Arevalo et al. 2004). K_B for these materials was used since PVC and LCI walls have little demand and were located upstream of the unlined metallic pipes. W for each of the pipe materials was calculated for by least-square non-linear regression using the dummy variables to separate the data. A temperature correction coefficient, θ, derived from the Arrhenius equation, was used to incorporate the effect of temperature. The value of θ was also obtained using non-linear regression.

The decay constants used to incorporate the effect of phosphate and silicate inhibitors were found to be statistically insignificant, with p-values of 0.85 and 0.4 respectively, and were eliminated from the model. After running the model again, all the terms were significant at the 95% confidence level as indicated by the p-values being lower than 0.05. The R^2 obtained for the model was 0.75. The final model is shown in Equation 6.5 and the parameter values are listed in Table 6.7.

$$Cl_{2(t)} = Cl_{2(0)} * \exp\left[\left(\begin{array}{l} K_B * UV + K_H * H * DV_H + \dfrac{W_{PVC} * DV_{PVC}}{D_{PVC}} \\ + \dfrac{W_{LCI} * DV_{LCI}}{D_{LCI}} + \dfrac{W_{UCI} * DV_{UCI}}{D_{UCI}} + \dfrac{W_G * DV_G}{D_G} \end{array}\right) * \theta^{(T-20)} * time\right] \qquad \textbf{Equation 6.5}$$

where $Cl_{2(t)}$ = chlorine concentration at time t (mg/L as Cl_2)
$Cl_{2(0)}$ = initial chlorine concentration (mg/L as Cl_2)
K_B = bulk decay constant (cm/hr)
K_H = coefficient for H^+ term
W_{PVC} = wall decay constant for PVC pipe (in/hr)
W_{LCI} = wall decay constant for LCI pipe (in/hr)
W_{UCI} = wall decay constant for UCI pipe (in/hr)
W_G = wall decay constant for G pipe (in/hr)
UV = UV254 (cm^{-1})
H = molar concentration of H^+ (mol/L)
DV_i = dummy variable for parameter i (H^+, PVC, LCI, UCI and G)
D_i = pipe diameter of pipe material i (inches)
θ = temperature correction coefficient
T = temperature in degrees C
time = time expressed in hours

Table 6.7 Parameter Values for Chloramine Decay Model

Parameter	Value	p-value
θ	1.11	<0.0001
W_{PVC}	-0.025	<0.0001
W_{LCI}	-0.014	<0.0001
W_{UCI}	-0.103	<0.0001
W_G	-0.051	<0.0001
K_H	-106403.7	0.022

The model shows that chloramine decay is dependent on the initial chloramine concentration, the organic content of the water, the pipe material and diameter, water temperature and time.

Plots of predicted versus actual chloramine residual for the data used to develop the model are presented in Figure 6.9 to Figure 6.12 for PVC, LCI, UCI and galvanized steel, respectively. Each of these figures show an acceptable prediction of chloramine residual as shown by the fit of the data to the "ideal" 45^{o} trend line.

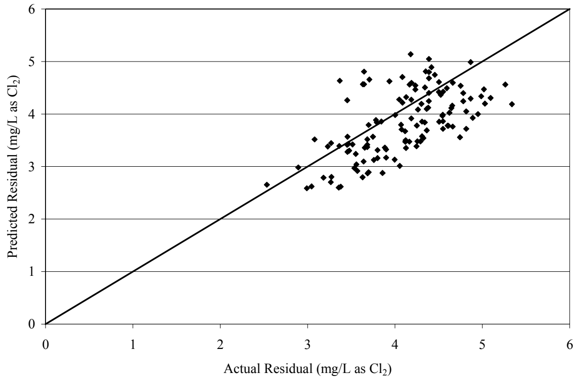

Figure 6.9 Predicted Versus Actual Chloramine Residual for PVC Pipes

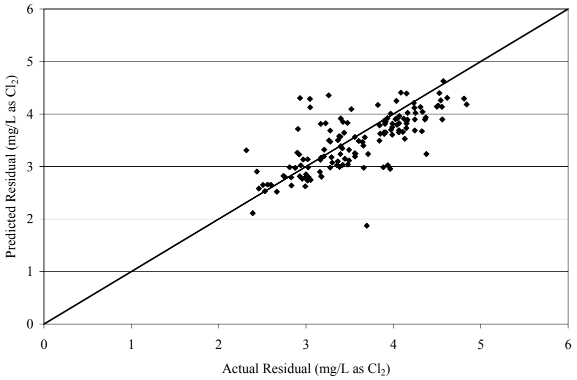

Figure 6.10 Predicted Versus Actual Chloramine Residual for LCI Pipes

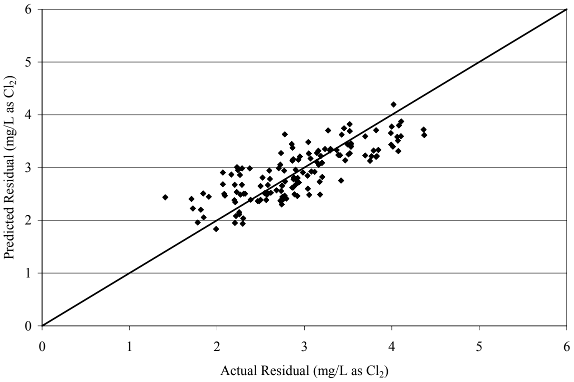

Figure 6.11 Predicted Versus Actual Chloramine Residual for UCI Pipes

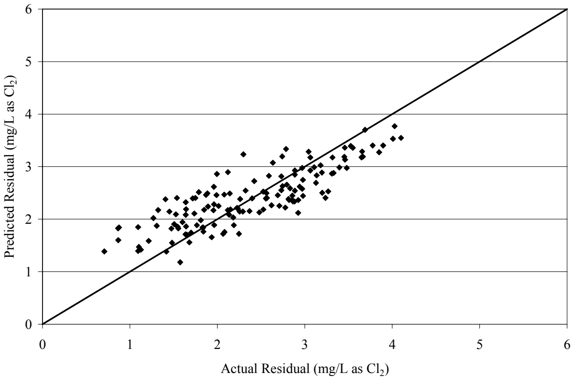

Figure 6.12 Predicted Versus Actual Chloramine Residual for G Pipes

Galvanized steel pipes have a W that is roughly two and three times greater than W for PVC and LCI. The wall decay rate of the UCI pipe is greater than the wall decay rates for any pipe material used in this work. The W for UCI pipes is 0.103 in/h and is 4 and 7 times greater than W for the PVC and LCI pipes and twice the W for G pipes. The higher wall demand of the LCI and G pipe surfaces might be due to the greater chemical reactivity of iron and zinc as well as higher surface roughness, corrosion and higher biofilm densities relative to LCI and PVC pipes. The decay of chloramine in UCI and G pipes is mainly due to wall decay since the effect of W is much greater than the effect of K_B and K_H, however, for PVC and LCI pipes the effect of wall effects, organics and pH are all important.

Figure 6.13 shows the predicted effect, over time, of pipe material on water with a organic content of 3 mg/L as C, a temperature of 25°C, a pH of 8.0 and an initial chloramine residual of 4 mg/L as Cl_2 running through 6-inch diameter PVC, LCI, UCI and G pipes. The water is predicted to maintain a chloramine residual of about 1.0 to 1.5 mg/L as Cl_2 after five days in the PVC and LCI pipes respectively. Within the UCI pipe, the residual drops to 0.3 mg/L as Cl_2 after 80 hours and is completely depleted after 120 hours. The G pipe is predicted to maintain a residual of 0.4 mg/L as Cl_2 after 120 hours.

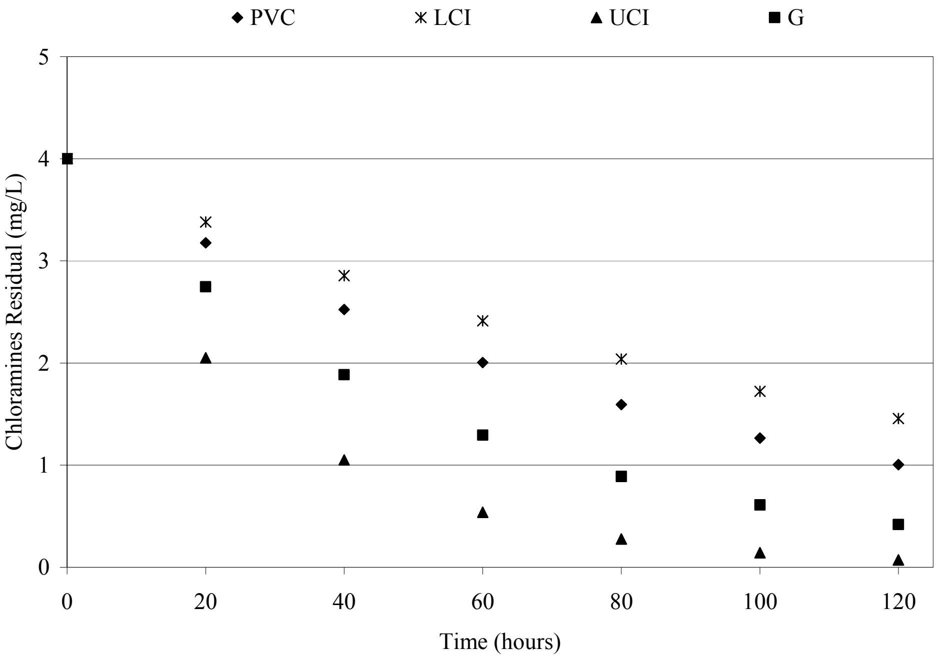

Figure 6.13 Predicted Effect of Pipe Material on Chloramine Residual Decay

For all pipe materials, the effect of the pipe wall is dependent on the pipe diameter. It increases when the pipe diameter is small and decreases for larger diameter pipes. Figure 6.14 shows the effect of the pipe diameter on chloramine decay for LCI and UCI pipes with diameters of 6, 24 and 48 inches. The predictions were calculated for water at 25°C, an organic content of 3 mg/L, a pH of 8.0 and an initial chloramine residual of 4 mg/L as Cl_2.

Figure 6.14 shows a predicted chloramine residual of 1.5, 2.1 and 2.2 mg/L as Cl_2 for LCI pipes with diameters of 6, 24 and 48 inches respectively after 120 hours (5 days). For the unlined cast iron (UCI) pipe, the predicted chloramine residuals after 120 hours are 0.1, 1.0 and 1.5 mg/L as Cl_2 for pipes with diameters of 6, 24 and 48 inches respectively.

