CORROSION IN NEW CONSTRUCTION: ELEVATED COPPER, EFFECTS OF ORTHOPHOSPHATE INHIBITORS, AND FLUX INITIATED MICROBIAL GROWTH

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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

Master of Science
in
Environmental Science and Engineering

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March 10, 2010
Blacksburg, VA

Keywords: Corrosion, Chloramine Decay, Blue Water, Phosphate Corrosion Inhibitor

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ABSTRACT

It is generally acknowledged that a variety of problems affecting aesthetics, health, and corrosivity of potable water can arise during installation of building plumbing systems. These include 'blue water', microbial infestation, and rapid loss of disinfectant residual, among other things. Frequently cited causes of the problems include metallic fines left in the plumbing lines from deburring, cutting and product fabrication; solder flux residuals (water soluble and petroleum based flux); and solvents for CPVC. Mechanistically, some materials such as flux contain high chloride, high ammonia and cause low pH, which can increase the corrosivity of water held in the lines. Indirect effects are also suspected to be important. For example, ammonia from flux and organic carbon from flux or PVC solvents can spur microbial growth, which in turn can reduce pH or otherwise increase corrosivity. Recent work has also demonstrated that problems with lead leaching to water from brass in modern plumbing can actually be worse in PVC/plastic than in copper systems, if certain types of microbes such as nitrifiers proliferate and drop pH. Some of the problems initiated by construction practices can persist indefinitely, causing higher levels of lead and copper in water, or longer term, contributing to failures of the plumbing system.

Blue water from high copper concentrations is a confounding problem that continues to arise in some locales of the United States. One public elementary school in Miami Dade County is experiencing blue water issues as manifested by blue ice cubes and sink staining. In addition to the aesthetic problems, copper levels are above the EPA's Copper Action Level of 1.3 ppm. Bottled water has been substituted for tap water consumption, which has created a financial burden. The pH of the school's water ranges from 7.15 - 7.5 and the school itself is located 1 ½ miles off the main distribution line resulting in a very low chlorine residual of between 0.06 mg/L Cl_2 and 0.18 mg/L Cl_2. On site water was shipped to Virginia Tech from Miami to be used in this study. Preliminary testing showed that an increase in the pH of the water would decrease copper leaching. Several pH's were tested which revealed that increasing the pH of the water to 8.5 would drop copper below 1.3 mg/L. When these recommendations were implemented at the school, the high alkalinity and calcium rich water caused calcite scales to form which clogged the chemical feed nozzles. Further bench scale testing indicated that adding 2 mg/L orthophosphate corrosion inhibitor would effectively decrease copper to a level that would comply with the EPA's Copper Action Limit.

Orthophosphate corrosion inhibitors are used by utilities to limit lead and copper corrosion from consumer's plumbing. An evaluation comparing the effects of both 100% orthophosphate inhibitor and orthophosphate/polyphosphate inhibitor blends was performed to study the effects they have on galvanic corrosion, metallic corrosion, microbial growth and the decay of chloramine disinfectant. On site water was sent to Virginia Tech from UNC for use in this bench scale study. The results from this study indicated that 100% orthophosphate inhibitor was the most effective corrosion inhibitor at decreasing metallic corrosion.

It has long been known that microbial activity can have significant effects on water quality. This study evaluated nitrifying and heterotrophic bacterial growth in water systems containing copper pipes, a common plumbing product, and flux which is used in soldering copper pipes together in new construction. There are several types of commercially available fluxes which are often used when soldering new pipes together. Flux ingredients vary and can include extremely high concentrations of ammonia, zinc, chloride, tin, copper and TOC. Flux containing high amounts of ammonia can be detrimental to water quality because it can accelerate the occurrence of nitrification, thus creating a cascading set of problems including, but not limited to, pH decrease and copper corrosion. The results from this case study indicated that flushing a pipe system can effectively decrease the high concentrations of flux present in a new construction system; however, high levels of ammonia from flux can create an environment in which nitrifiers may proliferate within the system.

Many water utilities in the United States are switching disinfection type from chlorine to chloramine due to the increased stability, longer residual time, and overall safety benefits of chloramine. Although chloramines have been found to be a desirable means for disinfection, chloramine decay is an issue of great concern because if the chloramine residual decays, it can leave a water system unprotected against microbial infestation. A preliminary examination of this issue was performed in a laboratory setting to evaluate the many components that effect the stability of chloramine decay, including alkalinity, phosphate, temperature, and various pipe materials. The results from this experiment revealed that temperature increase, pH increase, and aged tygon tubing all accelerated the rate of chloramine decay.

ACKNOWLEDGEMENTS

First and foremost I would like to thank my advisor, Dr. Marc Edwards, for all the guidance he showed me throughout my assistantship. I would also like to thank my other committee members Dr. Jeffrey Parks and Dr. Amy Pruden-Bagchi for their direction and support.

A huge thank you to Dr. Yan Zhang and the rest of the Edwards' Lab for lending me a helping hand and for making this experience one that I'll never forget.

I will be eternally grateful to my dear friends and loved ones, who never stopped challenging me and pushing me towards achieving my goals.

I would also like to extend my deepest gratitude to my mother, brothers, and extended family who have given me endless encouragement and everlasting love throughout my life.

Finally, thank you to the Water Research Foundation, Copper Development Association, and United States Environmental Protection Agency for their funding and support for these projects.

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AUTHOR'S PREFACE

The chapters in this thesis are a compilation of different case studies and co-authored papers published in professional journals. Chapter 1 evaluates a case study involving a Miami Dade Public School experiencing blue water. Chapter 2 involves a case study evaluating phosphate corrosion inhibitors. Chapter 3 is based on one part of an AwwaRF proposal *4164: Lead and Copper Corrosion in New Construction*. Chapter 4 compiles several bench scale studies evaluating chloramine decay. Appendices A through C list three different published research papers in which the author of this thesis is co-author of.

CHAPTER 1: MIAMI DADE COUNTY PUBLIC SCHOOL BLUE WATER CASE STUDY

ABSTRACT

Blue water is a phenomenon that has spurred confusion and concern in various locations through the United States in past history. The evaluation of several case studies has revealed that copper corrosion is a strong contributing factor to this problem. The topic of this thesis chapter is a Miami Dade County Public Elementary School which has been experiencing blue water problems. Water samples were sent to Virginia Tech for evaluation and a bench scale study was performed using brand new 2 ½ foot copper pipe sections. Initial water quality parameters were evaluated and metal analysis revealed copper concentrations exceeding EPA’s Copper Action Limit of 1.3 ppm by up to 3.5 times in some locations throughout the Public School.

This case study examined the role that pH, chlorine, orthophosphate corrosion inhibitor, and carbon filtration plays with copper leaching. Although the blue water was never replicated within the laboratory setting, after several failed attempts the copper levels eventually dropped below EPA’s Copper Action Limit.

INTRODUCTION

Virginia Tech was contacted in March, 2009 to assist in resolving a problem with excessive blue water and ice staining in a newly constructed Miami elementary school. The blue water caused aesthetic concerns for parents of students attending the school, faculty, and students themselves. Bottled water had to be purchased by the school which became both a financial and environmental burden. School officials provided pictures of the blue ice cubes and the staining that occurred in the sinks as a result of the blue water (Figure 1-1). There are two newly built schools of similar age within this school/water system and only one is experiencing blue water. The particular school with the problem is 1.5 years old and sits at the end of a 1.5 mile water main of which the school is the only user. School officials initially hypothesized that the problem could be attributed to lightning striking the school or grounding.

The occurrence of blue water is a rare phenomenon and extensive research has revealed major contributing factors. Edwards et al. (2000) discussed copper corrosion extensively and separated the problem into two categories: soluble copper and particulate copper. Problems with particulate blue water occur in high pH and low alkalinity water supplies with low levels of disinfectant residual, and the problem does not solve itself with time [1,2]. It is hypothesized that particulate blue water results from a combination of microbiological and chemical factors. Oddly, this type of problem can become worse at higher pH values.

Problems with soluble copper result from formation of the high solubility $Cu(OH)_2$ on copper pipes [2]. For typical pH and temperature ranges found in distribution systems the formation of this solid can lead to dissolved copper concentrations in the 2-10 mg/L range. This problem tends to occur in relatively low pH and high alkalinity waters. Oftentimes, the problem goes away with time as the $Cu(OH)_2$ solid transitions to less soluble malachite or tenorite scales on the pipe surface. After the transition occurs copper levels can drop by one or two orders of magnitude, but the presence of sulfate or NOM can prevent these less soluble solids from forming [2,3].

The objective of this study was to diagnose and resolve problems associated with elevated copper levels in the Miami school. To achieve this objective field sampling was conducted as well as numerous bench-scale experiments.

METHODS AND MATERIALS

Sample Collection. School officials collected water samples from ten locations throughout the school and shipped the samples to Virginia Tech for analysis. These locations included a domestic backflow prevention valve prior to the school's premise plumbing, five sinks, three hose bibs, and following an in-line filter in the school's kitchen. Chlorine concentrations and pH measurements were determined in the school prior to shipment.

Analytical Methods. Samples were analyzed for total copper using a Thermo Electron X-Series inductively coupled plasma with mass spectrometry (ICP-MS) according to Standard Methods 3125-B [4]. The pH was monitored by using a pH electrode according to Standard Method 4500-H^+ B [4]. The dissolved copper concentration was determined by passing an aliquot through a 0.45 micrometer pore-size nylon syringe filter with subsequent analysis by ICP-MS. Heterotrophic Plate Counts (HPC) were conducted to monitor microbial activity of bacteria known to thrive in water systems according to Standard Method 9215[4]. Biological Activity Reaction Tests (BART) were used to test the water samples for Sulfate Reducing Bacteria

(SRB), Heterotrophic Aerobic Bacteria (HAB), and Slime Forming Bacteria (SLYM). The BARTs were administered in the field and sent back to Virginia Tech for monitoring.

Bench Scale Study. Testing under rigorously controlled conditions was conducted using new ½"copper pipes. The pipes were cut into 30 inch sections and sealed with rubber stoppers at each end. Four sets of pipes were used, with triplicates of each condition. This study was set up in two phases of work. Phase I used water from two different locations in the school, which included water from the domestic backflow valve and at the kitchen tap following an inline filter. Phase II focused solely on the backflow valve water unaffected by the building plumbing system.

During Phase I of this experiment the pH of the water was adjusted to 7.15 and pH 7.5 using CO_2 gas to examine the role of pH at constant alkalinity. These pH levels were selected as representative of the range of pH encountered in the school (Figure 1-4). In Phase II different pH levels were tested within the four sets of copper pipes purchased for the study, including targets which might mitigate the copper leaching. These pH levels were 7.15, 7.5, 7.8, 8.0, and 8.5.

Additional bench-scale testing was conducted to determine if chlorine might have a role in reduced copper leaching. Another school in close proximity to the school in this study has not observed any copper leaching problems. One key difference is that school is located near the water main and a chlorine residual of approximately 1.4 mg/L was measured. Water from the backflow prevention device was used for this study. Four water quality conditions were tested. These included pH 7.15, pH 7.5 with 0.5 mg/L chlorine, pH 7.8, and pH 7.8 with 0.5 mg/L chlorine.

A follow up bench-scale experiment was performed comparing the benefits of orthophosphate inhibitor and carbon filtered water in terms of copper leaching. A condition using carbon filtered water was used because the groundwater in question had high TOC, which interferes with aging of copper pipes [3]. A granular activated carbon filter was prepared using a two foot section of tygon tubing. A plastic stopper with a small hole drilled into it sealed the bottom of the tubing, a one inch layer of glass wool was placed above the stopper, and then an eight inch layer of activated carbon was placed above the glass wool (Figure 1-8). The Miami water was filtered through the carbon filter two times and TOC measurements showed that 70% of the carbon and 72% of the UV_{254} was removed from the water.

A new 10 foot section of copper pipe was purchased for this experiment and was cut into ten one-foot sections. It was important to use the same [10 foot] piece of copper pipe for all conditions within this experiment because previous studies have revealed that copper leaching is sometimes inconsistent among individual copper pipes purchased seperately. Testing was conducted in triplicate for both the orthophosphate condition and the carbon filtered condition, and four pipes were used for the control condition. Water was changed Monday through Friday and samples were taken daily.

RESULTS AND DISCUSSION

A school official took chlorine measurements at 10 different locations throughout the school and sent us the results. The chlorine levels indicated an extremely low level of disinfectant in flushed samples (Figure 1-3). Low chlorine levels are probably due to the fact that the school is located so far from the main distribution line. Microbial monitoring results indicated the presence of SRB and HAB in the water, but overall relatively low microbial activity was found in the school water (Table 1-1) despite the low chlorine concentrations. Lead concentrations were measured and in four of the ten sampling locations the concentrations of lead in the water exceeded EPA's Lead Action Limit of 15 ppb (Figure 1-2).

Effects of pH on Copper release

Copper concentration data showed little variation between the unfiltered and filtered samples, indicating the copper is mostly dissolved (Figure 1-5). The copper concentration exceeded the EPA action limit of 1.3 ppm in nine of the ten sampling locations. As expected, the influent water to the school (as measured at the backflow prevention device) had virtually undetectable copper. This confirmed that the high copper concentrations were coming from the copper pipes in the schools, which is not surprising because there is no copper pipe in the water distribution system before the school.

A study was conducted to test the hypothesis that increasing the pH would cause a decrease in copper leaching. Three sets of triplicate pipes were used and pH levels of 7.15, 7.5 and 7.8 were tested. These pH levels were used because they fall within the pH range that was observed in the school (Figure 1-4). An average was determined for each set of triplicates and error bars represent the standard deviation within each set (Figure 1-6). The results confirmed that the copper concentration decreased as the pH increased. The pipes with a pH of 7.15 had 2.4

times higher copper concentrations compared to the pipes held at pH 7.8. The pipes with a pH of 7.5 showed a decrease in copper concentration compared to the lower pH of 7.15, but the results were not as dramatic as observed for the pH 7.8 pipes.

This study demonstrated that increasing the water's pH level could prevent high levels of copper leaching into the water. Although the increase in pH will not solve this problem completely and there will likely still be some copper release, it could get the copper levels below the EPA Copper Action Limit of 1.3 ppm and hopefully mitigate the blue water problem. A modest increase in pH from 7.15 to 7.5 with additional chlorine resulted in a 35% decrease in copper leaching (Figure 1-6).

Copper Release as a Function of Time

Copper release as a function of time was also considered. Water quality conditions for this experiment were pH 7.15, pH 7.5 + 0.5 mg/L chlorine, pH 8.0, and pH 8.5 + 0.5 mg/L chlorine. These parameters were used in order to examine a wide range of pH levels and to consider the effects that chlorine has under these conditions. After each water change, water samples were taken at 2 hours, 4 hours, 8 hours, and 72 hours for ICP-MS analysis.