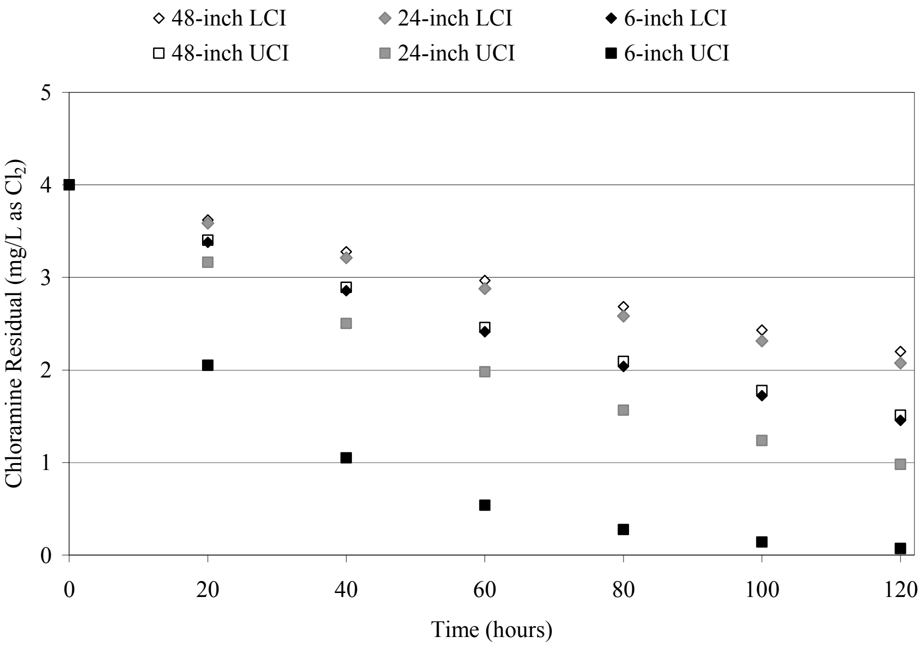

Figure 6.14 Predicted Effect of Pipe Diameter on Chloramine Decay

Even though the pipe diameter effect affects all the types of pipe, the pipe materials with the highest W show the largest improvements with the increase of pipe diameter. When the UCI pipe diameter is increased from 6 to 48 inches, the chloramine residuals are predicted to increase from 0.1 to 1.5 mg/L as Cl_2 while for LCI, it goes from 1.5 to 2.2 mg/L as Cl_2. In pipes with diameters less than 1 foot, the wall effect becomes more significant since the wetted surface area to volume ratio is more elevated. When the diameter of the pipes is big enough, the wall effect diminishes and the effluent residual would be similar regardless of the type of pipe used.

The value of the temperature correction factor, θ, was determined by regression and was 1.11, which means that the decay constants will double for an increase of temperature of 7 ^{o}C. Figure 6.15 shows the effect of temperature on water with an organic content of 3 mg/L, a pH of 8.0 and an initial chloramine residual of 4 mg/L as Cl_2 running through 6-inch LCI and UCI pipes. In the LCI pipe, when the temperature increases from 10 ^{o}C to 25 ^{o}C the chloramine residual is predicted to decrease from 3.2 mg/L as Cl_2 to 1.7 mg/L as Cl_2 after 120 hours. Similarly, in the UCI pipe, the effluent chloramine residual is predicted to go from 1.5 mg/L as Cl_2 at 10 ^oC to 0.1 mg/L as Cl_2 for a water temperature of 25 ^oC.

Predictions of chloramine residual decay for pH values of 7.6, 7.9 and 8.2 are shown in Figure 6.16. The predictions were done for 6-inch PVC and UCI pipes for water with an influent chloramine residual of 5 mg/L as Cl_2, temperature of 25^oC, and UV254 of 0.08 cm^{-1}. Figure 6.16 shows that in PVC pipes, the chloramine residual would increase from 0.9 to 1.2 and 1.4 mg/L as Cl_2 when the pH increases from 7.6 to 7.9 and 8.2, respectively. For UCI pipes, however, the increase on pH would not have an appreciable effect since the wall effect is dominant making the influence of pH change to be negligible. It is necessary to warn the reader not to use the model outside the range of pH used to develop the model (7.6 to 8.3).

As mentioned before, no effect of inhibitor type or dose was found and the parameters for phosphate and silicate dropped from the model. Several other variations of the model were tested which included the effect of inhibitor type and dose. In all the regressions, the terms used for inhibitor effect had to be discarded because the constants obtained were not significant. This result is not surprising based on the chloramine demand information and overall rate of decay supplied in previous sub-sections.

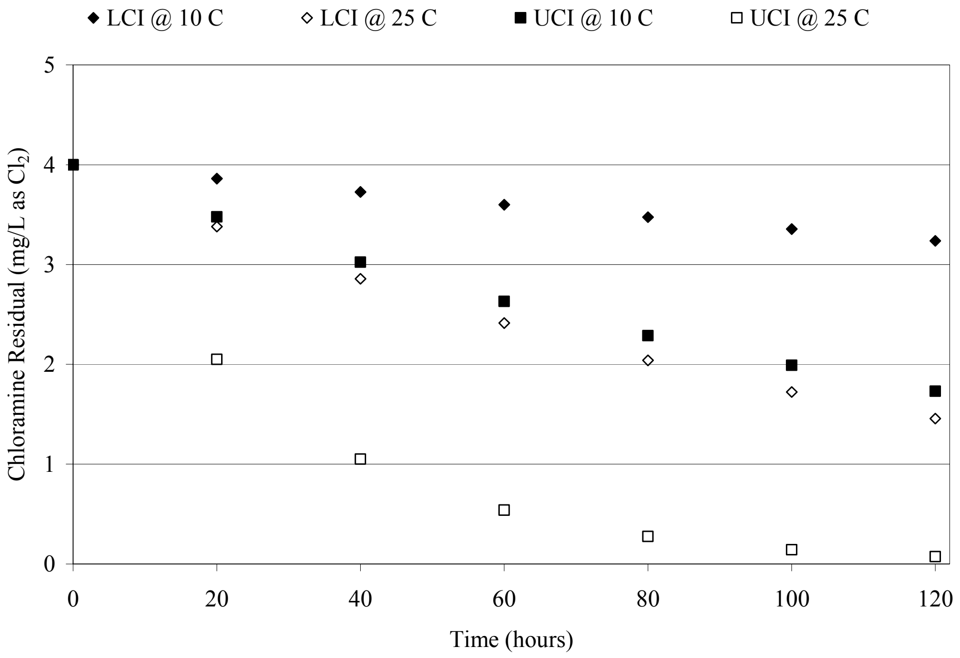

Figure 6.15 Predicted Effect of Temperature on Chloramine Residual Decay

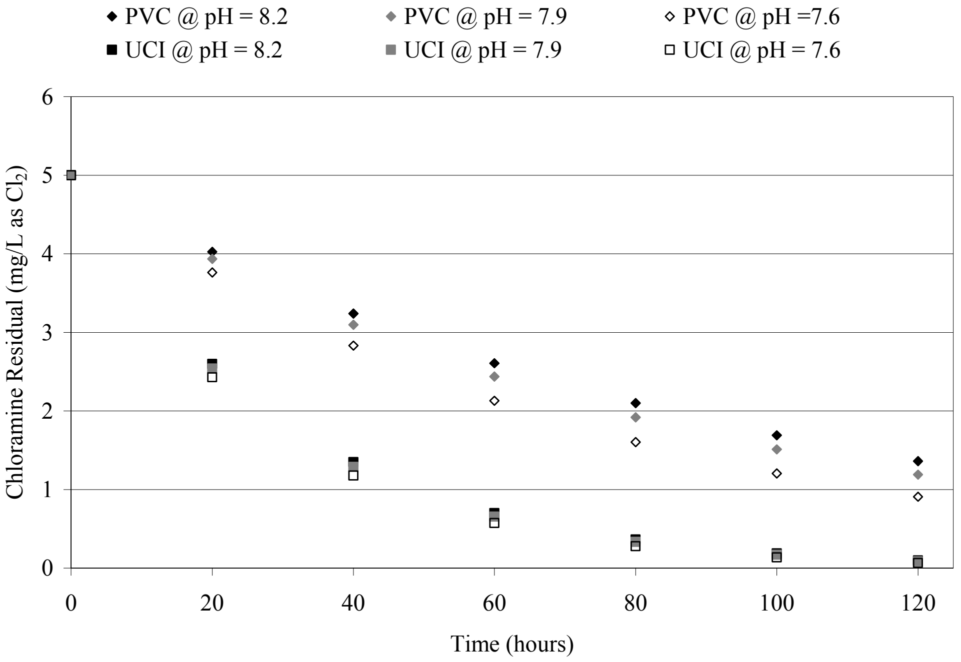

Figure 6.16 Predicted Effect of pH on Chloramine Residual Decay

6.4.6 Model Verification

The chloramine residual decay model was verified using data obtained from the distribution system that was not used for model development. Figure 6.17 shows actual chloramine concentration compared to the predicted concentration using the model. The data used for verification was collected from the influent and the effluent of the pilot distribution system. Since the PDSs had sections of PVC, LCI, UCI and G, the model was used incrementally for the corresponding pipe material. The influent chloramine residual to the PDS was used as the starting point and the coefficients and HRT for the PVC sections was used to predict the residual of the water entering the LCI section of the PDS. The same approach was used for the LCI, UCI and galvanized pipes using the residence time of the water in each section of pipe.

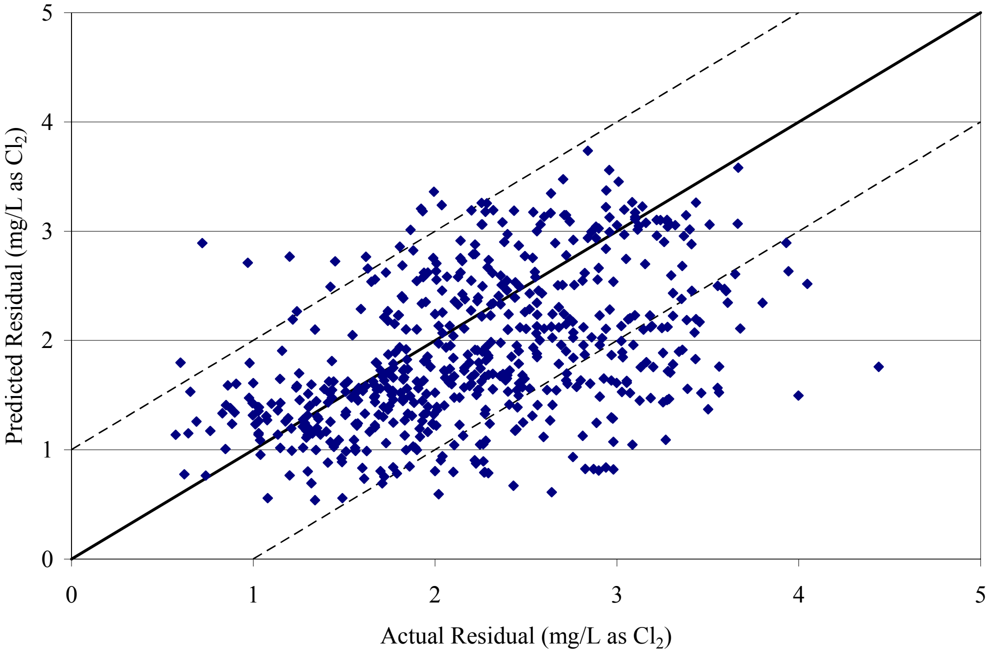

Figure 6.17 Verification of Chloramine Residual Model Using Independent Data

The average of the absolute error between the actual and the predicted effluent chloramine residual was 0.6 mg/L as Cl_2. The black solid line represents the line of perfect agreement between actual and predicted values and the dotted lines are located plus and minus 1 mg/L as Cl_2 from that line.