A low pH and longer contact time with copper pipe corresponds to higher copper levels in the water (Figure 1-7). The copper levels at 2 hours were below the EPA Copper Action Limit in three of the four conditions. When 72 hours had passed the copper levels had increased by more than a factor of two for all conditions. The copper concentrations exceeded the EPA Copper Action Limit in three out of the four conditions after 72 hours. On the basis of these results it was believed that raising pH to 7.8 would be effective in reducing copper levels below 1.3 mg/L. Unfortunately, when chemical feed was tested to adjust pH to this range, the chemical feed nozzles clogged rapidly due to precipitation of calcite (Figure 1-9 and 1-10), making it desirable to find other remedial strategies.

Copper Release Relative to Carbon Filtered Water and Orthophosphate Inhibitor

Benefits of orthophosphate and activated carbon in reducing copper levels were tested. Both activated carbon filtered water and the orthophosphate were successful at decreasing the copper concentration when compared to the control. Although 1 mg/L orthophosphate caused the greatest decrease in copper leaching (Figure 1-11) the levels did not drop below the EPA Copper Action Limit of 1.3 ppm. Thereafter, orthophosphate dosing was increased to 2 mg/L in an attempt to bring the copper concentration below the EPA Copper Action Limit. The increase dropped the copper levels to 1.27 ppm, which is quite low considering the 48-72 hour stagnation time that was tested (Figure 1-12). The water treated to 70% organic matter removal with activiated carbon did not drop below the action limit, and had slightly higher variability amongst the replicate pipes compared to the condition with orthophosphate (Figure 1-11).

CONCLUSIONS

- Bench-scale testing, in conjunction with field sampling, indicated that an increase in pH (7.8 or above) and/or a boost in chlorine residual will reduce copper leaching. But unfortunately, preliminary testing revealed serious scaling problems on chemical feed nozzles when adjusting pH to this level.
- Stagnation time has a dramatic effect on the amount of copper that gets released into the water (Figure 1-7). If water is left stagnant in a copper pipe system for a long period of time, the amount of copper that inevitably leaches into the water will also increase. In order to reduce the amount of copper in the school's water, flushing the system is recommended after long periods of stagnation.
- Treating the water with granular activated carbon to remove TOC produced less copper leaching.
- Addition of orthophosphate at 2 mg/L as P was effective in reducing copper leaching below the EPA Action Limit for the high alkalinity, high hardness Miami water.

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3. Boulay, N. and Edwards, M. 2000. Role of Temperature, Chlorine, and Organic Matter in Copper Corrosion By-Product Release in Soft Water. *Water Research* 35(3): 683-690.

4. APHA, AWWA, and WEF (American Public Health Association, American Water Works Association, and Water Environment Federation). 1998. *Standard Methods for Examination of Water and Wastewater*, 20th ed. Washington, D.C.: APHA.

Table 1-1. Microbiological presence in water samples showing little activity found.

Location	SRB	HAB	SLYM
Domestic Backflow, Incoming Water	550 cfu/mL	No Activity	No Activity
Kitchen, Following Inline Filter	Water Spilled in Transit	7000 cfu/mL	No Activity
2-045B (Sink)	550 cfu/mL	No Activity	No Activity
4-SE (Hose Bib)	5000 cfu/mL	No Activity	No Activity
5-301 (Sink)	Water Spilled in Transit	No Activity	No Activity
3-065 (Hose Bib)	550 cfu/mL	Very Little Activity, Close to 0 cfu/mL	No Activity

Table 1-2. Water chemistry of domestic backflow water.

Parameter	Value
Alkalinity (mg/L as CaCO3)	197
TOC (mg/L as C)	2.1
Sulfate (mg/L)	18.9
Sodium (mg/L)	24.73
Silica (mg/L)	2.6
Phosphate (ppb)	6.2
Chloride (mg/L)	44.8
Nitrate (mg/L)	2.02
Magnesium (mg/L)	5.9
Calcium (mg/L)	87.4
Iron (ppb)	6.2
pH	7.15
Chlorine range	0.06 to 0.18
UV	0.046

Figure 1-1. Pictures of blue ice cubes from Miami Public School and blue staining in sink.

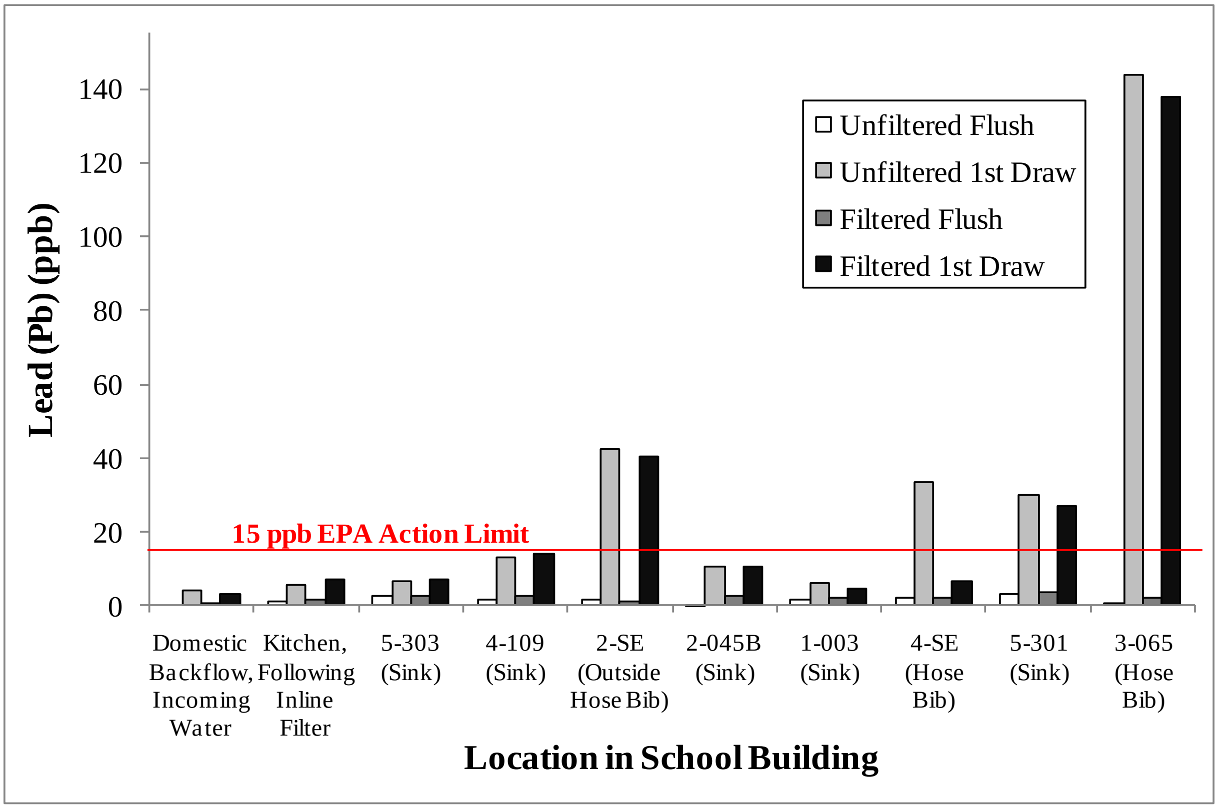

Figure 1-2. Lead Concentration in water from Miami Public School.

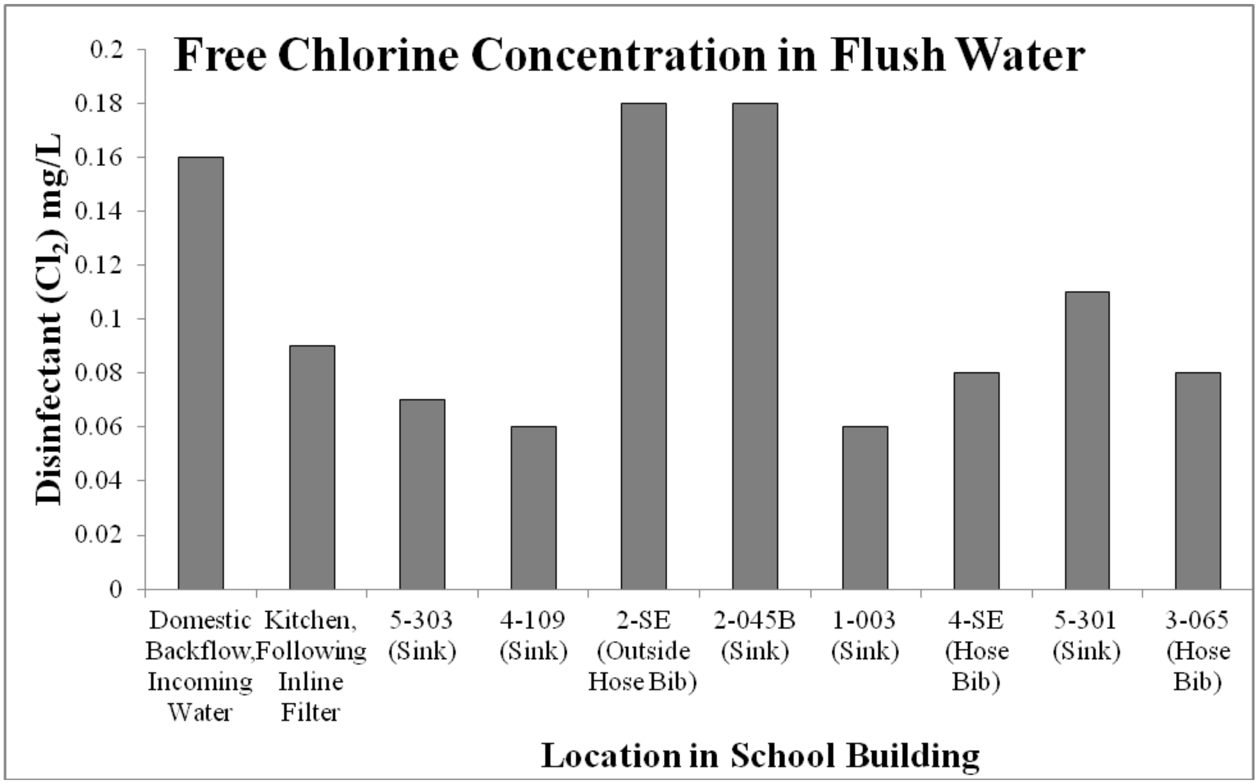

Figure 1-3. Disinfectant (free chlorine) concentration in Miami Public School flush water (water was flushed for 10 minutes).

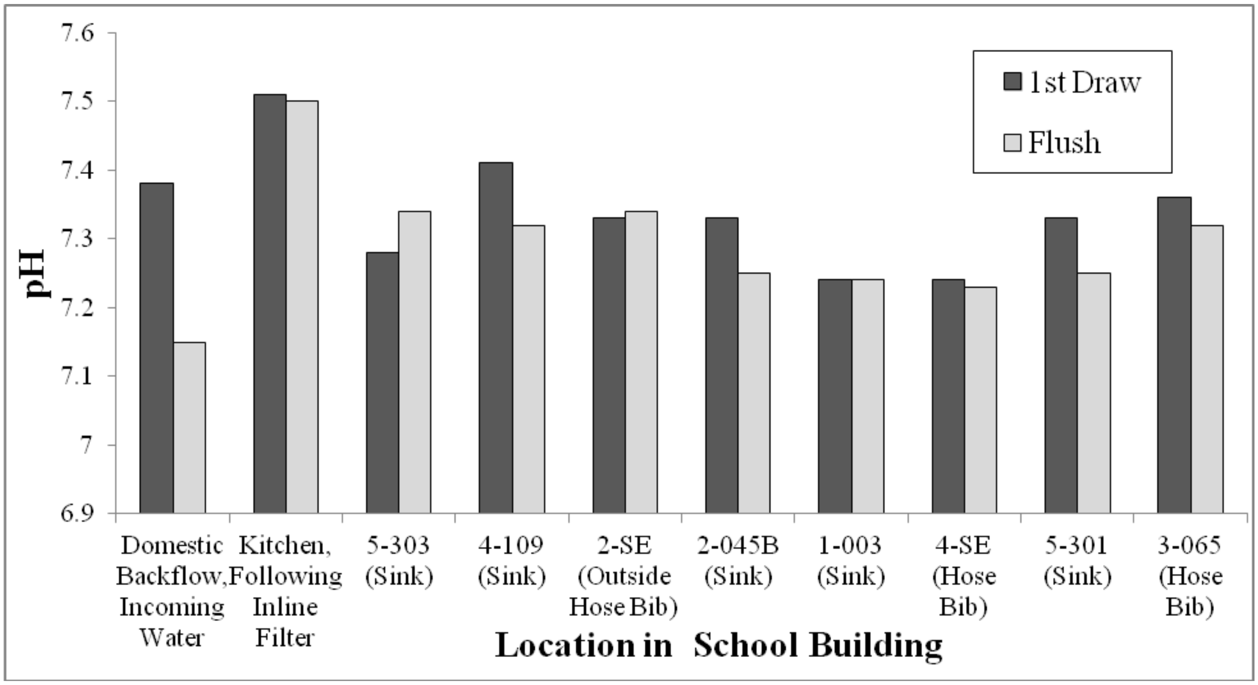

Figure 1-4. pH of water in different School locations for first draw and flush samples. Values taken onsite.

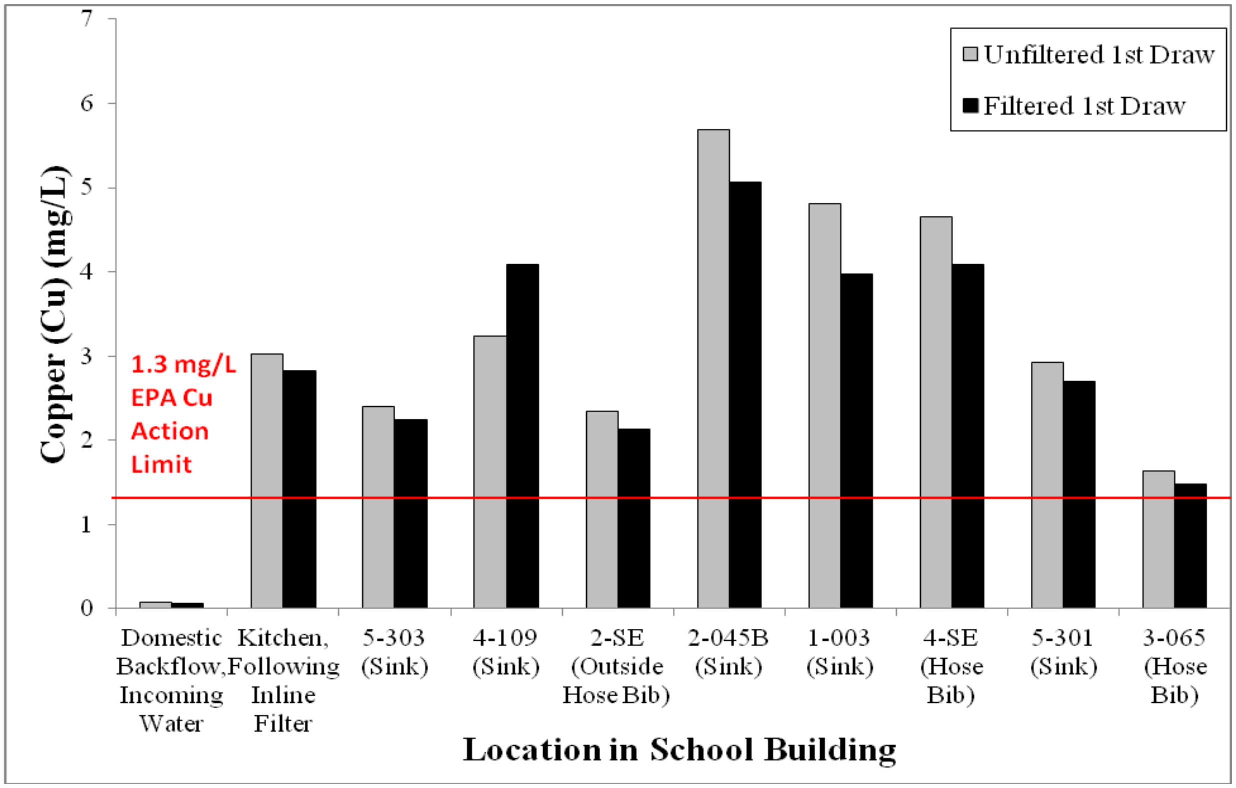

Figure 1-5. Copper concentrations in first draw filtered and unfiltered samples showing copper concentrations exceeded EPA Action Limit in nine out of the ten locations.

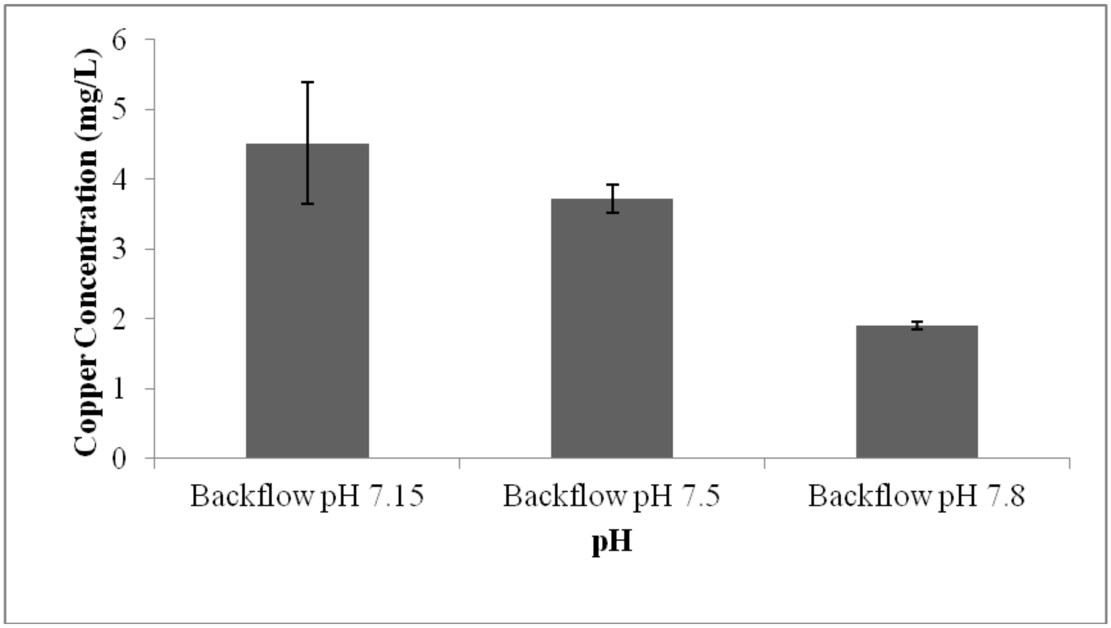

Figure 1-6. Copper release relative to water pH (error bars represent 95% confidence).

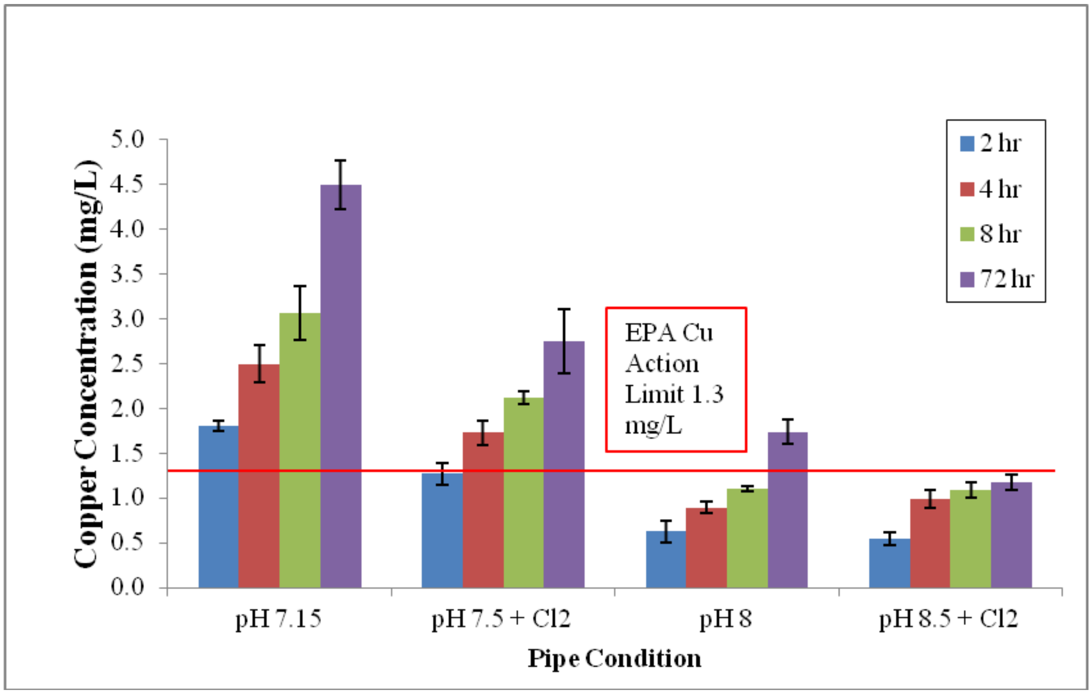

Figure 1-7. Copper release relative to time (error bars represent 95% confidence).

Figure 1-8. Carbon filtered water filter.

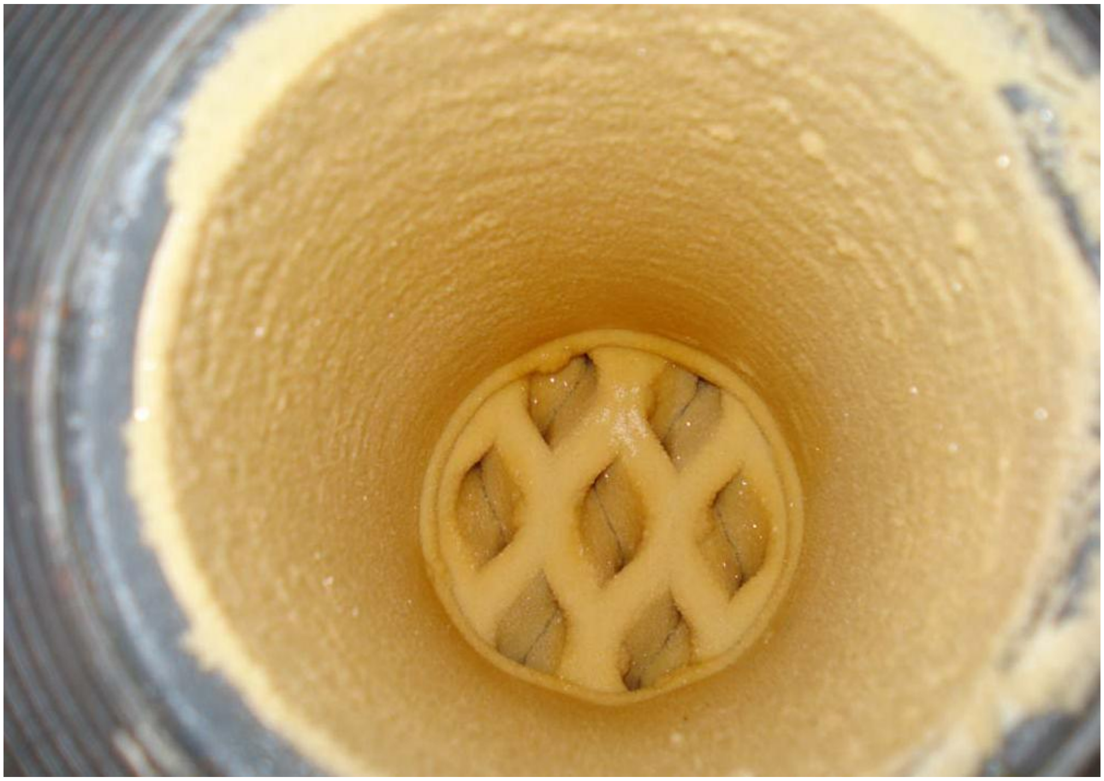

Figure 1-9. Calcite scale clogging pipes in Miami Public School.

Figure 1-10. Calcite scale in Miami Public School.

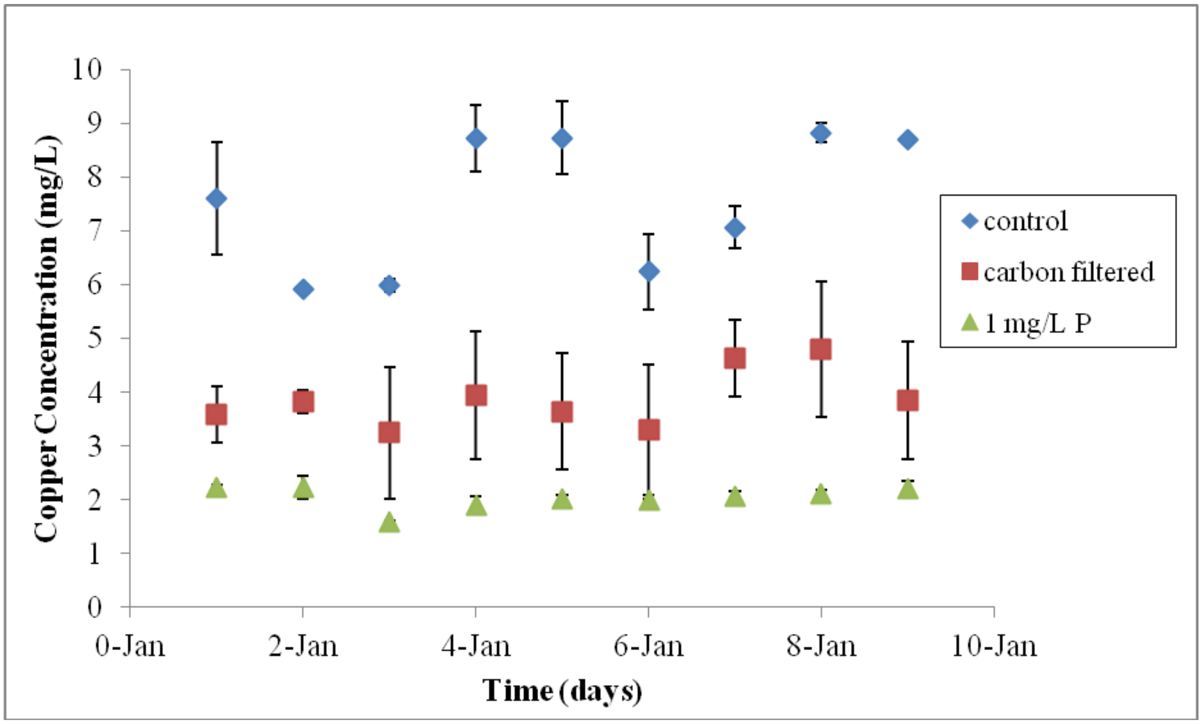

Figure 1-11. Comparison of copper release from control, carbon filtered water, and water with 1 mg/L orthophosphate inhibitor (error bars represent 95% confidence).

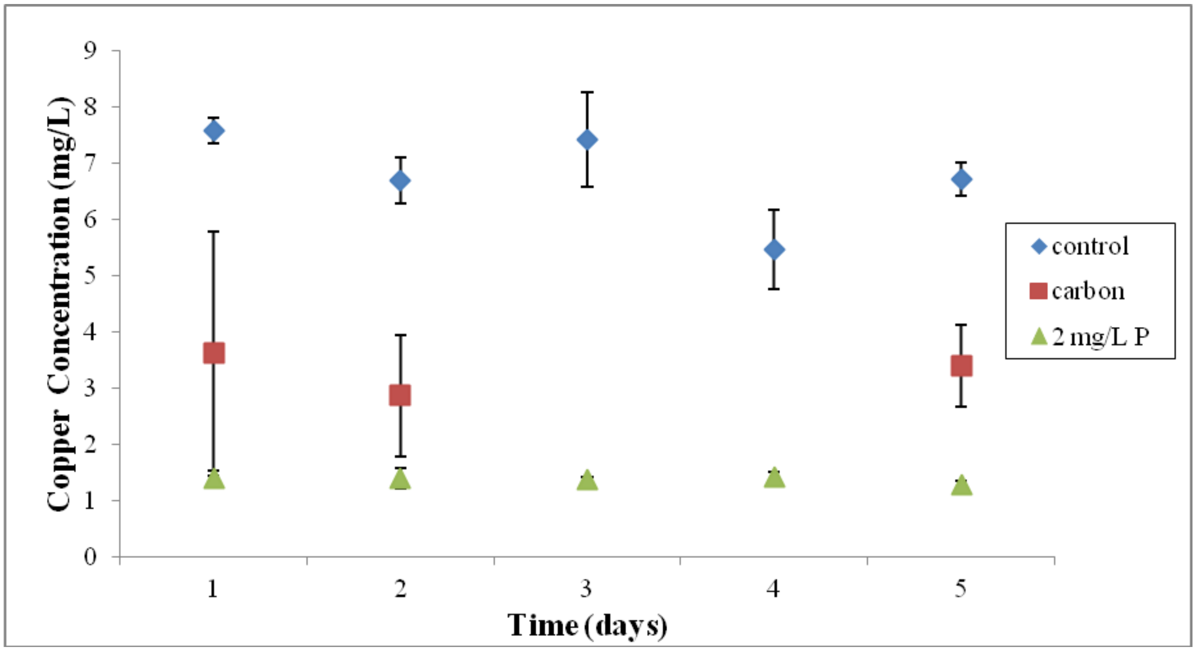

Figure 1-12. Comparison of copper release from control, carbon filtered water, and water with 2 mg/L orthophosphate inhibitor (error bars represent 95% confidence).