6.5 Conclusions

The use of phosphate or silicate based corrosion inhibitors did not have an effect on chloramine residual decay in the pilot distribution system as the chloramine demand in the PDS did not change by inhibitor type or dose. Only the pH control had an effect on chloramine residual decay with the rate of decay decreasing with the increase of pH of the water.

Chloramine decayed at different rate depending on the material of the pipe. PVC and lined cast iron (LCI) pipes showed a rate of chloramine decay lower than unlined cast iron (UCI) and galvanized steel (G) pipes. The order of the decay rate was LCI<PVC<<G<UCI. Chloramine was observed to decline faster during the summer months than in winter.

A first-order model for chloramine dissipation was developed, using non-linear regression, as a function of pipe material, pipe geometry, initial chlorine dose, water quality (temperature, pH and UV254) and time. The model contains a bulk decay rate constant (K_B), a pH effect constant (K_H), a wall decay rate constant (W) and a temperature correction factor (θ). The model uses a common K_B, θ and K_H for all types of pipe as well as an individual W for each pipe material.

LCI and PVC pipes had W of 0.014 and 0.025 cm/h. UCI and G have W that are four and nine times greater than W for LCI. The decay of chloramine in UCI and G pipes is mainly due to wall decay since the effect of W is much greater than the effect of K_B and K_H, however, for PVC and LCI pipes the effect of wall reactions, organics and pH are all important.

The diameter of the pipe affects the rate of chloramine decay because the effect of W is proportional to the wetted surface area to volume ratio. The relative effect of W decreases when the pipe diameter increases. This effect is more noticeable for unlined metallic pipes since their W is more elevated.

The rate of chloramine decay was found to increase with the increase of temperature. The temperature correction factor, θ, was 1.11, which means the rate of decay would double for each 7 ^{o}C increment of the water temperature. The pH of the water was the only corrosion control measure to have an effect on the rate of chloramine decay in the PDSs. The decay of chloramine residual was found to be slower when the pH of the water increased. The effect of pH is more noticeable in LCI and PVC pipes but almost negligible in UCI and G pipes. The model for chloramine was adequate to predict chloramine residual in the pilot distribution system at the 95% confidence level and was verified using independent data that was not used to develop the models.

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7 DETERMINATION OF CHLORAMINE DECAY RATES UNDER DIFFERENT FLOW VELOCITIES IN A PILOT DISTRIBUTION SYSTEM

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7.1 Abstract

Experiments were conducted to evaluate the effect of flow velocity on chloramine decay in a pilot distribution system (PDS) for different pipe materials and water qualities. The pipes used to build the PDS were 20-40 years old and taken from actual distribution systems. The pipes used were PVC, unlined cast-iron (UCI), and lined cast-iron pipes (LCI) with a diameter of 6 inches and galvanized steel pipes (G) with a diameter of 2 inches. The waters used were conventionally treated groundwater (GW) from the Floridian aquifer and reverse osmosis desalinated water (RO). A set of experiments also included the addition of blended orthophosphate corrosion inhibitor (BOP) at a dose of 1.0 mg/L as P to evaluate the effect of the inhibitor on chloramine decay.

The flow velocity of the water was varied to obtain Reynolds' numbers from 50 to 8000. Water quality parameters, such as free and total chlorine, free ammonia, temperature, UV254, dissolved oxygen, apparent color, turbidity, nitrites, and pH, were monitored at different points within the PDS. The effect of Reynolds' number on the overall chloramine

decay rate (K) and the wall decay rate constant (W) was assessed for PVC, LCI, UCI, and G pipes.

PVC and LCI showed no change on the rate of chloramine decay at any flow velocity. UCI and G pipes showed a rapid increase on the wall decay rate constant (W) under laminar conditions (Re < 500) followed by a more gradual increase under fully turbulent flow conditions (Re > 2000). The use of the BOP inhibitor did not have an effect on the rate of chloramine decay for any of the pipe materials studied. Linear correlations between Reynolds' number and W were developed to adjust the rate of chloramine decay at the pipe wall for UCI and G depending on the flow conditions.

7.2 Introduction

Chloramine residual decays in distribution systems due to reactions in the bulk and the pipe wall (Biswas, Lu and Clark 1993; Rossman, Clark and Grayman 1994). In the bulk, chloramine is consumed by autodecomposition and reactions with NOM or natural organic matter (Duirk et al. 2002), and also due to reactions with iron (Vikesland and Valentine 2000, Frateur et al. 1999), bromides and nitrites (Vikesland, Ozekin and Valentine 2001), phosphates and sulfates (Valentine and Jafvert 1988). At the pipe wall, chloramines decay due to reactions with the pipe surface, corrosion products, deposits, and biofilms (Vikesland and Valentine 2000, Vikesland and Valentine 2002a, Gauthier et al. 1999). Lined and synthetic material pipes have been shown to have low chloramine demand compared to unlined metallic pipes (Kiéné et al. 1998, Hallam et al. 2002) partly because unlined pipes are more reactive with chloramines, have higher biofilm densities, and accumulate more deposits due to the presence of tubercles (Frateur et al. 1999, Vikesland and Valentine 2002b, Hallam et al. 2001).

Disinfection loss due to reactions at the pipe wall must take into consideration the rate of reactions at the pipe wall, mass transfer limitations of the disinfectants from the bulk liquid to the wall and the available wetted surface area to volume geometry (Frateur et al. 1999; Vikesland, Ozekin and Valentine 2001; Hallam et al. 2002). An expression for the wall reaction rate as stated by Rossman, Clark and Grayman (1994) is shown in Equation 7.1. For a pipe full with water, V/A (pipe volume/surface area) is equal to the pipe diameter divided by 4.

$$\left(\frac{dC}{dt}\right)_{Wall} = -\left(\frac{A}{V}\right) \times K_{W1} \times C_W = -\frac{4}{D_p} \times K_{W1} \times C_W$$

Equation 7.1

where K_{W1} = Wall reaction rate constant (L/T)
A = Surface area (L^2)
V = Pipe volume (L^3)
Dp = pipe diameter
C_W = chlorine concentration at the pipe wall

The decay of disinfectant residuals in distribution systems have been correlated to the flow velocity inside the pipes (Rossman, Clark, and Grayman 1994; Vasconcelos et al. 1997; Hallam et al. 2002; Doshi, Grayman, and Guastella 2003; Clark and Haught 2005; Mutoti et al. 2007). Some authors use a mass-transfer limited approach, which assumes chlorine reacts as it reaches the pipe wall with no accumulation. This approach limits the rate of chlorine decay at the pipe wall to the transfer of chlorine from the bulk liquid to the pipe wall as shown in Equation 7.2 (Rossman, Clark, and Grayman 1994; Vasconcelos et al. 1997; Hallam et al. 2002).

$$\left(\frac{dC}{dt}\right)_{Wall} = \left(\frac{dC}{dt}\right)_{Mass\ transfer} = -\frac{4}{D_p} \times K_F \times (C - C_W)$$ **Equation 7.2**

where K_F = mass transfer coefficient
D_p = pipe diameter
C = chlorine concentration in the bulk
C_W = chlorine concentration at the pipe wall

The coefficient K_F is the mass transfer coefficient and has to be determined for the flow conditions. Since the chloramine concentration at the pipe wall (C_W) is difficult do determine, Equation 7.2 was manipulated to obtain an expression based on the bulk chlorine concentration, which is shown in Equation 7.3. An overall wall decay constant, W, can then be obtained by combining the mass transfer constant, K_F, and the wall reaction constant, K_{W1}.

$$\left(\frac{dC}{dt}\right)_{Wall} = -\frac{4}{D_p} \times \frac{K_{W1} K_F}{(K_{W1} + K_F)} \times C = -\frac{W}{D_p} \times C$$ **Equation 7.3**

where K_F = mass transfer coefficient
K_{W1} = wall reaction rate constant
K_W = overall wall decay constant
D_p = pipe diameter
C = chlorine concentration in the bulk

The rate at which chlorine moves towards the pipe wall is dependent on the flow conditions. Rossman, Clark and Grayman (1994) provided a relationship between the mass transfer constant, K_F and the dimensionless Sherwood number, Sh, as shown in Equation 7.4.

$$K_F = Sh \times \frac{d}{D_p}$$ **Equation 7.4**

where d = molecular diffusivity of the species being transported (L^2/T)
D_p = pipe diameter (L)

The Sherwood number has been defined as shown in Equation 7.5 and Equation 7.6 for laminar and turbulent flow (Rossman 2000), respectively. Equation 7.7 and Equation 7.8 show the expressions for the Reynolds' and the Schmidt numbers.

$$Sh = 3.65 + \frac{0.0668 \times \left({}^{Dp}\!/_{L} \right) \times \left(\mathrm{Re} \times Sc \right)}{1 + 0.04 \times \left[\left({}^{Dp}\!/_{L} \right) \times \left(\mathrm{Re} \times Sc \right) \right]^{0.67}} \qquad \text{for Re} < 2{,}300 \qquad \textbf{Equation 7.5}$$

$$Sh = 0.0149 \times \mathrm{Re}^{0.88} \times Sc^{0.333} \qquad \text{for Re} > 2{,}300 \qquad \textbf{Equation 7.6}$$

$$\mathrm{Re} = \frac{u \times Dp}{\nu} \qquad \textbf{Equation 7.7}$$

$$Sc = \frac{\nu}{d} \qquad \textbf{Equation 7.8}$$

where Sh = Sherwood number
Dp = pipe diameter (L)
L = pipe length (L)
Re = Reynolds' number
Sc = Schmidt number
u = flow velocity in pipe (L/T)
ν = kinematic viscosity of water
d = molecular diffusivity of chlorine in water

Based on Equation 7.3, Equation 7.4, Equation 7.5, and Equation 7.6, as the flow velocity increases, Reynolds' number, Sherwood's number and the mass transfer rate of chlorine towards the pipe wall increase resulting on a higher wall decay rate, K_W. Clark and Haught (2005) showed that K_W would approach a limiting value at high flow velocities (Re > 7,500).

Recent studies show that the rate of decay is directly dependent on the Reynolds number and specifically the flow velocity for free chlorine (Doshi, Grayman, and Guastella

2003; Clark and Haught 2005) and chloramines (Mutoti et al. 2007). However, contrary to Rossman, Clark and Grayman (1994), the recent studies have found that K_W does not reach a fixed value and instead keeps increasing with the Reynolds' number (Doshi, Grayman, and Guastella 2003; Clark and Haught 2005; Mutoti et al. 2007). Doshi, Grayman, and Guastella (2003) found the half-life of chlorine at the higher flow rates to be in the order of just several minutes. Some of the values obtained for the overall wall decay constant, K_W, were so high that they were higher than the mass transfer coefficient, K_F, making the value for the wall reaction rate constant, K_{W1}, negative. The same behavior was observed by Mutoti et al. (2007) and the authors assumed it was due to an increase in surface area associated with the release of particulate corrosion products from the pipe wall at elevated velocities. The additional decay in the metallic pipes resulted in an increased wall reaction rate constant (kw).

Chloramine decays in the presence of iron corrosion products by reacting with ferrous iron, Fe^{2+}, either at the pipe wall or in solution to form ferric iron, Fe^{3+} (Vikesland and Valentine 2002, Frateur et al. 1999). Phosphate-based corrosion inhibitors create a protective layer on the surface of metallic pipes that protects against corrosion (Benjamin et al. 1990) and should reduce the rate of residual decay (Butterfield et al. 2002). However, phosphorous is also a nutrient for bacterial growth and the addition of phosphate-based inhibitors could increase biofilm populations in some distribution systems (Miettinen, Vartiainen and Martikainen 1997). The presence of phosphates has also been mentioned as a catalyst for monochloramine disproportionation (Valentine and Jafvert 1988). Limited literature is available relating chloramine decay and the use of corrosion inhibitors. Volk et al. (2000) compared control water (at treatment plant conditions) with the same water dosed with ZOP at 0.7 mg/L as PO_4 and found the effluent chloramine residual was the same for the test and the control waters and there was no difference in biofilm density or the bulk HPC. Other study found the addition of phosphate inhibitors did not affect biofilm densities or composition, however the phosphate concentration in the biofilm doubled (Batté et al. 2003).

This study found that the rate of chlorine decay at the pipe wall is dependent on the flow velocity for UCI and G pipes and it did not change for PVC and LCI pipes. In the unlined metallic pipes, chloramines decayed faster as flow velocity and Reynolds' number increased. The increase of the wall decay constant was faster under laminar conditions and slower for fully turbulent flow. The use of blended orthophosphate inhibitor at a dose of 1 mg/L as P was found to have no effect on chloramine decay rates.

7.3 Methods and Materials

Eighteen (18) distribution system lines or PDS were built with poly vinyl chloride (PVC), lined cast iron (LCI), unlined cast iron (UCI) and galvanized steel (G) pipes obtained from existing full-scale distribution systems. The PDSs were numbered sequentially from PDS 1 to PDS 18. Fourteen of the lines were constructed using the pipe material in series and were called hybrid lines, these lines were not used and will not be mentioned again. The other four PDSs were called single material PDSs and were constructed one for each of the different pipe materials. PDS 15 was made using eight (8) 12-foot long sections of 6-inch UCI pipes for a total of 96 feet. PDS 16 was composed by five (5) 18-foot long pieces of 6-inch LCI for a total of 87 feet. PDS 17 had five (5) 19-foot long sections of PVC pipe for 100 feet. PDS 18 was built with 2-inch diameter G pipes of different lengths for a total of

163 feet. The principal characteristics of the single material PDSs are presented in Table 7.1. A picture of the pilot distribution system is shown in Figure 7.1.

Table 7.1 Characteristics of Single Material Lines

PDS #	Length (ft)	Diameter (inches)	Material
15	97	6	Unlined cast iron
16	87	6	Lined ductile iron
17	95	6	PVC
18	163	2	Galvanized steel

Figure 7.1 Picture of Single Material PDS Lines

The single material PDSs (PDS 15 to PDS 18) were used to conduct experiments in which Reynolds number was varied from 50 to 200 by varying flow velocity to assess the effect of turbulence on chloramine decay. Data obtained previously by Mutoti et al (2007) from the same UCI and G pipes was also used to expand the dataset to obtain a range of Reynolds' number from 50 to 8,000. A set of experiments included the addition of blended orthophosphate (BOP) inhibitor at a dose of 1.0 mg/L as P to evaluate if the inhibitor had an effect on the rate of chloramine decay.

Two types of water were used for the experiments, groundwater (GW) and reverse osmosis desalinated water (RO). The GW was prepared by conventionally treating of raw groundwater from the Floridian Aquifer. The treatment consisted of aeration followed by disinfection with free chlorine to obtain a minimum chlorine residual of 5 mg/L as Cl_2 after a 5 minutes contact time. Ammonium chloride (NH_4Cl) was added to form monochloramines (NH_2Cl). The Cl_2 to ammonia-N ratio used was 5:1 to avoid excess ammonia in the PDSs. RO was prepared by desalination of raw groundwater by reverse osmosis (RO) membranes. After membrane filtration, the RO water was aerated and dosed with calcium chloride, sodium bicarbonate and sea salt to simulate the water quality of the water produced at the Tampa Bay Water Regional Seawater Desalination Plant. The pH of the RO finished water was adjusted to achieve a LSI greater than 1 using sodium hydroxide. The RO water was disinfected in the same way than GW water. A summary of the water quality of raw groundwater, finished groundwater and RO is presented in Table 7.2.

Table 7.2 Summary of Test Waters Average Water Quality

Parameter	Raw GW	Finished GW	Finished RO
pH	7.4	7.7	7.9
Alkalinity*	215	211	70
Ca Hardness*	216	214	63
UV-254 (cm^{-1})	0.077	0.073	0.029
Color (CPU)	8	4	0
Turbidity (NTU)	0.1	0.2	0.1
Diss. Oxygen (mg/L)	0.3	7.4	8.3
Sulfates (mg/L)	30	29	2
Chlorides (mg/L)	14	36	92
TDS (mg/L)	318	357	285
Temperature (°C)	23	23	23

* measured in units of mg/L as $CaCO_3$

PDSs samples were analyzed immediately after collection in a properly equipped field laboratory. All the samples were collected in 1-L borosilicate bottles that were cleaned previously at the main UCF laboratory. Before being used in the field, each bottle was pre-rinsed thoroughly several times with distilled water and then three times with the sample to be collected. After these pre-rinses, the sample to be analyzed was actually collected. Several water quality parameters such as free and total chlorine, free ammonia, temperature, UV254, dissolved oxygen, apparent color, turbidity, nitrites, and pH, were monitored to determine the effect of turbulence on overall chloramine decay in the PDS. The effect of Reynolds' number on the wall decay rate constant (W) for PVC, LCI, UCI, and G pipes was assessed for different water quality and temperatures. Table 7.3 presents the analytical methods followed to analyze the samples during the study. The methods followed were obtained from the 20th edition of the Standards Methods for the Examination of Water and Wastewater (APHA, AWWA, and WEF 1999).

Table 7.3 Analytical Methods Used During Study

Parameter	Method	Method Reference	Approximate Range
Free Chlorine	DPD colorimetric	HACH 8021	0 – 2 ppm
Total Chlorine	DPD colorimetric	HACH 8167	0 – 2 ppm
Temperature	Direct reading	SM-2550 B	0 – 100 deg C
UV-254	UV spectrometry	HACH 10054	0 – 0.5200 cm^{-1}
NPDOC	Persulfate/UV oxidation	SM 5310C	0.1 to 20 mg/L
pH	Electrometric	SM-4500-H^+ B	2 - 13
Color, apparent	Visible spectrometry	SM 2120 B	1 – 50 cpu
Turbidity	Nephelometric	SM 2130 B	0.02 – 200 NTU

Quality control was assessed by taking duplicate samples equal to at least 10% of the samples analyzed with at least one duplicate taken any time sampling was conducted. The precision of the samples was evaluated by determining the range or difference between the sample and its duplicate. Dynamic control charts, also known as Shewart charts, were used to monitor the results. Warning and control limits were set equal to two and three standard deviations calculated from the last 30 duplicate samples analyzed. When available, accuracy was determine using known standards and calculating the recovery. Known standards were also used to calibrate and verify the instruments.

7.4 Results and Discussion

An empirical model to predict chloramine residual in a pilot distribution system with time was developed during the AwwaRF project "Control of Distribution System Water Quality in a Changing Water Quality Environment using Inhibitors" (Taylor et al. 2007). The resulting model allows the prediction of the chloramine residual based on the pipe material and pipe diameter, as well as the organic content, pH and temperature of the water.

The general form of the model is shown in Equation 7.9 with the parameter values being showed in Table 7.4.

$$Cl_{2(t)} = Cl_{2(0)} * \exp\left[\left(\begin{array}{l} K_B * UV + K_H * H * DV_H + \dfrac{W_{PVC} * DV_{PVC}}{D_{PVC}} \\ + \dfrac{W_{LCI} * DV_{LCI}}{D_{LCI}} + \dfrac{W_{UCI} * DV_{UCI}}{D_{UCI}} + \dfrac{W_G * DV_G}{D_G} \end{array}\right) * \theta^{(T-20)} * time\right] \qquad \textbf{Equation 7.9}$$

where $Cl_{2(t)}$ = chlorine concentration at time t (mg/L as Cl_2)
$Cl_{2(0)}$ = initial chlorine concentration (mg/L as Cl_2)
K_B = bulk decay constant (cm/h)
K_H = coefficient for H^+ term (L/mol-h)
W_{PVC} = wall decay constant for PVC pipe (in/h)
W_{LCI} = wall decay constant for LCI pipe (in/h)
W_{UCI} = wall decay constant for UCI pipe (in/h)
W_G = wall decay constant for G pipe (in/h)
UV = UV254 (cm^{-1})
H = molar concentration of H^+ (mol/L)
DV_i = dummy variable for parameter i (H^+, PVC, LCI, UCI and G)
D_i = pipe diameter of pipe material i (inches)
θ = temperature correction coefficient
T = temperature in degrees C
time = time expressed in hours

Table 7.4 Parameter Values for Chloramine Decay Model

Parameter	Value	p-value
θ	1.11	<0.0001
W_{PVC}	-0.025	<0.0001
W_{LCI}	-0.014	<0.0001
W_{UCI}	-0.103	<0.0001
W_G	-0.051	<0.0001
K_H	-106403.7	0.022
K_B	-0.02	

LCI and PVC have the lowest W at 0.014 in/h and 0.025 in/h respectively since those materials are fairly inert, do not promote bacterial growth and in general have the lowest chloramine demand of the materials used in the study. UCI has a W of 0.103 in/h and G has a W of 0.051 in/h. The higher wall demand of the LCI and G pipe surfaces are due in part to the greater chemical reactivity of iron and zinc relative to LCI and PVC. Material wall demand also increases with roughness, biological film densities and corrosion by-products. The diameter of the pipe affects the rate of chloramine decay because the effect of W is proportional to ratio of the volume to wetted surface area. The relative effect of W decreases when the pipe diameter increases. This effect is more noticeable for unlined metallic pipes since their W is more elevated.