CHAPTER 2: EVALUATION OF GALVANIC CORROSION WITH VARIOUS PHOSPHATE CORROSION INHIBITORS USING OWASA WATER

ABSTRACT

There are several options when it comes to corrosion inhibitors, and phosphate based corrosion inhibitors are among the most common. Polyphosphate corrosion inhibitors contain a combination of orthophosphate and polyphosphate. This case study evaluates three different phosphate-based corrosion inhibitors: 100% orthophosphate, 50/50 orthophosphate/polyphosphate, and 70/30 orthophosphate/polyphosphate. Phosphate corrosion inhibitors are effective at reducing corrosion because a protective film layer is formed on the surface of the material, in this case the copper pipe and/or brass rod.

INTRODUCTION

This case study involved a laboratory evaluation of the effects of various phosphate based corrosion inhibitors on galvanic brass corrosion using Orange County Water and Sewage Authority (OWASA) water. The effect of these inhibitors on chloramine decay and the growth of microorganisms were also evaluated.

When two dissimilar metals are in contact, the galvanic connection between the two metals can cause them to corrode. Brass is an alloy of copper and zinc and in this experiment the corrosion results from a reaction between the copper cathode and the brass anode, with the brass sacrificed and the copper protected [1].

Phosphate corrosion inhibitors are used by water utilities to help mitigate water quality issues, such as metal corrosion. Phosphate based corrosion inhibitors are commonly used because they form a protective layer on the corrosive material and prevent further leaching into the water. There are several different options when it comes to choosing a phosphate corrosion inhibitor, but all have different effects on not only the corrosion factor but on the water quality itself. Polyphosphate and orthophosphate are both used in the field; however, polyphosphate often contains aggravating components and manufacturers do not list the specific ingredients in polyphosphate mixtures. Polyphosphate has been found to be less beneficial at reducing copper release when compared to orthophosphate [2].

METHODS AND MATERIALS

Water was shipped from Orange County Water and Sewage Authority (OWASA) to Virginia Tech in five gallon plastic containers for use in this study. Six inch long sections of copper and PVC pipe were exposed to the water. Plastic stoppers were used to seal the ends of the pipes and at one end of each pipe a brass rod was inserted into a hole in the stopper. The copper pipes were then connected to the brass rods with wires to facilitate measurements of galvanic corrosion between the anodic brass and the cathodic copper (Figure 2-1). The pipes were filled with water and placed horizontally on the bench.

Four inhibitor conditions were tested: control with no added inhibitor, orthophosphate inhibitor, 50/50 orthophosphate / polyphosphate inhibitor, and 70/30 orthophosphate/ polyphosphate inhibitor. The total concentration of phosphorus was 0.8 mg/L (as P) for each condition. Fresh stock solutions of the polyphosphate-containing inhibitors were prepared every two weeks to ensure that the polyphosphate did not revert to orthophosphate. Triplicate pipes were used for each condition so that statistical analyses could be performed.

Before the water was added to the pipes during each water change, 1 mg/L chloramine was added to the water using ammonia and chlorine stock solutions (individual concentrations were 0.5 mg/L ammonia and 0.5 mg/L chlorine). Ammonia was added to the water and chlorine was slowly added while the solution was stirred rapidly. Ammonia, total chlorine, and free chlorine levels were measured to confirm targeted levels were achieved. Ammonia levels were measured on a Hach DR2000 spectrophotometer according to Standard Method 4500-NH_3 [3]. Total and free chlorine were also measured on a Hach DR 2000 spectrophotometer according to Standard Method 8167 [3]. The pH was adjusted to 8.2, a target level in the UNC system (using 1 N sodium hydroxide), and measured with a pH electrode according to Standard Method 4500-H^+ B [3].

The water was then poured into four plastic containers and the inhibitors were added to their respective containers before adding the water to the pipes. The final concentration of inhibitor was 0.8 mg/L (as P) for each test condition. The ‘dump-and-fill’ method was used for each water change on Monday, Wednesday and Friday.

Heterotrophic Plate Counts (HPC) were performed every week to track the microbial activity in the pipes. R2A agar plates were made fresh each week and plated using dilutions of

10^4, duplicates of 10^3, and 10^2. The plates were left to sit at room temperature and colonies were counted one week later.

Total metal release was measured by analyzing samples preserved with 2 % nitric acid on a Thermo Electron X-Series Inductively Coupled Plasma Mass Spectrophotometer (ICP-MS) per Standard Method 3125 [3]. Chloramine decay was measured in all pipes after each water change. Total chlorine, free chlorine, and ammonia were measured to track the decay rate. Measurements were taken at 30 minutes, 3 hours, 24 hours, and 48 hours to get a decay curve for the chloramine.

RESULTS AND DISCUSSION

Effects of Phosphate Inhibitors on Metal Leaching and fate of Phosphorous

Results from this case study indicated that 100 % orthophosphate inhibitors were more effective at reducing metal release than orthophosphate/polyphosphate inhibitor mixtures in both copper and PVC pipes, both containing a brass rod inside. Lead release was highest in both PVC and copper pipes containing no inhibitor and lowest in pipes containing 100% orthophosphate inhibitor (Figure 2-3). Lead release was lower in PVC pipes compared to copper pipes under all inhibitor conditions, indicating accelerated leaching of lead due to galvanic corrosion. The starting pH was 8.2 and decreased in both the copper and PVC pipes after a three day stagnation period (Table 2-1).

There was very little difference in copper release between the ortho/poly combination inhibitors. There was a slight benefit to using 100% orthophosphate (Figure 2-2). For PVC pipes, brass was the only copper source and the 100% orthophosphate inhibitor had the lowest average copper release while the control pipes with no inhibitor had the highest average copper release. In all cases copper release was less than the EPA action level of 1.3 ppm.

A large amount of phosphate disappeared from the water during the early stages of the experiment in the copper pipes galvanically connected to brass rods (Figure 2-5). Specifically, about 75% of the phosphate was removed during the first two water changes, and 50% was removed in the next two water changes, and thereafter about 25% was removed during each testing period. The phosphate was presumably consumed in reactions with the copper and brass pipe surface that formed scale on the pipe wall, since little phosphate precipitated in the PVC pipes (Figure 2-6).

Effects of Phosphate Inhibitors on Microbial Growth

HPCs were performed each week in order to compare the microbial activity within the copper and PVC pipes (Figure 2-4). During the first four weeks of the experiment, 1 mg/L chloramine was added to the water prior to each water change. After the first four weeks the chloramine level was increased to 2 mg/L chloramine (0.5 mg/L ammonia plus 2.0 mg/L chlorine). The results showed that during the first four weeks the HPCs in the copper pipes were higher than the HPCs in the PVC pipes, indicating that in this experiment the bacteria grew better in the copper pipes compared to the PVC pipes.

Effects of Phosphate Inhibitors on Chloramine Decay

Chloramine decay was tracked throughout the experiment. Initial chloramine concentrations were 1 mg/L and were increased to 2 mg/L after the first month. Chlorine concentrations began to decrease within the first hour after each water change (Figure 2-8). Ammonia concentrations showed very little decrease until about 48 hours (Figure 2-9). The rate of chloramine decay did not differ significantly between the different phosphate inhibitors. The chloramine in the copper pipes did show a slightly faster decay rate compared to the PVC pipes, providing a potential explaination for the higher levels of bacteria in copper pipes measured in the preceeding section.

Effects of Phosphate Inhibitors on Galvanic Corrosion

A galvanic connection was made between the copper pipes and the brass rod inserted using a Fluke 189 True RMS Multimeter and recorded as microAmps/cm^2 (Figure 2-7). Galvanic measurements were taken at two hours, two days, and three days (Figure 2-7). The results indicated significant galvanic currents at all time periods, but there were only subtle differences between conditions exposed to different inhibitors.

CONCLUSIONS

The most effective inhibitor at preventing metal leaching was 100% orthophosphate. The orthophosphate inhibitor caused a significant decrease in both copper and lead leaching in copper pipes when compared to the control, 50/50 orthophosphate/polyphosphate inhibitor, and 70/30 orthophosphate/polyphosphate inhibitor (Figures 2-2 & 2-3). The PVC pipes had similar copper and lead leaching trends, except that the levels were much less because the only source of metal leaching was from the brass rod.

The HPC data indicated that there was a significantly higher amount of heterotrophic activity in the copper pipes containing inhibitors when compared to the PVC pipes containing inhibitors. The control PVC and copper pipes had similar HPC levels.

None of the phosphate inhibitors showed a significant difference in chloramine decay. The chlorine decayed by about 50% within the first hour and reached zero by 24 hours in all but one condition, the PVC control. The ammonia had a very slow decrease over the 24 hour period and levels dropped from ~0.5 mg/L-NH_3 to about 0.4 mg/L-NH_3 in the PVC 70/30 Orthophosphate/Polyphosphate condition.

There was not a significant difference in the rate of chloramine decay amongst the different phosphate inhibitors compared to the control without inhibitors. The chlorine decayed to 0 mg/L in all conditions over the 24 hour period except for the PVC control condition which dropped to approximately 0.04 mg/L. The ammonia concentrations all decayed at a similar rate over the 24 hour period.

There was not a noticeable difference in the galvanic corrosion between the 50/50 orthophosphate/polyphosphate inhibitor and the 70/30 orthophosphate/polyphosphate inhibitor but both caused the biggest decrease in galvanic corrosion compared to the control and 100% orthophosphate inhibitor when tested two hours after changing the water. The levels changed drastically between the times tested. After 2 and 3 days the control and 100% orthophosphate levels were almost identical and the other phosphate inhibitor mixtures were within a similar range.

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Table 2-1. Change in pH after three day stagnation.

Pipe Conditions	Initial pH	pH after 3 days stagnation
Copper control	8.2	7.86
Copper Orthophosphate	8.2	7.86
Copper 50:50 Orthophosphate: Polyphosphate	8.2	7.67
Copper 70:30 Orthophosphate: Polyphosphate	8.2	7.83
PVC control	8.2	7.69
PVC Orthophosphate	8.2	7.72
PVC 50:50 Orthophosphate: Polyphosphate	8.2	7.69
PVC 70:30 Orthophosphate: Polyphosphate	8.2	7.42

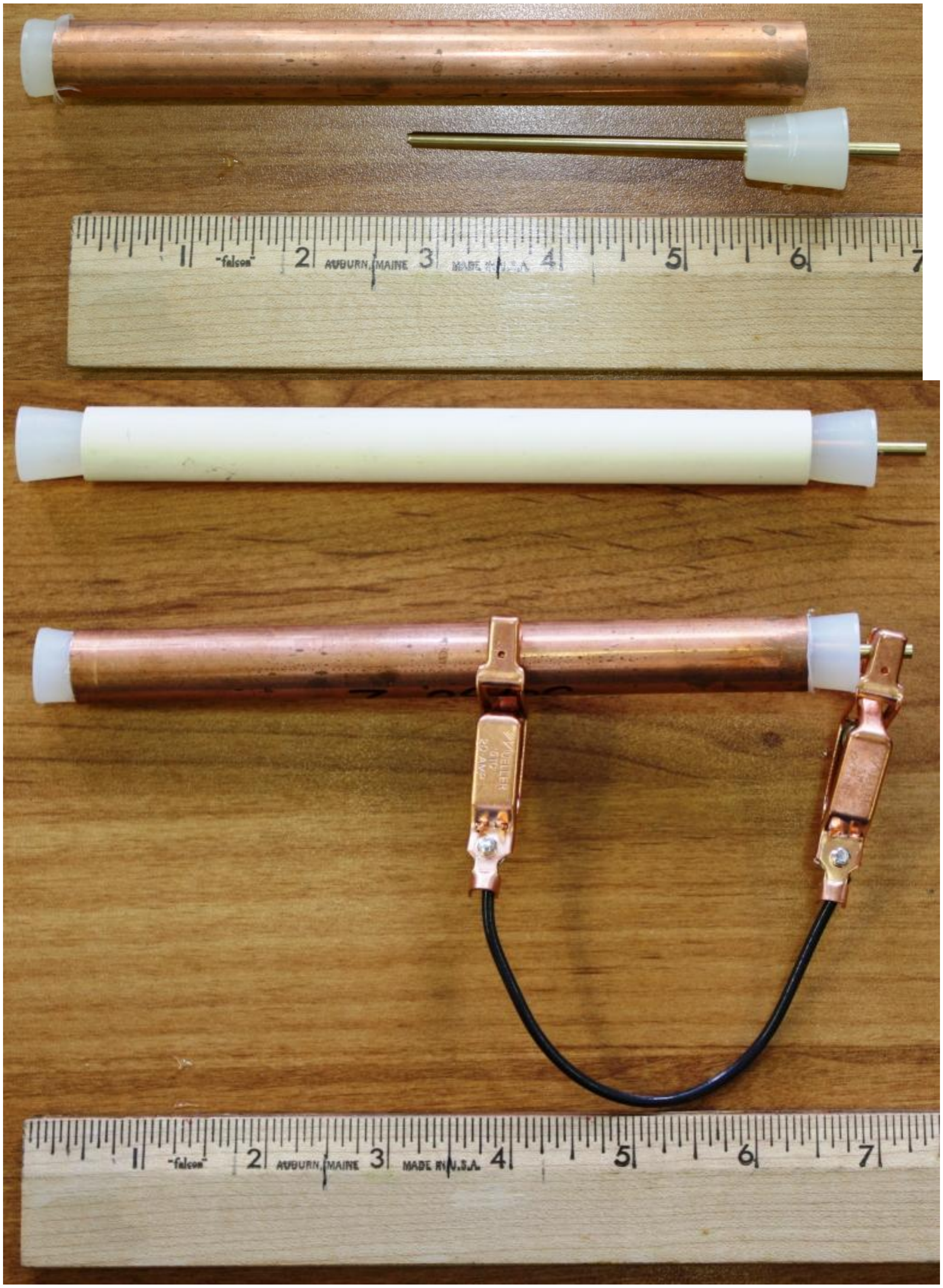

Figure 2-1. Pipe and leaded brass experiment to consider the ability of various phosphate corrosion inhibitors to reduce lead leaching.

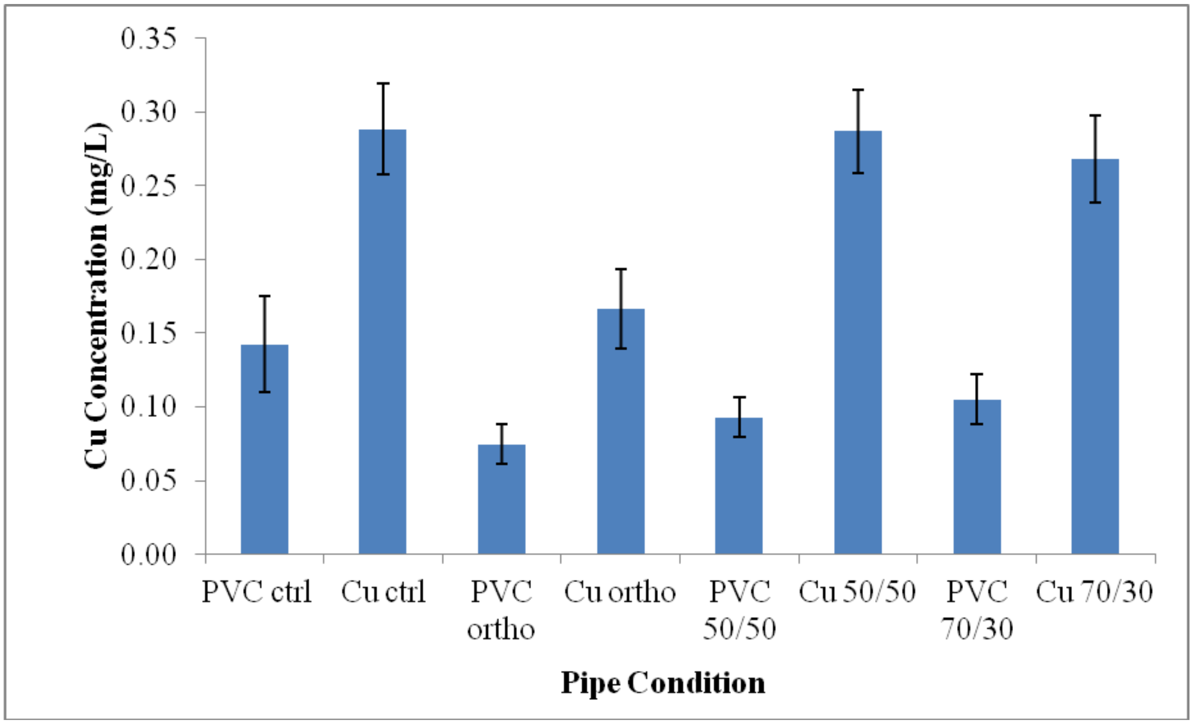

Figure 2-2. Copper release for copper pipe galvanically connected to brass rod (error bars represent 95% confidence).

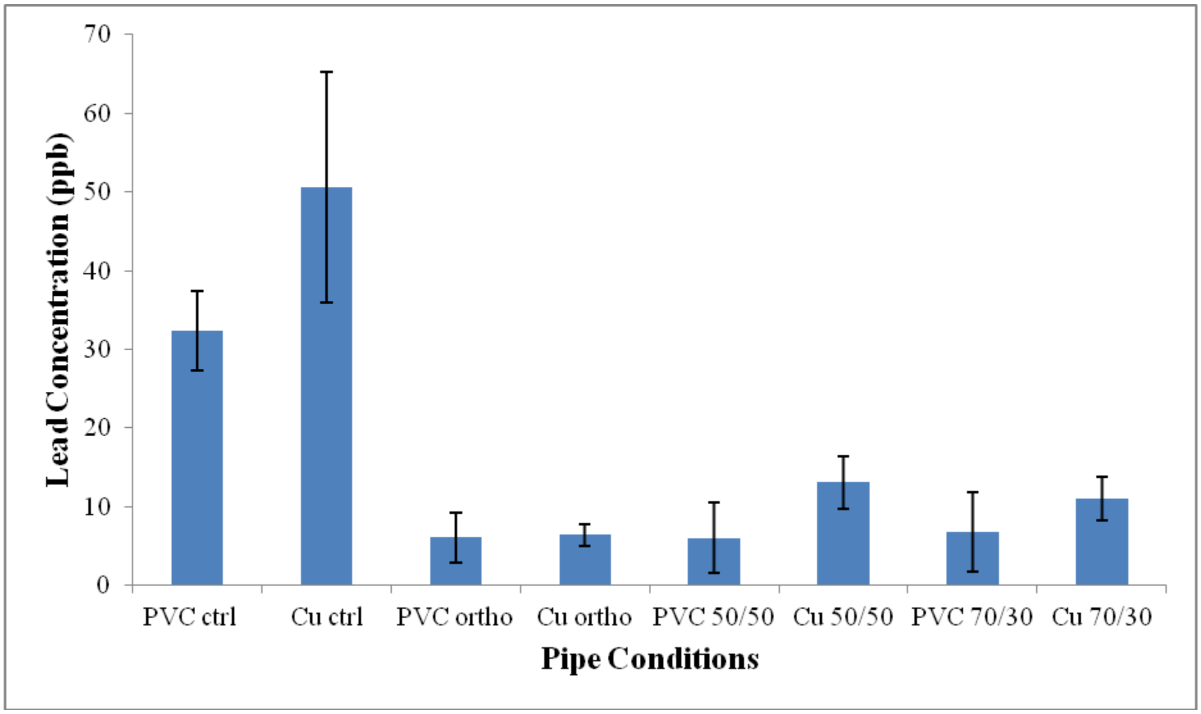

Figure 2-3. Lead release for copper pipe galvanically connected to brass rod (error bars represent 95% confidence).

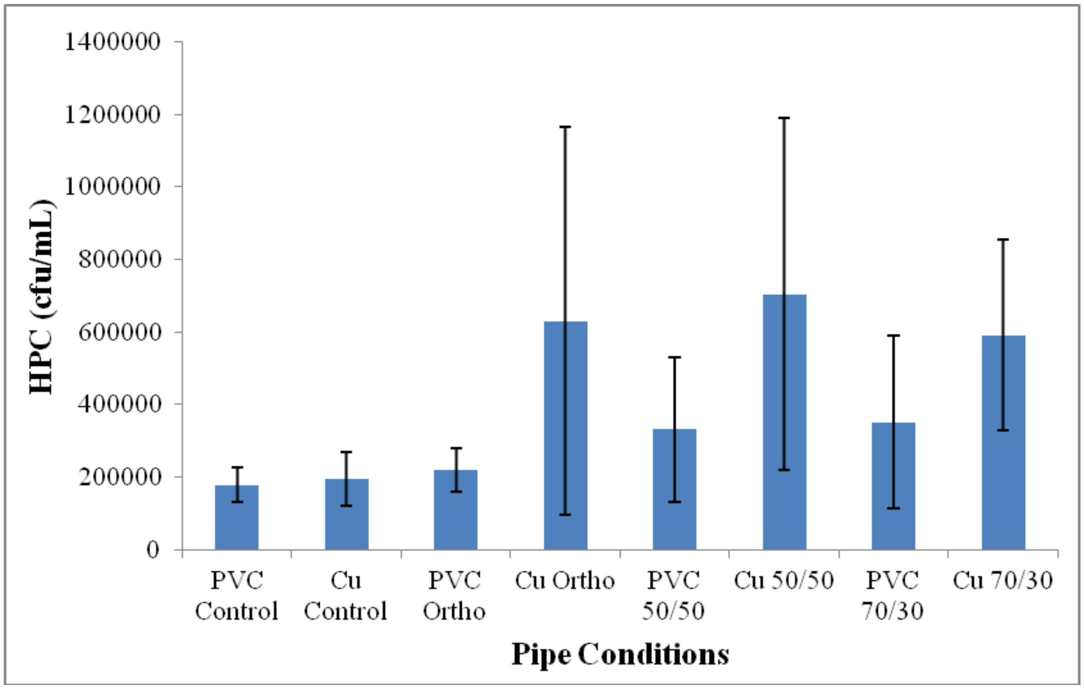

Figure 2-4. Heterotrophic Plate Count's (cfu/mL) among PVC and copper pipes with different phosphate inhibitors. These averages represent data from the first four weeks (error bars represent 95% confidence).

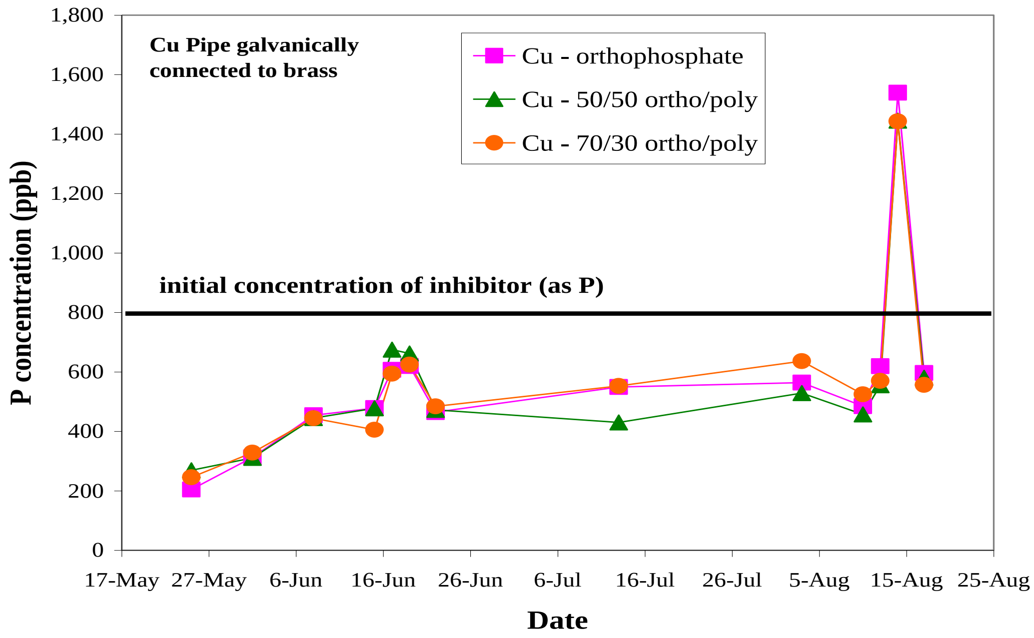

Figure 2-5. Phosphorus concentration as a function of time for copper pipe galvanically connected to brass. There is a substantial uptake of phosphorus early in the experiment followed by a near constant uptake after about 3 weeks. Spike was caused by improper dosing.

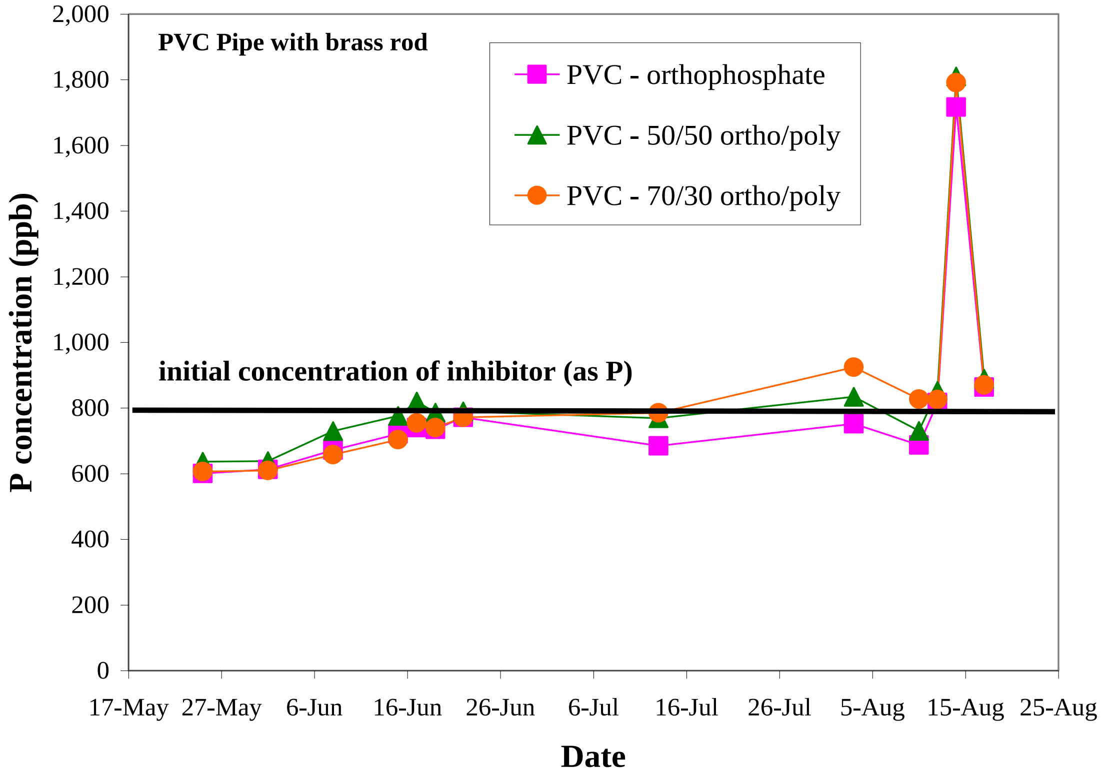

Figure 2-6. Phosphorus concentration as a function of time for PVC pipe with inserted brass rod. There is a little uptake of phosphorus early in the experiment; however, after 3 weeks no further uptake was observed. Spike was caused by improper dosing.