The rate of chloramine decay was found to increase with the increase of temperature. The temperature correction factor, θ, was obtained to be 1.11 that means the rate of decay would double for each $7^{o}C$ increment of the water temperature. The decay of chloramine residual was found to be slower when the pH of the water increased or the organic content was lower. The effect of pH and organic is more noticeable in LCI and PVC pipes than in UCI and G pipes.

K_B and K_H are rate constants that are dependent on UV254 (surrogate for organic content) and the pH of the water, which are intrinsic to the type of water and are not likely to change with the flow velocity. The wall decay constants for PVC (W_{PVC}), UCI (W_{UCI}), LCI (W_{LCI}), and G pipes (W_G) are probably dependent on the flow conditions and mass transfer of chloramine towards the pipe wall. The combination of K_B, K_H, and W for the respective pipe material results on an overall first-order decay rate, K, as shown in Equation 7.10. K can be calculated from initial or influent chloramine residual, the final or effluent chloramine residual, the hydraulic residence time and temperature from the field experiments as shown in Equation 7.11.

$$K = K_B * UV254 + K_H * \left[H^+\right] + \frac{W}{D}$$ **Equation 7.10**

$$K = \frac{Ln\left(\frac{Cl_{2(t)}}{Cl_{2(0)}}\right)}{\theta^{(T-20)} \times time}$$ **Equation 7.11**

where $Cl_{2(t)}$ = chlorine concentration at time t (mg/L as Cl_2)
$Cl_{2(0)}$ = initial chlorine concentration (mg/L as Cl_2)
K_B = bulk decay constant (cm/h)
K_H = coefficient for H^+ term (L/mol-h)
W = wall decay constant for pipe material (in/hr)
K = overall decay rate (1/h)
θ = temperature correction coefficient
UV254= UV254 (cm^{-1})
H = molar concentration of H^+ (mol/L)
T = temperature in degrees C
time = time expressed in hours
D = pipe diameter (in)

All data used to determine the effect of velocity and turbulence on loss of chloramine residual was normalized to remove the effect of temperature as shown in Equation 7.11. Normalization was done by using the temperature correction factor listed in Table 6.7 to adjust the overall chloramine decay rate to 20 ^{o}C from the actual temperature of the experiment. As mentioned previously, the reaction rate K is the sum of the wall reaction rate, W, and bulk reaction rates, K_B and K_H. The wall reaction rate could then be determined for varying TOC concentrations and pH by using Equation 7.12 and the values of K_B and K_H from Table 7.4. This method was used to calculate W at the different Reynolds' number and water qualities for each of the pipe materials.

$$W = D * \left(K - 0.02 * UV254 - 106644 * \left[H^+\right]\right)$$ **Equation 7.12**

where W = overall wall decay constant (in/h)
D = pipe diameter (inches)
K = overall decay rate (h^{-1})

7.4.1 Unlined Cast Iron Pipes

A total of 18 experiments were conducted using the UCI PDS as shown in Table 7.5. Reynolds' number experiments conducted previously by Mutoti et al. (2007) were used to obtain a range of Reynolds' number from 50 to 8,000. Table 7.5 lists the Reynolds number for each experiment, the corresponding HRT, the flow rate, the flow velocity, the calculated overall decay rate constant (K) and the overall wall decay constant (W). The experiments are also identified when BOP inhibitor was used at a total phosphorus dose of 1.0 mg/L as P.

Table 7.5 Information on Reynolds' Number Experiments in UCI Pipes

Re	Flow rate (gpm)	Velocity (ft/min)	HRT (h)	Inhibitor?	K (h^{-1})	W (in/h)
50	0.10	0.07	24	No	0.012	0.064
50	0.10	0.07	24	No	0.024	0.124
50	0.10	0.07	24	Yes	0.025	0.134
100	0.19	0.13	12	No	0.027	0.155
100	0.19	0.13	12	No	0.012	0.053
100	0.19	0.13	12	Yes	0.017	0.090
150	0.29	0.20	8	No	0.019	0.101
150	0.29	0.20	8	Yes	0.029	0.159
200	0.38	0.26	6	No	0.046	0.254
200	0.38	0.26	6	Yes	0.035	0.193
245	0.47	3.17	4.70	No	0.021	0.113
772	1.47	10.0	1.49	No	0.048	0.273
1224	2.33	15.9	0.94	No	0.026	0.141
2449	4.66	31.7	0.47	No	0.105	0.614
3079	5.86	39.9	0.37	No	0.040	0.228
3263	6.21	42.3	0.35	No	0.078	0.457
6051	11.52	78.4	0.19	No	0.063	0.364
8045	15.31	104.2	0.14	No	0.083	0.483

1 gpm = 0.063 L/s
1 ft/min = 0.005 m/s
1 in/h = 0.025 m/h

To better observe the effect of Re number on the wall decay rate constant, W was plotted with relation to Reynolds' number as shown in Figure 7.2. The overall wall decay constant, W, was found to increase with the Reynolds' number. The data in Figure 7.2 is grouped into a low and high region, which matches the flow regime categories based on flow velocity in that laminar flow occurs at Re numbers less than 200 and turbulent flow occurs at Re numbers greater than 2000. Two regions can be observed depending on the flow regime, one for laminar flow and the second for turbulent flow. W increased rapidly with the increase of the Reynolds' number under laminar flow conditions and a more gradual increase was observed under fully turbulent flow conditions. There might be a transition region for the effect of Re number on W, however not enough data was collected within the transition zone as seen in Figure 7.2. No effect of the BOP corrosion inhibitor was observed on the rate of chloramine decay in the UCI pipes as can be seen by comparing the overall and wall decay constant for the experiments at the same Re number and information obtained from a 1-year long side by side comparison conducted by Taylor et al. (2007).

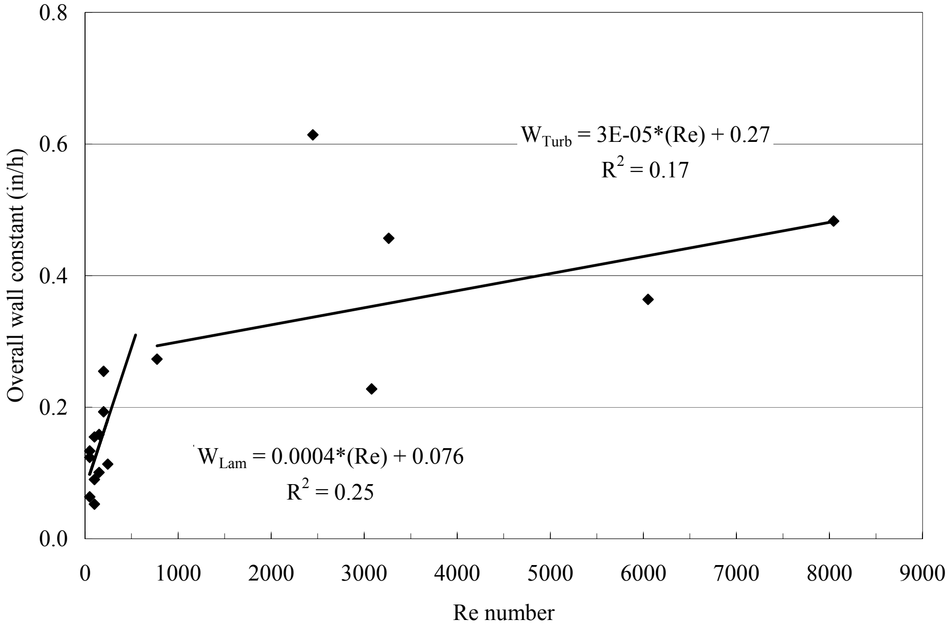

Figure 7.2 Effect of Reynolds' Number on Overall Wall Decay Rate (W) for UCI Pipes

The relationships between Re and W were found to be described by simple linear equation of W as a function of Re. The equations for laminar and turbulent flow are shown in Equation 7.13 and Equation 7.14 respectively. The slope of the lines fitted to the data shows that W increases 17 times faster during laminar that it does during turbulent flow for each increment in Reynolds' number. Graphically, it can be seen that the two trend lines intercept at a W of 0.3 in/h corresponding to a Reynolds number of approximately 500.

$W_{Lam} = 0.00044*Re + 0.076$ **Equation 7.13**

$W_{Turb} = 0.000026*Re + 0.27$ **Equation 7.14**

where: W_{Lam} = overall wall decay rate under laminar conditions (in/h)
W_{Turb} = overall wall decay rate under turbulent conditions (in/h)
Re = Reynolds' number

7.4.2 Galvanized Steel pipes

A total of 14 experiments were conducted using the galvanized steel PDS as shown in Table 7.6. Table 7.6 shows general information about the experiments such as the Reynolds' number used, the flow rate, the flow velocity, the HRT, the overall and wall rate of decay observed and whether inhibitor was used during the experiment. The use of BOP inhibitor at a total phosphorus dose of 1 mg/L as P did not affect the rate of chloramine decay in the G pipes. The experiments conducted at Re of 50 had identical overall and wall decay rates irrespective of the use of inhibitor. When the Re number was 100 the water without inhibitor had K and W greater than the water with the inhibitor, however, when Re number was 150 and 200, K and W were greater when BOP inhibitor was used.