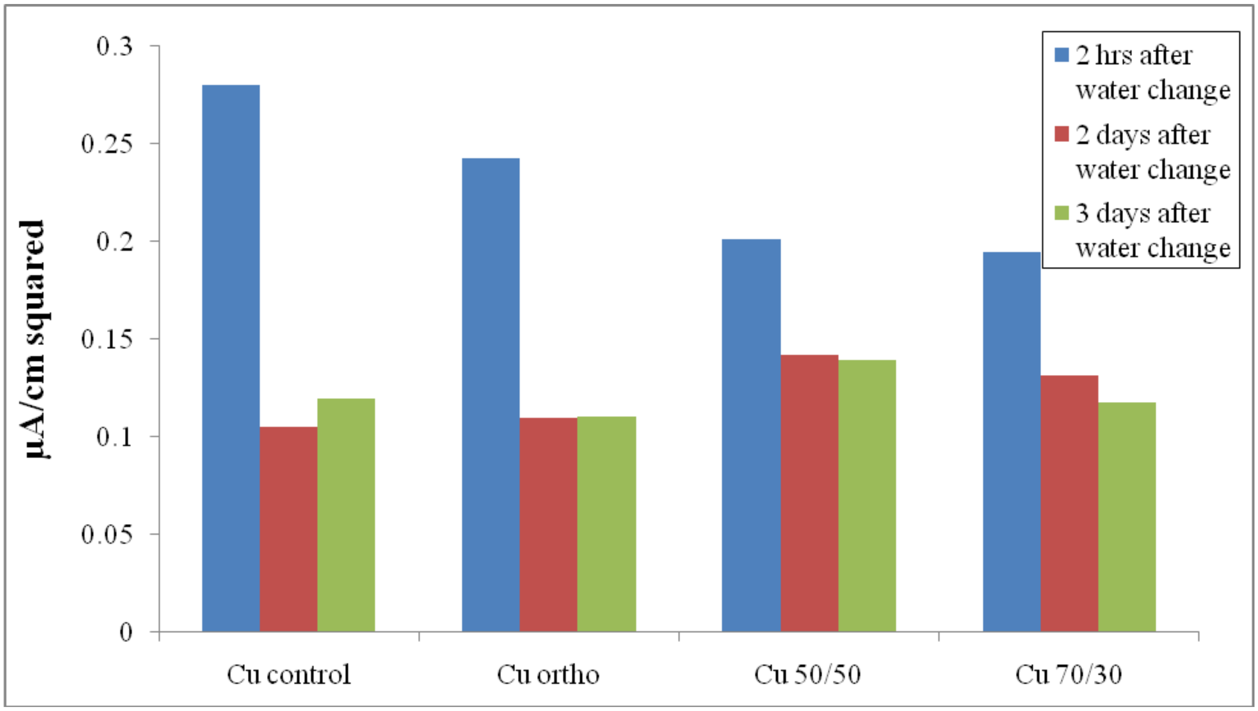

Figure 2-7. Effects of phosphate inhibitors on galvanic corrosion relative to time.

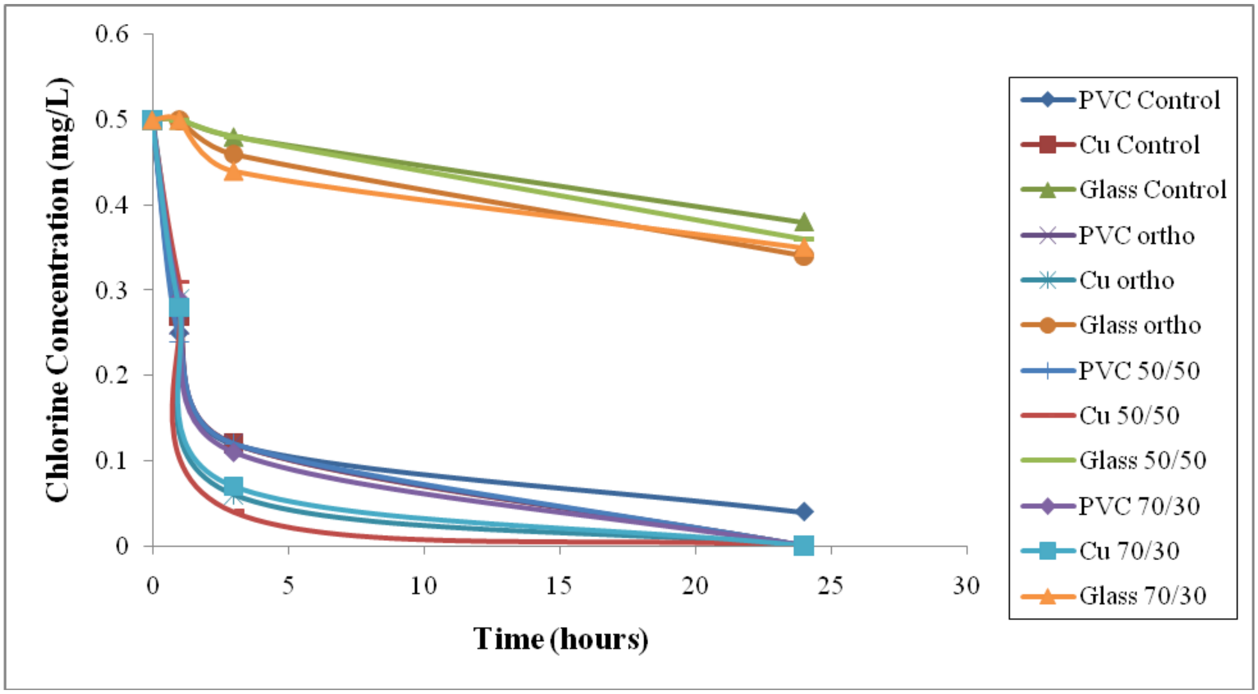

Figure 2-8. Chloramine decay as chlorine concentration in PVC pipes, copper pipes, and control glass bottles.

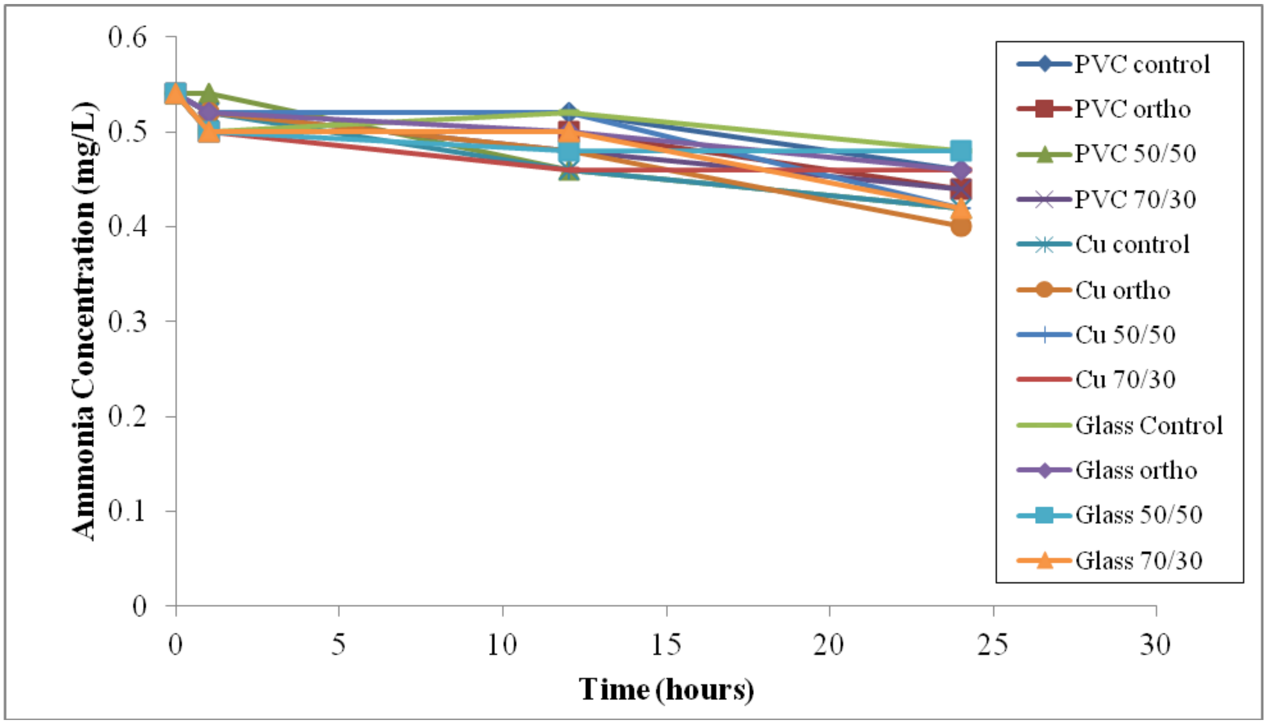

Figure 2-9. Chloramine decay as ammonia concentration in PVC pipes, copper pipes, and control glass bottles.

CHAPTER 3: FLUX AS INHIBITORS/INITIATORS OF MICROBIAL GROWTH

ABSTRACT

Overuse of plumbing flux, coupled with inadequate rinsing of plumbing lines, can create a situation with high levels of ammonia in building plumbing systems which allow nitrifiers to proliferate. Resulting water quality problems in buildings can include exceedance of the 1 mg/L nitrite standard, higher levels of lead and copper leaching, higher levels of bacteria, and more rapid loss of disinfectant. Problems can be reduced by following guidelines that minimize flux use and that carefully rinse plumbing.

INTRODUCTION

Occurrence of nitrification in premise plumbing can create problems with rapid disinfectant decay, higher microbial re-growth potential, increased lead/copper leaching, and reduced control of premise plumbing pathogens[1,2]. The precise factors that allow nitrifiers to establish in copper premise plumbing systems have not been defined, because prior work indicated that copper is highly bacteriostatic to nitrifiers [1]. Better understanding of factors which allow nitrifiers to colonize copper pipes is of high interest.

One earlier case study of copper corrosion problems in brand new construction identified high levels of nitrifier activity in a situation where excessive petroleum based flux had been used [3]. Flux is a chemical used to prepare metal surfaces for effective soldering, and is used at all copper-copper or copper-brass soldered joints in premise plumbing. A wide variety of water based and petroleum based flux is commercially available. A key ingredient in many flux mixtures is ammonia, which is the primary substrate for nitrifying bacteria. It has been reported that excessive amounts of flux is often used during soldering and the residual flux can create water quality problems [4]. It was considered likely that high levels of ammonia and possibly other constituents in flux could, under some circumstances, initiate rampant nitrifier colonization of new copper premise plumbing systems. The goal of this research was to test this hypothesis under realistic circumstances.

METHODS AND MATERIALS

Flux in Water

A range of commercially available flux was obtained and tested by adding one gram of flux to 100 mL of reagent grade water. Ammonia was measured using a Hach DR2000 spectrophotometer salicylate method, according to Standard Method 4500-NH_3 [5]. The pH was measured using a pH electrode according to Standard Method 4500-H^+ B [5]. Samples were analyzed for metal concentrations using a Thermo Electron X-Series Inductively Coupled Plasma Mass Spectrometer (ICP-MS) according to Standard Method 3125-B [5]. Total Organic Carbon (TOC) was also measured according to Standard Method 5310 [5]. After analyzing the results three examples of flux were selected to represent extremes of ammonia, pH and chloride levels (Table 3-1). At the outset we note that typically, ammonia levels in potable water are rarely over 1 mg/L NH3-N due to use of chloramines in potable water systems [6, 7], yet nitrification can still be problematic. The water contacting two fluxes used in this study contained ammonia levels at least 200 times the levels commonly encountered in potable water systems.

Flux in Copper Pipe

Copper joints were soldered together using the different fluxes to produce plumbing assemblies with 2 elbows and 1 straight joint for experimentation. Rubber stoppers were used to seal each end of the assembly and tygon tubing and metal clamps were used to hold the joints together so that the assemblies could be disassembled and the inside surface of the pipes evaluated (Figure 3-1).

The three types of flux were tested in pipe rigs in a variety of methods including: 1) very high flux application without any flushing, 2) very high flux application that had been thoroughly flushed for one week, and 3) no flux at all. One gram of flux was used to solder each individual joint together and therefore each copper pipe assembly contained a total of six grams of flux and 200 mL's of water. Triplicate pipes were tested at each condition making 27 tests total (Figure 3-2). A parallel experiment used a set of PVC pipes with joints glued together as an additional control.

Inoculation of Nitrifying Bacteria into Copper Pipes

Synthetic water containing a seed of active potable water nitrifying bacteria that had colonized premise plumbing systems in a prior research project was constituted (Table 3-2) [1]. A Nitrifier Biological Activity Reaction Test (N-BART) was performed to verify that the original nitrifier stock water had viable nitrifiers present. N-BART's use a colorimetric method of showing nitrifier activity by measuring nitrate production, and provide results associated with four semi-quantitative levels of nitrifiers in samples: 0 cfu/mL, 1,000 cfu/mL, 10,000 cfu/mL, and ≥100,000 cfu/mL. The nitrifier seed water in this study tested positive for nitrifiers at a level of ≥100,000 cfu/mL. The copper pipes were then filled with this nitrifier stock water and held stagnant for three weeks, as might occur in new building pre-occupancy, in order to provide an opportunity for inoculation.

Water Chemistry Measurements

The water was changed in the pipes twice each week, and once each week samples were collected and analyzed according to Standard Method procedures [5]. Heterotrophic Plate Counts (HPCs) were conducted in order to monitor microbial activity according to Standard Method 9215 [5], and nitrate, nitrite, chloride and sulfate levels were monitored using Ion Chromatography (IC) according to Standard Method 4110 [5].

RESULTS AND DISCUSSION

Effect of flux on water quality after 3 week stagnation

After the initial three week stagnation, the water removed from the copper pipe rigs with unflushed low ammonia flux and the unflushed petroleum flux exhibited a greenish blue color and contained chunks of flux that had flushed out of the pipes (Figure 3-3). The unflushed high ammonia flux did not show the same color change as the other two fluxes but there was visible turbidity in the water and small particles of flux were also visible. This color effect continued to decrease as the water was changed bi-weekly. The pipe samples that had been thoroughly flushed for one week prior to the three week stagnation time had no issues with high copper or color, highlighting the benefits of thorough flushing.

The flux impacted the aesthetic value of the water as well as the water quality itself. Concentrations of chloride, zinc, and ammonia increased in response to the addition of flux

(Table 3-3). The ammonia concentration increased in all conditions when compared to the control pipe assemblies, which contained no flux and had negligible amounts of ammonia (0.02 mg/L). The low ammonia flux caused a slight increase in ammonia concentrations in both the unflushed flux and flushed flux conditions, 0.36 mg/L and 0.33 mg/L, respectively. The high ammonia flux generated an ammonia concentration of 31 mg/L in the unflushed flux condition and a concentration of 22 mg/L in the flushed flux condition. The petroleum flux conditions produced a remarkable increase in ammonia: the ammonia in the flushed petroleum flux condition increased to 25 mg/L and the ammonia in the unflushed petroleum flux condition increased to 200 mg/L (Table 3-3, Figure 3-4).

The chloride concentrations also showed remarkable increases when compared to the control condition, which contained 63 mg/L chloride. The low ammonia flux flushed condition was similar to the control with 72 mg/L chloride. All other conditions contained significant increases in chloride concentrations with the most remarkable increase to 1750 mg/L in the unflushed petroleum flux condition (Table 3-3, Figure 3-5).

The three week stagnation period also caused increases in zinc concentrations under all conditions. The control condition contained the lowest zinc concentration of 19 ppb zinc and the unflushed high ammonia flux condition contained the highest zinc concentration of 13,750 ppb zinc (Table 3-3, Figure 3-6).

The increasing concentrations of ammonia, chloride and zinc confirmed that the addition of flux to a pipe system can dramatically affect the water quality if water is allowed to sit stagnant for a significant period of time.

Effect of water changes on water quality

During periods of stagnation, some constituents settle and can build up. As water was changed twice per week, the high concentration of constituents in flux gradually decreased. After the three week stagnation and the subsequent three weeks of water changes the ammonia concentration had decreased to undetectable levels in all conditions (Figure 3-7). The ammonia was initially highest in the petroleum flux, which reached 200 mg/L, but after three weeks the water showed no sign of such high ammonia levels.

Chloride is a highly soluble component of the flux, therefore monitoring the decrease in chloride concentration over the three weeks is an accurate method of illustrating the effectiveness of flushing. The control condition had low concentrations of chloride compared to the flux conditions and showed little change over the three week test; however, each of the conditions containing flux showed substantial decreases in chloride concentrations over the three week period (Figure 3-8).

Zinc is listed as a contaminant in the EPA secondary drinking water regulations with a secondary maximum contaminant level set at 5 mg/L [8]. Flushing had a similar effect on zinc concentrations as it did on the ammonia and chloride concentrations. The high ammonia flux contained the highest concentration of zinc, measuring 13.8 mg/L after one week of water changes. After three weeks of water changes, the zinc levels had decreased by more than 50%; however, the zinc concentration did not quite fall below the secondary standard of 5 mg/L. The other conditions had very low amounts of zinc present throughout the testing period (Figure 3-9).

Microbial growth after stagnation and water changes (Nitrification)

Nitrification involves the conversion of ammonia to nitrite and lastly into nitrate. Monitoring nitrification is most accurately done by keeping track of each parameter [9]. Partial nitrification can occur when ammonia conversion stops at nitrite. A drop in pH due to the consumption of alkalinity is a common result of nitrification [9]. In order to monitor nitrification activity in the different conditions, these key parameters were examined (in addition to the nitrifying BARTs).

After three weeks of stagnation, water samples were collected (Table 3-3) and testing for nitrifying bacteria through BARTs was also conducted. No ammonia was added to the water during these three weeks of water changes. The flushed pipe conditions resulted in a decrease in pH and showed nitrite presence between weeks one and three. The pH levels dropped in all conditions but showed the most prominent decreases in the low ammonia flux and high ammonia flux flushed pipe conditions (Figure 3-10). Nitrite data confirmed nitrification was occurring in the unflushed high ammonia flux condition and all three flushed flux conditions (Figure 3-11).

Microbial Growth and Monitoring (Heterotrophic Bacteria)

In addition to reducing pH, nitrification produces assimilable organic carbon (AOC) which can stimulate heterotrophic bacteria colonization in drinking water systems [1]. Heterotrophic bacteria can cause health implications in drinking water systems and heterotrophic plate counts (HPC) is a procedure used to estimate the amount of viable heterotrophs present in a water sample [10]. The EPA reports that a well treated water system will generate low HPCs and vice versa [10].

The unflushed pipes in this experiment showed a significant variation in HPCs over the three week testing period. The control condition had the least amount of variation between week one (211,500 cfu/mL) and week three (983,333 cfu/mL) resulting in an increase of 447%. The unflushed low ammonia flux condition showed an increase from 2100 cfu/mL to 3,660,000 cfu/mL from week one to week three, resulting in an increase of 174,285%. HPCs in the unflushed petroleum flux condition increased from 200 cfu/mL at week one to 35,000 cfu/mL at week three, an increase of 17,400%. HPCs in the unflushed high ammonia flux condition increased from 155,000 cfu/mL to 6,600,000 cfu/mL for an increase of 4,158% (Figure 3-12).

The percent increases in HPC for the flushed pipe conditions were not as extreme as those observed in the unflushed pipes. The high ammonia flux condition had the greatest increase, by 3,246%, in HPCs from week one to week three. The petroleum flux condition also showed a slight increase, from 920,000 cfu/mL to 1,640,000 or 78%, in HPC activity. The HPC in the low ammonia flux condition decreased from 2,470,000 to 1,430,000, representing the only decrease (by 72%) in HPCs among all conditions tested (Figure 3-13).

It was hypothesized that some of the residuals (such as ammonia flux) could enhance nitrification, whereas in other instances high concentrations of other constituents in the flux (or mobilized by flux, such as copper) could hinder nitrification. Nitrifier activity was monitored after three weeks and again after eleven weeks using nitrifying BART's to determine the effects that the different fluxes had on nitrifier activity. Nitrifier activity was confirmed in several of the pipes and the extent of the colonization varied markedly among the conditions tested (Figures 3-14 & 3-15).

To examine the effects of unflushed flux on nitrifiers, water with > 100,000 cfu/mL nitrifiers was added to each of the pipes and left to sit stagnant for three weeks. All nitrifier activity was undetectable in the unflushed pipes after three weeks, except for the control condition with no flux addition, suggesting that the high levels of copper and other constituents in the water (Table 3.3) inactivated the nitrifying bacteria. In order to test the hypothesis that the flux could serve to initiate nitrification, after the three weeks of water changes without additional ammonia, a dose of 1 mg/L ammonia was added to the water for the subsequent six weeks.

After twelve weeks of water changes without adding additional nitrifier inoculant, the nitrifier levels increased appreciably, indicating that flushing water through the pipes eventually created an environment highly suitable for nitrifier growth. The nitrifiers reached the maximum BART detection limit in the unflushed petroleum flux and unflushed low ammonia flux conditions. Nitrifier activity also increased to 10,000 cfu/mL in the control and unflushed high ammonia flux conditions (Figure 3-14).

In pipes in which potentially toxic contaminants were pre-flushed, the low ammonia and petroleum fluxes had high nitrifier activity at week three through week eleven ($\geq$ 100,000 cfu/mL). The flushed pipe with high ammonia flux had no nitrifier activity after three weeks of water changes but had detectable nitrifier activity (~1,000 cfu/mL) after eleven weeks. The control condition had slight nitrifier activity of ~1,000 to 10,000 cfu/mL (Figure 3-15). For the control condition, apparently the nitrifier stock used for inoculation provided enough nutrients to sustain nitrifier growth until 1 mg/L ammonia was dosed to the water after week three.

Effects of pH on Copper Release

The incidence of nitrifiers dropping pH and causing copper leaching is of great concern. Copper concentration and pH were strongly correlated in the unflushed high ammonia flux condition (Figure 3-16). The pH of the water was adjusted to 8 prior to each water change and progressively decreased with each water change (i.e. at week one the pH dropped from 8 to 6.74, at week two the pH dropped from 8 to 6.65, and at week three the pH dropped from 8 to 6.34). The decreasing pH resulted in the copper concentration exceeding the EPA Copper Action Limit of 1.3 ppm after three weeks [11].

CONCLUSIONS

- Excessive flux can result in aesthetic, chemical, and microbial water quality issues.

- Thorough flushing might be an effective way to reduce adverse consequences of flux; however, in this work flux still created microbial problems even with flushing.

- Initiation of nitrification and associated pH drops can create problems with copper leaching.

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Table 3-1. Flux constituent concentrations. One gram of flux was dissolved in 100 mL of nanopure water and heated for an hour to dissolve flux.

Sample ID	B813 Compliant	TOC mg/L	NH_3 mg/L	pH	Cl mg/L	Cu ppb	Zn ppb	Sn ppb	P ppb
High Ammonia Water Soluble Flux	Yes	4560	500	6.7	109	2.6	186	18	72.6
Low Ammonia Water Soluble Flux	Yes	2350	6.8	8.7	21	5.2	279	60	138.2
Traditional Petroleum Flux	No	7	230	8.3	108	1,501	96,690	364	0.0

Table 3-2. Water quality parameters for flux in copper pipe experiment.

	Concentration (mg/L)
Na	50
Ca	6.8
Mg	20
Si	20
K	0.6
SO_4	85
PO_4	3
NO3	24
NaHCO3	7.9
pH	8.0

Table 3-3. Water quality constituents after three week stagnation period in copper pipes.

Sample ID	TOC mg/L	NH_3 mg/L	pH	Cl mg/L	Cu ppb	Zn ppb	P ppb
Control	7.8	0.02	7.64	63	1200	19	457
Unflushed low ammonia	1.5	0.36	8.77	645	8500	20	451
Unflushed high ammonia	8.0	31	6.74	739	640	13,750	325
Unflushed petroleum	1.9	200	8.28	1750	1100	45	112
Flushed low ammonia	26.4	0.33	8.23	72	2000	31	173
Flushed high ammonia	3.4	22	7.67	226	1500	159	27
Flushed petroleum	5.9	25	6.78	441	300	11,260	207

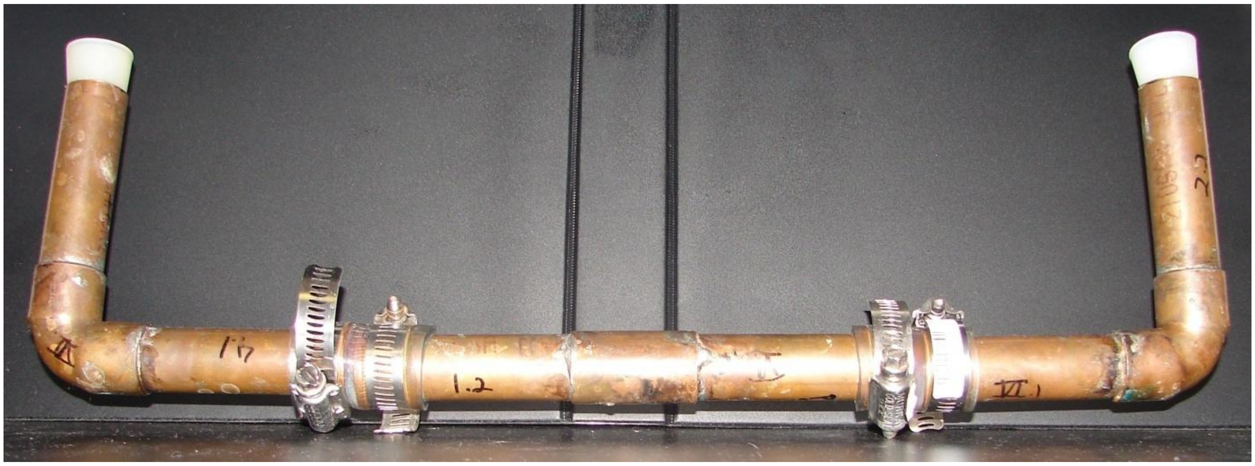
Figure 3-1. Copper pipe flux joints soldered together and then joints connected together using tygon tubing and metal clamps, and sealed at each end with rubber stoppers.


Figure 3-2. Complete set of pipes used in flux experiment.

Figure 3-3. Visible effects of flux on water after an initial three week stagnation period in unflushed copper pipes.

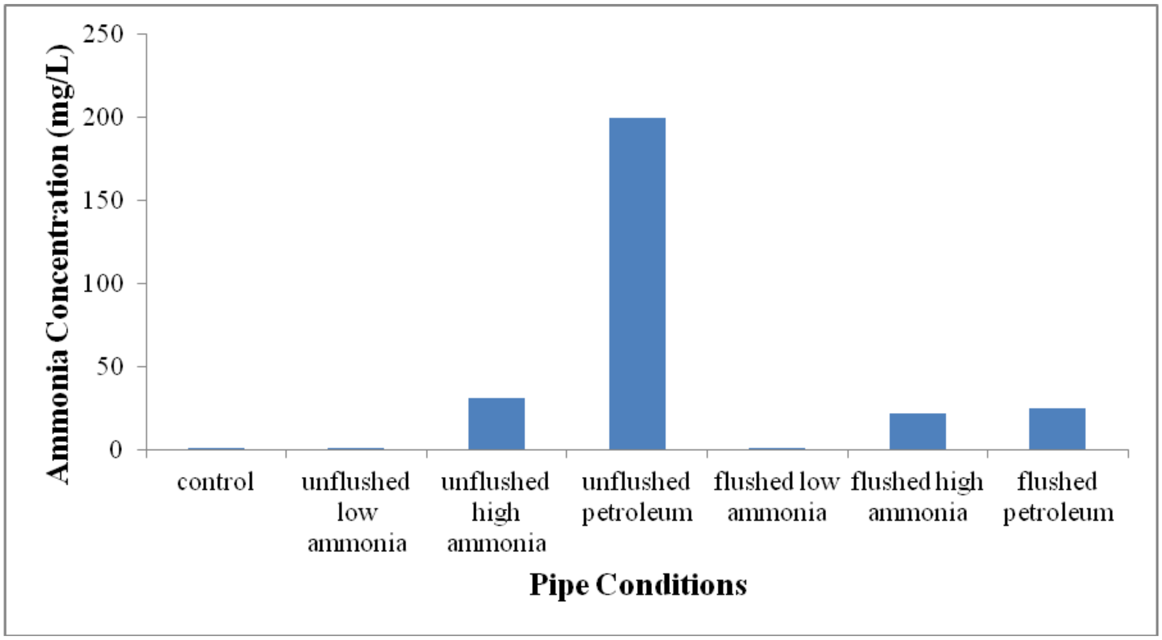

Figure 3-4. Ammonia concentrations in pipe conditions after three week stagnation.

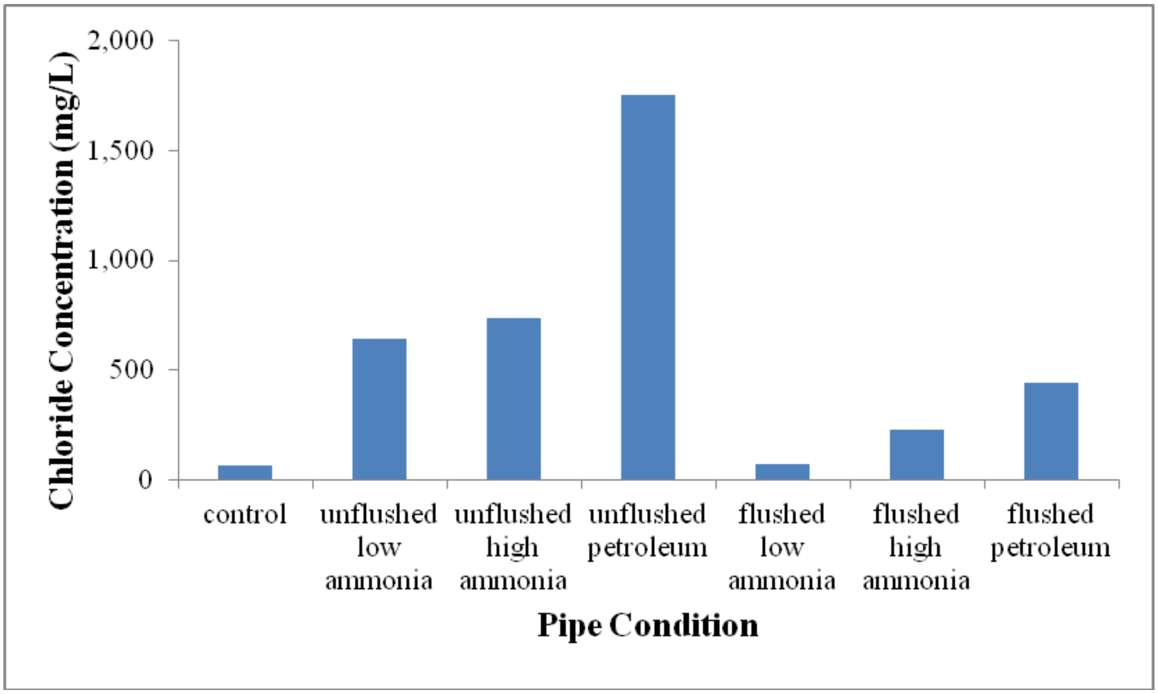

Figure 3-5. Chloride concentrations in pipe conditions after three week stagnation.