Table 7.6 Information on Reynolds' Number Experiments in G Pipes

Re	Flow rate (gpm)	Velocity (ft/min)	HRT (h)	Inhibitor?	K (h^{-1})	W (in/h)
50	0.06	0.44	12	No	0.059	0.113
50	0.06	0.44	12	Yes	0.058	0.113
100	0.13	0.87	6	No	0.088	0.171
100	0.13	0.87	6	No	0.092	0.180
100	0.13	0.87	6	No	0.048	0.092
100	0.13	0.87	6	Yes	0.041	0.077
150	0.19	1.31	4	No	0.033	0.065
150	0.19	1.31	4	Yes	0.073	0.144
200	0.26	1.74	3	No	0.064	0.126
200	0.26	1.74	3	Yes	0.087	0.170
391	0.23	1.57	1.49	No	0.131	0.256
2279	1.34	9.11	0.26	No	0.167	0.329
2934	1.72	11.74	0.20	No	0.197	0.390
5025	2.95	20.10	0.12	No	0.435	0.866

1 gpm = 0.063 L/s
1 ft/min = 0.005 m/s
1 in/h = 0.025 m/h

Equation 7.11 and Equation 7.12 were used to calculate K and W shown in Table 7.6. W was plotted in relation to the corresponding Reynolds' number used as shown in Figure 7.3. Similar to UCI pipes, a fast increase of W with Re was observed at Re number corresponding to laminar flow conditions and a slower increase at Re greater than 2,000. The linear regression of Re versus W for laminar flow (W_{Lam}) and turbulent flow (W_{Turb}) are presented in Equation 7.15 and Equation 7.16 respectively.

$$W_{Lam} = 0.0004*Re + 0.08 \qquad \textbf{Equation 7.15}$$

$$W_{Turb} = 0.00009*Re + 0.12 \qquad \textbf{Equation 7.16}$$

Analysis of the coefficients for Re in the equations shows W increases 40 times faster under laminar flow conditions than under fully turbulent flow. Under transitional flow conditions (500 < Re <2000), W appears to be relatively stable around 0.3 in/h.

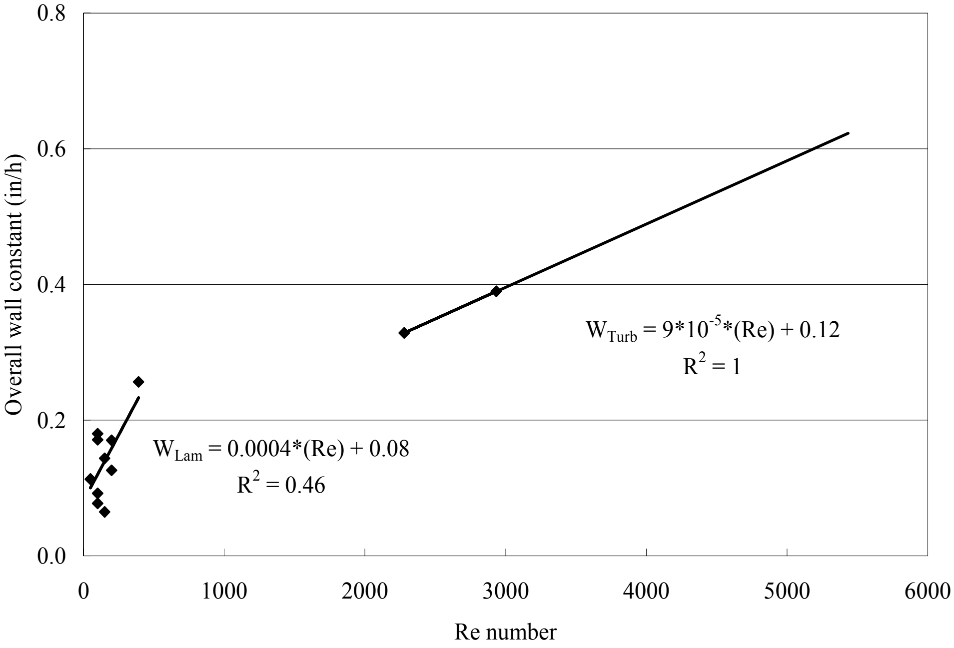

Figure 7.3 Effect of Reynolds' Number on Overall Wall Decay Rate (W) for G Pipes

7.4.3 PVC pipes

Seven (7) experiments varying Re number were conducted using the PVC PDS. Table 7.7 shows the Reynolds' number, the flow rate, flow velocity, HRT and the calculated rate constants for each of the experiments. Four (4) of the experiments were done with the addition of BOP at 1.0 mg/L as P and are identified in Table 7.7.

No correlation between Reynolds' number and the overall or the wall rate of chloramine decay in the PVC pipes can be observed in Table 7.7. This result is intuitive since the wall of PVC pipes have negligible chloramine demand and the bulk reaction rates are dominant (Hallam et al. 2002; Kiéné, Lu and Levi 1998). However, the results are not conclusive since for more than 50% of the experiments there was no or little change on the residual between the influent and the effluent due to the short retention time (6 to 24 hours). Figure 7.4 shows W in relation to Reynolds' number for the PVC PDS.

Table 7.7 Information on Reynolds' Number Experiments in PVC Pipes

Re	Flow rate (gpm)	Velocity (ft/min)	HRT (h)	Inhibitor?	K (h^{-1})	W (in/h)
50	0.10	0.07	24	No	0.006	0.025
50	0.10	0.07	24	Yes	0.000	0.000
100	0.19	0.13	12	No	0.018	0.092
100	0.19	0.13	12	Yes	0.001	0.000
150	0.29	0.20	8	Yes	0.001	0.000
200	0.38	0.26	6	No	0.018	0.094
200	0.38	0.26	6	Yes	0.000	0.000

1 gpm = 0.063 L/s
1 ft/min = 0.005 m/s
1 in/h = 0.025 m/h

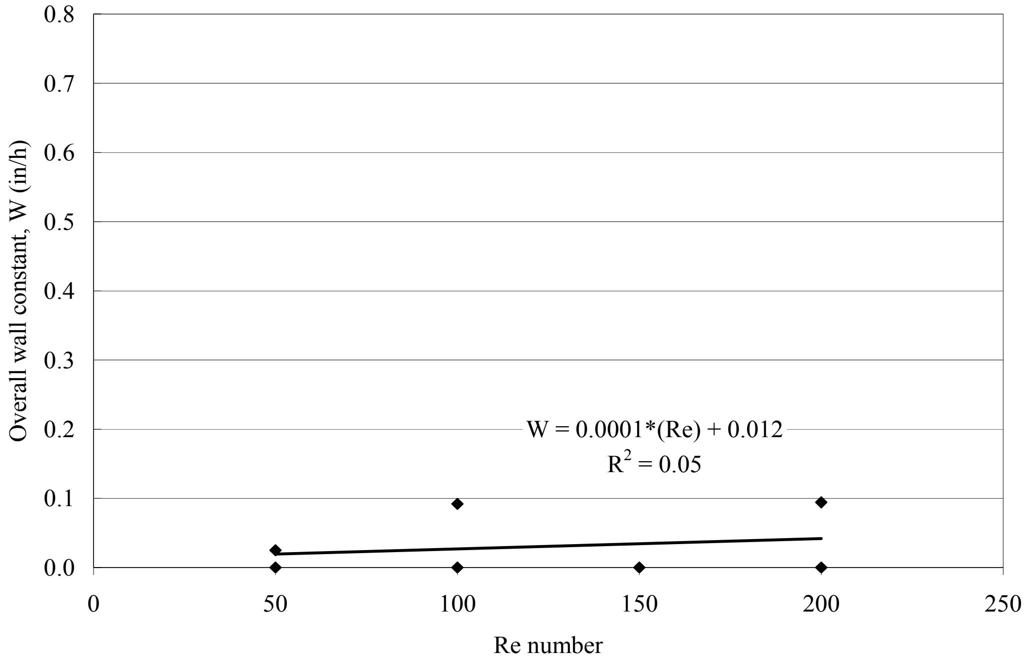

Figure 7.4 Effect of Reynolds' Number on Overall Wall Decay Rate (W) for PVC Pipes

7.4.4 Lined Cast Iron Pipes

A total of nine (9) experiments were conducted in the LCI PDS. The results were similar to the results obtained in the PVC pipes. Table 7.8 shows Re, flow rate and velocity as well as the corresponding HRT, K and W for each experiment. The experiments where BOP was utilized are also identified. No variation on K and W was observed with Re and the use of the BOP inhibitor did not have any effect on the rates of decay. Both decay constants were very low and almost flat for the range of Reynolds' number studied. As for the PVC pipes, the wall of the LCI pipes have a low demand and the results are not surprising. Figure 7.5 shows W plotted versus the Re number used for the experiments in the LCI PDS.

Table 7.8 Information on Reynolds' Number Experiments in LCI Pipes

Re	Flow rate (gpm)	Velocity (ft/min)	HRT (h)	Inhibitor?	K (h^{-1})	W (in/h)
50	0.10	0.07	24	No	0.0045	0.008
50	0.10	0.07	24	No	0.0011	0.000
50	0.10	0.07	24	Yes	0.0000	0.000
100	0.19	0.13	12	No	0.0000	0.000
100	0.19	0.13	12	Yes	0.0037	0.007
150	0.29	0.20	8	No	0.0021	0.000
150	0.29	0.20	8	Yes	0.0000	0.000
200	0.38	0.26	6	No	0.0026	0.000
200	0.38	0.26	6	Yes	0.0000	0.000

1 gpm = 0.063 L/s
1 ft/min = 0.005 m/s
1 in/h = 0.025 m/h

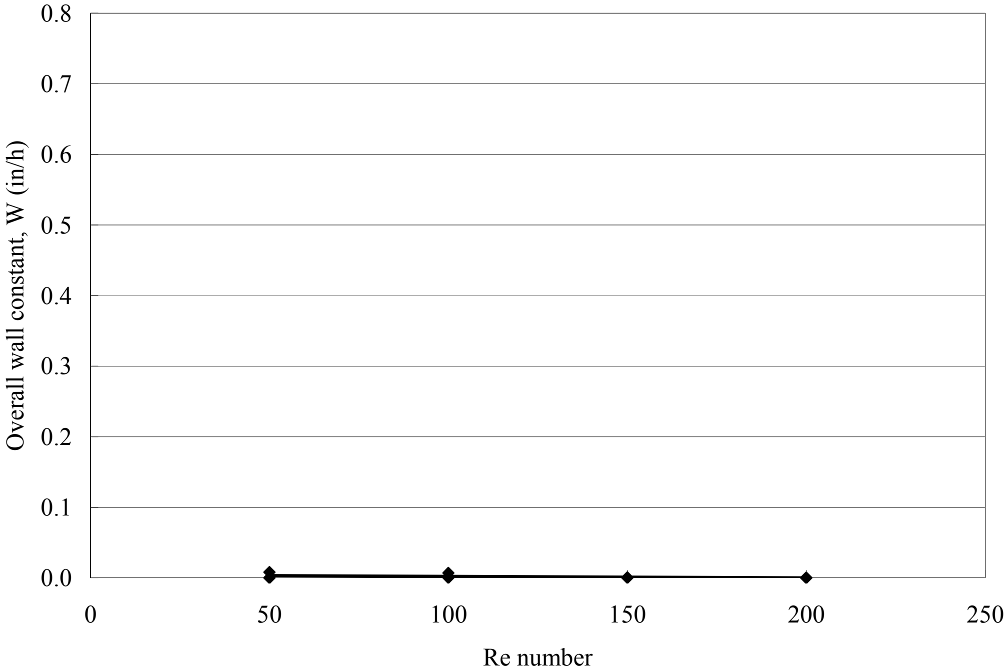

Figure 7.5 Effect of Reynolds' Number on Overall Wall Decay Rate (W) for LCI Pipes

7.4.5 Chloramine Decay Model Incorporating Reynolds' Number Effect

The effect of Reynolds' number on chloramine decay could be incorporated into the model by combining the model shown in Equation 7.9 with Equation 7.13 to Equation 7.16. A general form of the new model that can be adapted depending on the pipe material is presented in Equation 7.17. The parameter values for the model are included in Table 7.9. For PVC and LCI pipes, the parameter B takes a value of zero (0) since for those materials, W does not change with the Reynolds' number.

$$Cl_{2(t)} = Cl_{2(0)} * \exp\left(-\left(K_B * UV254 + K_H * \left[H^+\right] + \frac{B * \mathrm{Re} + C}{D} \right) * \theta^{(T-20)} * time \right)$$ **Equation 7.17**

where $Cl_{2(t)}$ = chlorine concentration at time t (mg/L as Cl_2)
$Cl_{2(0)}$ = initial chlorine concentration (mg/L as Cl_2)
K_B = bulk decay constant (cm/h) = 0.02 cm/h
K_H = coefficient for H^+ term (L/mol-h) = 106404 L/mol-h
B = wall decay material coefficient for Reynolds number (in/hr)
C = wall decay material constant (in/hr)
UV = UV254 (cm^{-1})
$[H^+]$ = molar concentration of H^+ (mol/L)
D = pipe diameter (inches)
θ = temperature correction coefficient
T = temperature in degrees C
time = time expressed in hours

Table 7.9 Model Parameters for Chloramine Model Modified Using Reynolds' Number

Pipe Material	K_B (cm/h)	K_H (L/mol-h)	θ	B (in/h)	C (in/h)
PVC	0.02	106403.7	1.11	0	0.025
LCI	0.02	106403.7	1.11	0	0.014
UCI					
Re < 500	0.02	106403.7	1.11	0.00044	0.076
Re > 500	0.02	106403.7	1.11	0.00003	0.27
G					
Re < 500	0.02	106403.7	1.11	0.0004	0.083
Re > 2000	0.02	106403.7	1.11	0.00009	0.12

Note: 1 inch = 2.54 cm

7.4.6 Predicted Effluent Residual Based on Reynolds' Number

Figure 7.6 and Figure 7.7 show the predicted residual for UCI and galvanized pipes, respectively, with a diameter of 6 inches (0.15 m) for different Reynolds' numbers ranging from 15 to 5000. The water used for the prediction have an organic content of 3 mg/L, a temperature of 20 ^{o}C, a pH of 8.0 and an initial chloramine concentration of 4 mg/L as Cl_2.

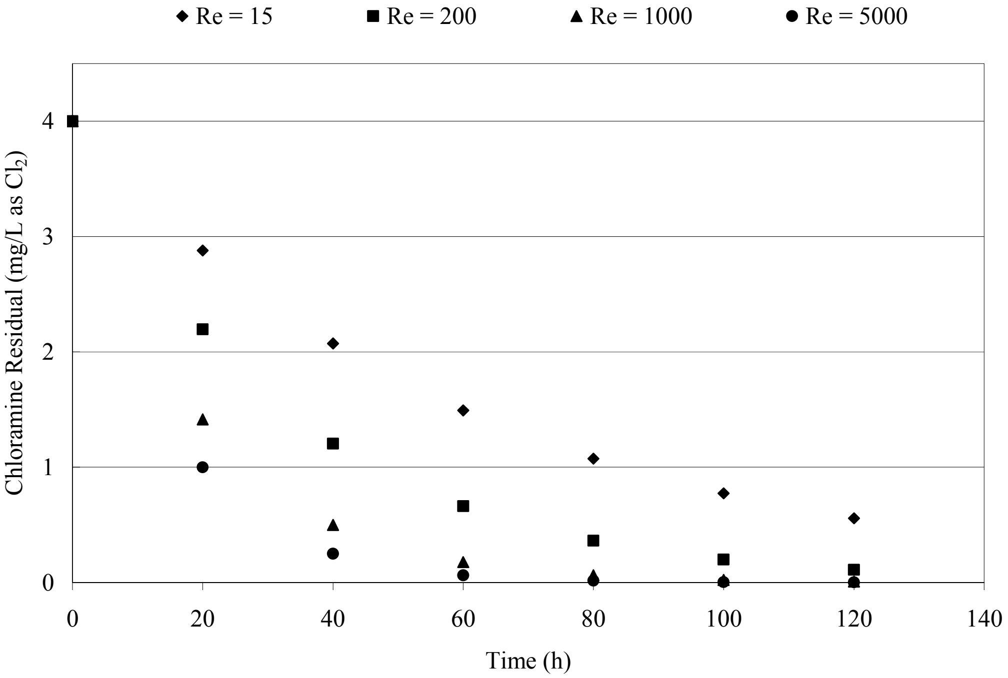

Figure 7.6 Predicted Chloramine Residual in 6-inch UCI Pipes vs Reynolds' Numbers

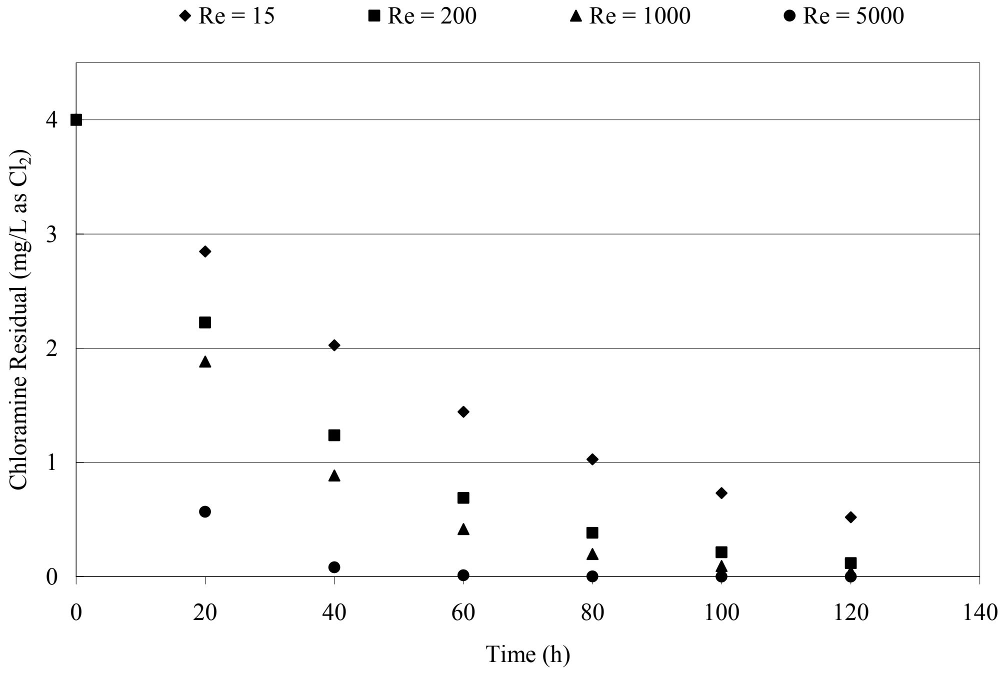

Figure 7.7 Predicted Chloramine Residual in 6-inch G Pipes vs Reynolds' Numbers

Figure 7.6 shows that for the UCI pipe, the chloramine residual is predicted to be below the regulatory minimum of 0.6 mg/L as Cl_2 in 40 hours under transitional (Re = 1000) and fully turbulent flow conditions (Re = 5000), and would be 1.2 mg/L as Cl_2 and 2.1 mg/L as Cl_2 for Reynolds' numbers of 200 and 15 respectively after the same 40 hours. Only when the Reynolds' number is 15, the water is predicted to maintain the chloramine residual for a period of 120 hours or 5 days. Figure 7.7 shows that for galvanized pipes with a diameter of 6 inches (0.15 m), the chloramine residual is predicted to be below the required minimum after 60 hours under transitional (Re = 1000) and 20 hours under fully turbulent flow conditions (Re = 5000), and would be 0.7 mg/L as Cl_2 and 1.4 mg/L as Cl_2 for Reynolds' numbers of 200 and 15 respectively, after the same amount of time. Even under fully laminar conditions, the water is predicted to fail to maintain the required minimum residual of 0.6 mg/L as Cl_2 for 120 hours.

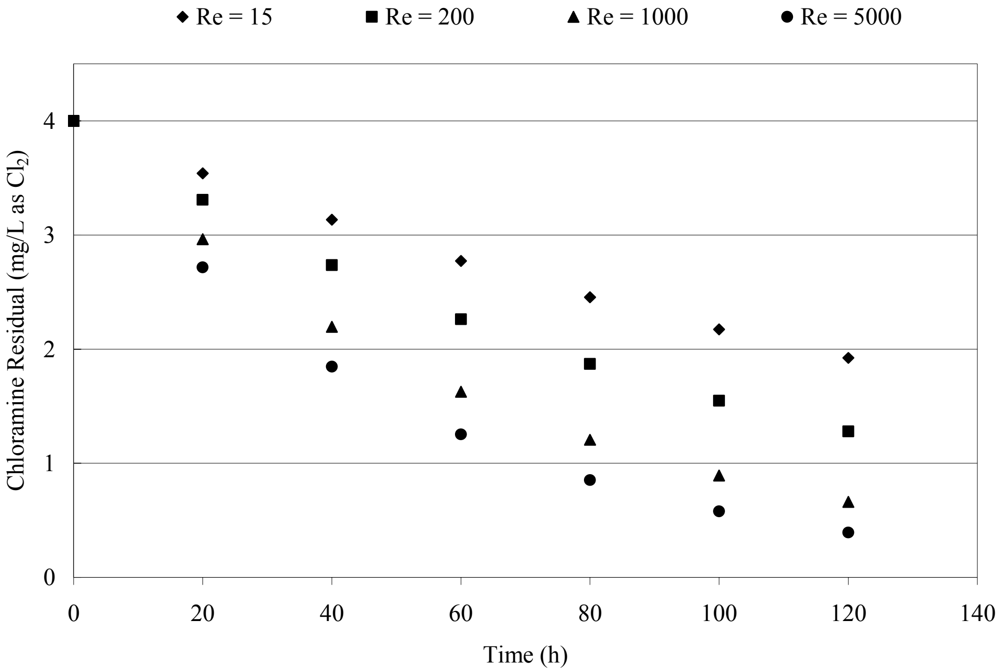

Figure 7.8 Predicted Chloramine Residual in 24-inch UCI Pipes vs Reynolds' Numbers

Figure 7.8 and Figure 7.9 show the predictions for UCI and G pipes with a diameter of 24 inches. Under this conditions, the water would maintain an adequate residual for laminar and transitional flow conditions, however residual is predicted to drop below the regulatory limit for fully turbulent flow. Since the effect of the wall decay constant decreases when the pipe diameter increases, the residual decays slower than for 6-inch pipes and higher effluent residuals are predicted. The effect of Re number on the residual decay is also diminished. The chloramine residual after 40 hours at Re number of 5,000 would be 60% of the residual when Re is 15 in the 24-inch diameter pipe compared with only 12% when the pipe diameter is 6 inches. For G, it would be 45% for the 24-inch pipe compared to 4% in the 6-inch pipe. This analysis show the importance of avoiding the use of small diameter UCI and G pipes to transport water over long distances and the need to replace the existing pipes, if possible.

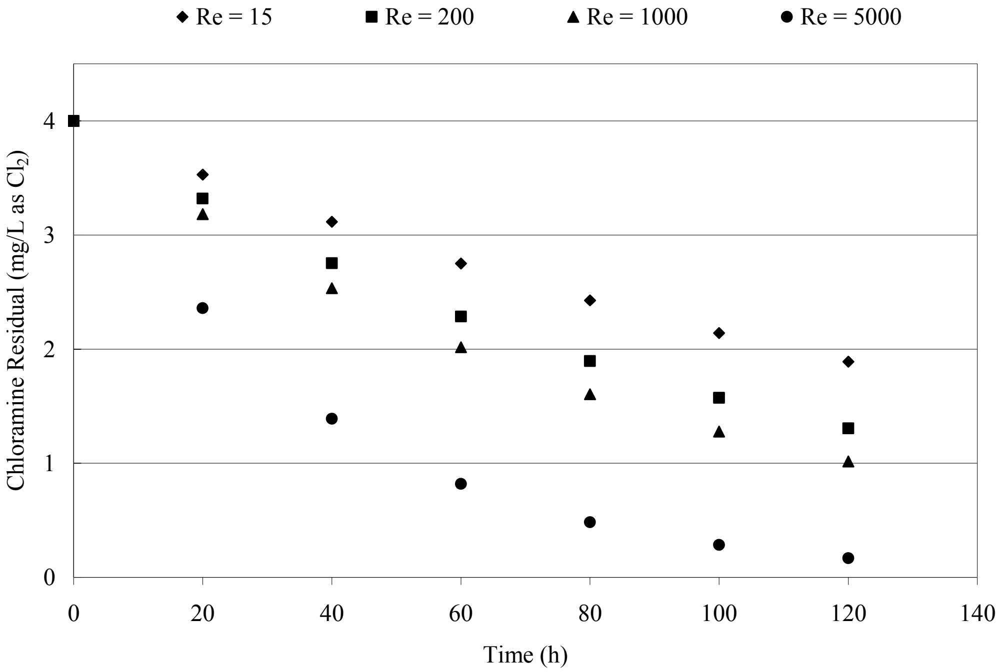

Figure 7.9 Predicted Chloramine Residual in 24-inch G Pipes vs Reynolds' Numbers

Even though the rate of chloramine decay in UCI and G pipes was found to increase with the Reynolds' number, that does not mean that the residual will reach farther at low velocities. Table 7.10 shows the distance that residual are predicted to reach in the distribution system before the residual is below the mandatory 0.6 mg/L as Cl_2. At a Re of 15, the residual will last for 116 hours, however it would only travel 138 feet whereas when Re is 5,000 the residual would disappear in 27 hours but travel more than 10,500 feet.

Table 7.10 Predicted Distances Covered by Chloramines at Different Re Number

Re	HRT (hours) to NH_2Cl = 0.6 mg/L	Flow Velocity (ft/min)	Distance (ft)
15	115	0.02	138
200	63	0.26	983
1000	36	1.3	2,808
5000	27	6.5	10,530

7.5 Conclusions

Flow velocity experiments in the single pipe material lines showed that the rate of chloramine decay at the pipe wall, W, did not change with increase of Reynolds' number for PVC and lined cast iron pipes. For UCI and G, the wall decay rate increased with the increase of the Reynolds' number. A region of rapid increase of W under laminar conditions was observed for both UCI and G pipes. W continued to increase with Reynolds' number under fully turbulent flow, however, the increase was more gradual. Chloramine residual in the PDS was not affected by the use of corrosion inhibitors. The increase in pipe diameter reduces the effect of Reynolds' number on wall decay rates. The use of UCI and G pipes of low diameter will result on rapid lost of chloramine residual in distribution systems.

7.6 Acknowledgements

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8 CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

An initial study was conducted to investigate the effect of blending waters of different water quality on the effluent water quality of a pilot distribution system. Within this study, the decay of free chlorine and chloramine was evaluated and modeled. Free chlorine and combined chlorine (monochloramines) decay in a pilot distribution system followed first-order kinetics with respect to initial chlorine concentration. The rate of chlorine dissipation was affected by the pipe material, temperature and organic content of the water.

The rate of free and combined chlorine dissipation in a distribution system is highly dependent on the pipe material. Free and combined chlorine decayed faster in iron-based pipes than in inert material pipes such as PVC and lined cast iron. PVC and lined iron pipes have similar low values for the decay constants while cast iron and galvanized steel present greater values due to the reactivity of chlorine with iron based pipes.

Water with low content of organics will maintain the chlorine residual longer than waters with high concentration of NOM in any type of pipe. The rate of chlorine dissipation in UCI distribution systems is dependent on aqueous organic concentration. The organic content of the water does not produce an effect of the same magnitude with chloramines as with free chlorine because chloramines are less reactive than free chlorine. A reduction in organics from 3.0 mg/L as C to 0.3 mg/L as C is predicted to increase the duration that water retains a free chlorine residual in UCI pipes by 71% and by 46% for a combined chlorine residual.

The rate of free chlorine dissipation is predicted to double for an increase of temperature between 5 and 17 ^{o}C. The rate of combined chlorine decay would double for an increase of 5 to 7 ^{o}C. Maintenance of combined or free chlorine residuals in unlined metallic pipes for 4 or more days is predicted to be difficult at temperatures above 20 ^{o}C.

A second and complementary study was conducted in the PDSs using blends of GW, SW and RO disinfected with chloramines. Corrosion control techniques, such as pH control and addition of phosphate-based and silicate-based corrosion inhibitors at different doses, were used to observe their effect on chloramine decay in the PDS. The use of phosphate or silicate based corrosion inhibitors did not have an effect on chloramine residual decay in the pilot distribution system as the chloramine demand in the PDS did not change by inhibitor type or dose. Only corrosion control by means of pH management had an effect on chloramine residual decay with the rate of decay decreasing with the increase of pH of the water.

Chloramine decayed at different rate depending on the material of the pipe. PVC and lined cast iron (LCI) pipes showed a rate of chloramine decay lower than unlined cast iron (UCI) and galvanized steel (G) pipes. The order of the decay rate was LCI<PVC<<G<UCI. Chloramine was observed to decline faster during the summer months than in winter time.

A first-order model for chloramine dissipation was developed using non-linear regression, as a function of pipe material, pipe geometry, initial chlorine dose, water quality (temperature, pH and UV254) and time. The model contains a bulk decay rate constant (K_B), a pH effect constant (K_H), a wall decay rate constant (W) and a temperature correction factor (θ). The model uses a common K_B, θ and K_H for all types of pipe as well as an individual W for each pipe material.

UCI and G pipes have W that are four and nine times greater than W for LCI pipes. The decay of chloramine in UCI and G pipes is mainly due to wall decay since the effect of W is much greater than the effect of K_B and K_H, however, for PVC and LCI pipes the effect of wall reactions, organics and pH are all important.

The diameter of the pipe affects the rate of chloramine decay because the effect of W is proportional to the wetted surface area to volume ratio. The relative effect of W decreases when the pipe diameter increases. This effect is more noticeable for unlined metallic pipes since their W is more elevated.

The rate of chloramine decay was found to increase with the increase of temperature. The temperature correction factor, θ, was 1.11, which means the rate of decay would double for each 7 ^{o}C increment of the water temperature. The pH of the water was the only corrosion control measure to have an effect on the rate of chloramine decay in the PDSs. The decay of chloramine residual was found to be slower when the pH of the water increased. The effect of pH is more noticeable in LCI and PVC pipes but almost negligible in UCI and G pipes. The model for chloramine was adequate to predict chloramine residual in the pilot distribution system at the 95% confidence level and was verified using independent data that was not used to develop the models.

Flow velocity experiments in the single pipe material lines showed that the rate of chloramine decay at the pipe wall, W, increased with the increase of the Reynolds' for UCI and G pipes. W did not change with increase of Reynolds' number for PVC and lined cast iron pipes. For UCI and G pipes, a region of rapid increase of W under laminar conditions was observed. W continued to increase with Reynolds' number under fully turbulent flow, however, the increase was more gradual. Chloramine residual in the PDS was not affected by the use of corrosion inhibitors. The increase in pipe diameter reduces the effect of Reynolds' number on wall decay rates. The use of UCI and G pipes of low diameter will result on rapid lost of chloramine residual in distribution systems.

8.2 Recommendations

Monitoring of free chlorine and chloramine residuals in the distribution system should be based on water age, water quality, season and pipe material. Locations with high residence times and dead end or near dead end locations should be monitored more frequently. Due to the high rates of free chlorine and chloramine decay in unlined cast iron and galvanized steel pipes, sections of the distribution system containing these type of pipe should be monitored frequently. Additionally, any unlined metallic pipes existing in the distribution system should be replaced as soon as possible to diminish the risk of complete loss of residual in the distribution systems. Monitoring of disinfectant residual should also be increased during the warm months of the year when the temperature rises above 20 ^{o}C.

The model for free and chloramine residual could be used to predict disinfectant residual concentrations at different points within the distribution system and can determine the locations where rechlorination, flushing or other means of residual maintenance should be implemented. The residual model developed should be calibrated and verified in actual distribution systems for varying seasons, pipe materials, water quality conditions, hydraulic conditions and pipe geometries to verify their accuracy.

The model for chloramine residual decay was developed under laminar regime conditions which might limit their use in full scale distribution systems. Furthermore, the limited length of pipe utilized in the development of the residual models constrained the velocity of flow that could be achieved while maintaining the required HRT. The experiments under turbulent flow conditions had short HRT that could have influenced the observed chloramine decay. Chloramine dissipation studies in full-scale distributions systems are required to verify the models especially under turbulent flow regimes.

The pipe materials were restricted to a single diameter used in the PDS construction. Verification of the effect of pipe diameter on chloramine dissipation rates would require a greater range of pipe diameters for each material.