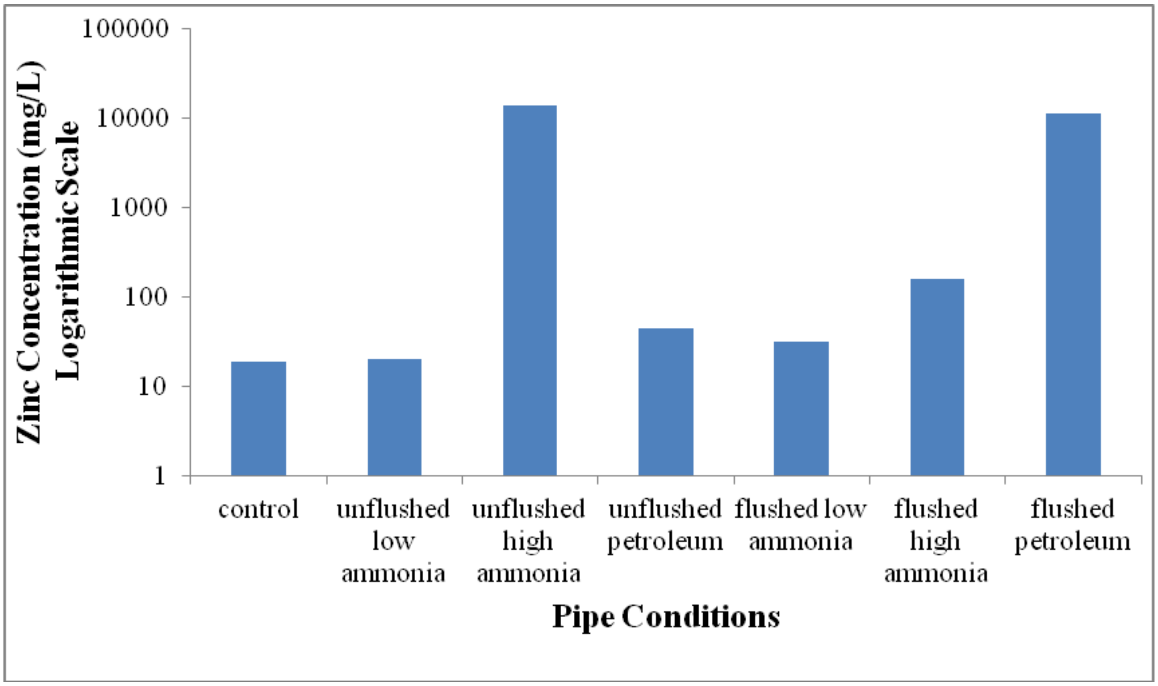

Figure 3-6. Zinc concentrations in pipe conditions after three week stagnation.

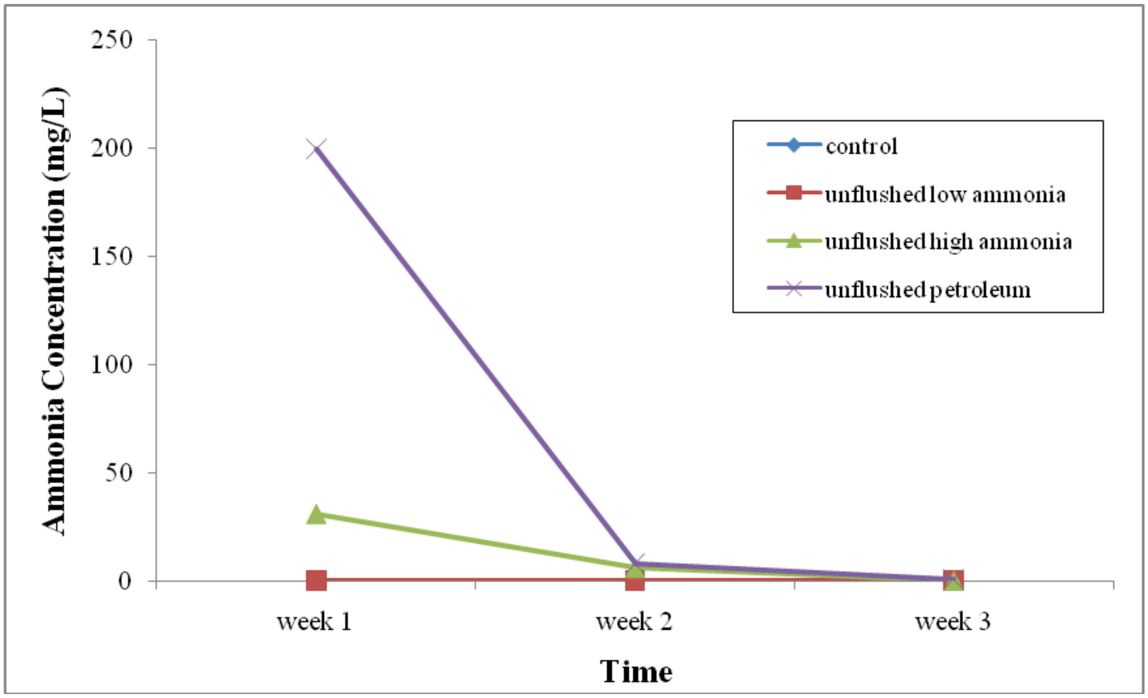

Figure 3-7. Ammonia concentration in unflushed pipes over the first three weeks of water changes during the experiment, after a three week stagnation period.

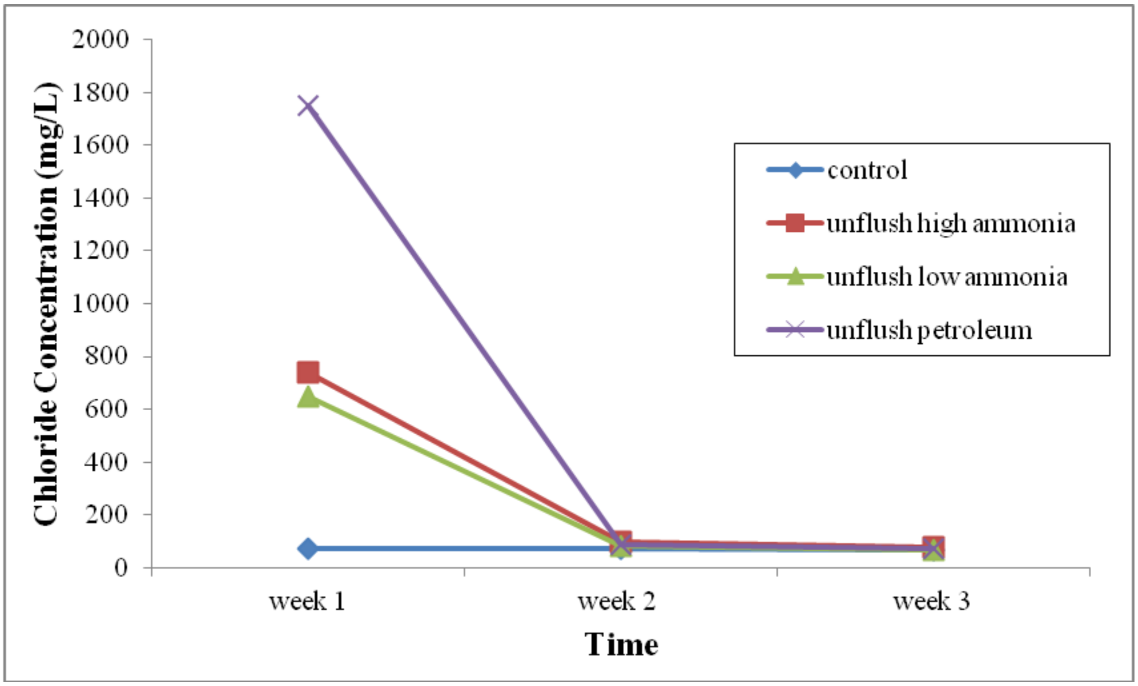

Figure 3-8. Chloride concentration in unflushed pipes over the first three weeks of water changes during the experiment, after a three week stagnation period.

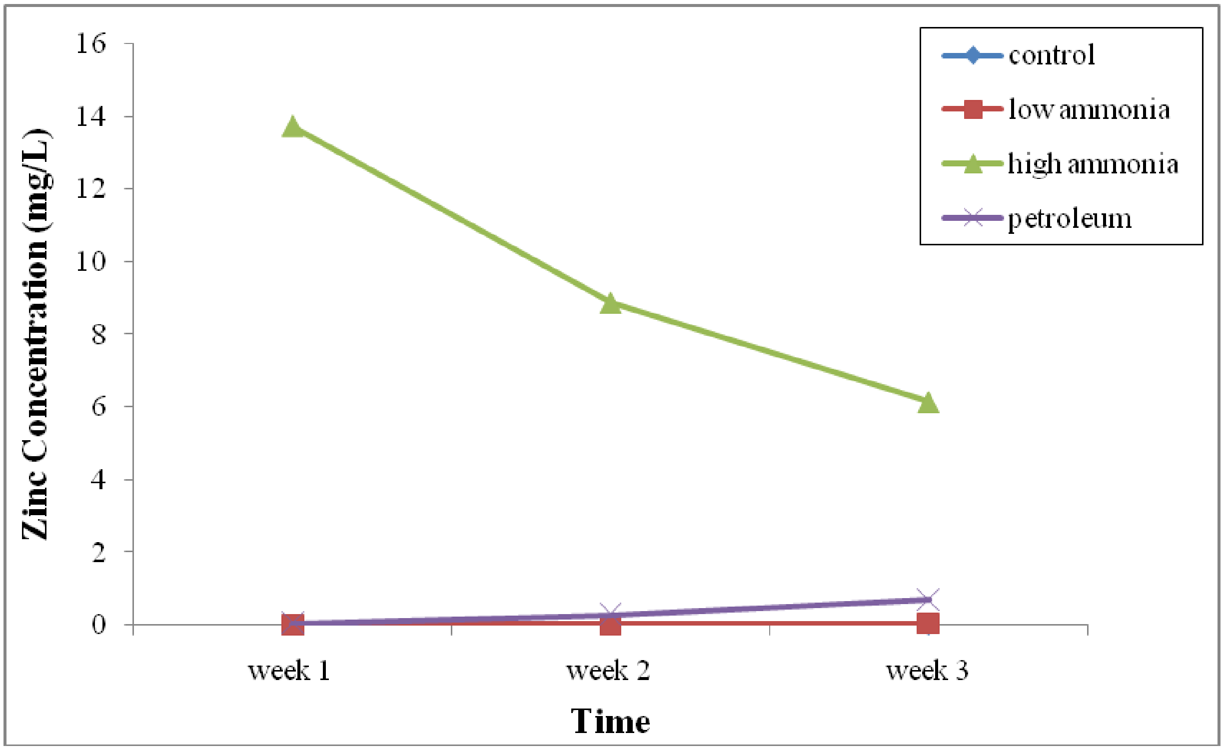

Figure 3-9. Zinc concentrations in unflushed copper pipes over the first three weeks of water changes during the experiment, after a three week stagnation period.

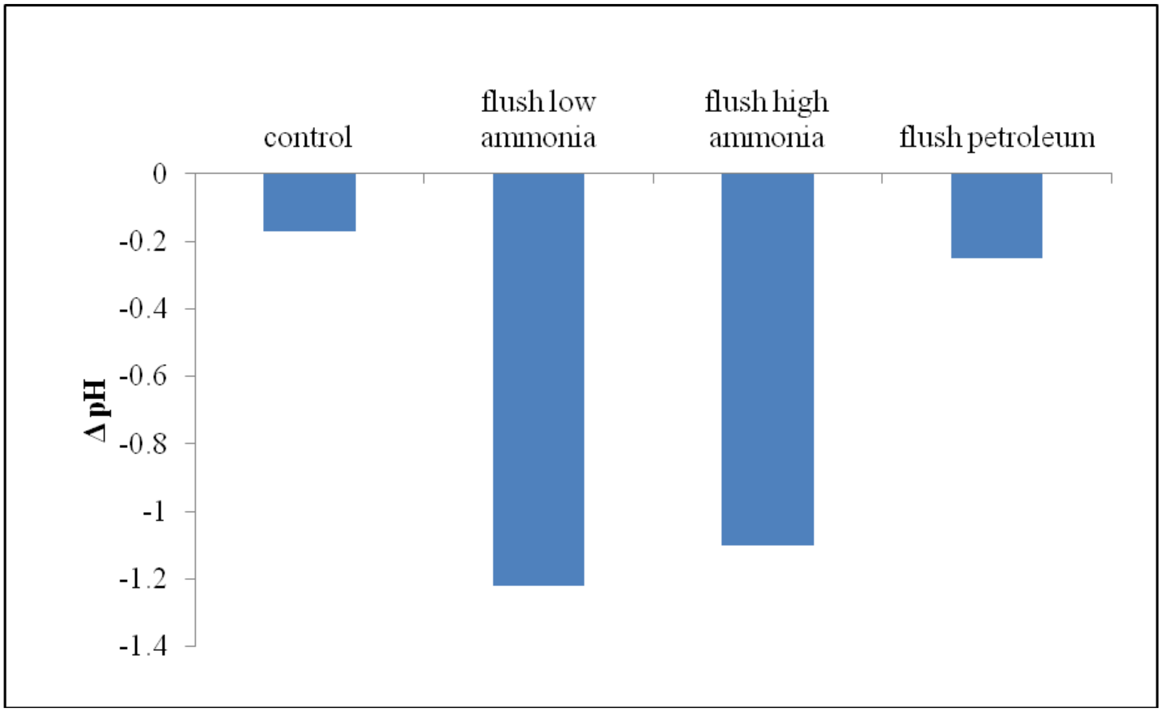

Figure 3-10. Change in pH values in flushed pipe conditions as a means of monitoring nitrification activity.

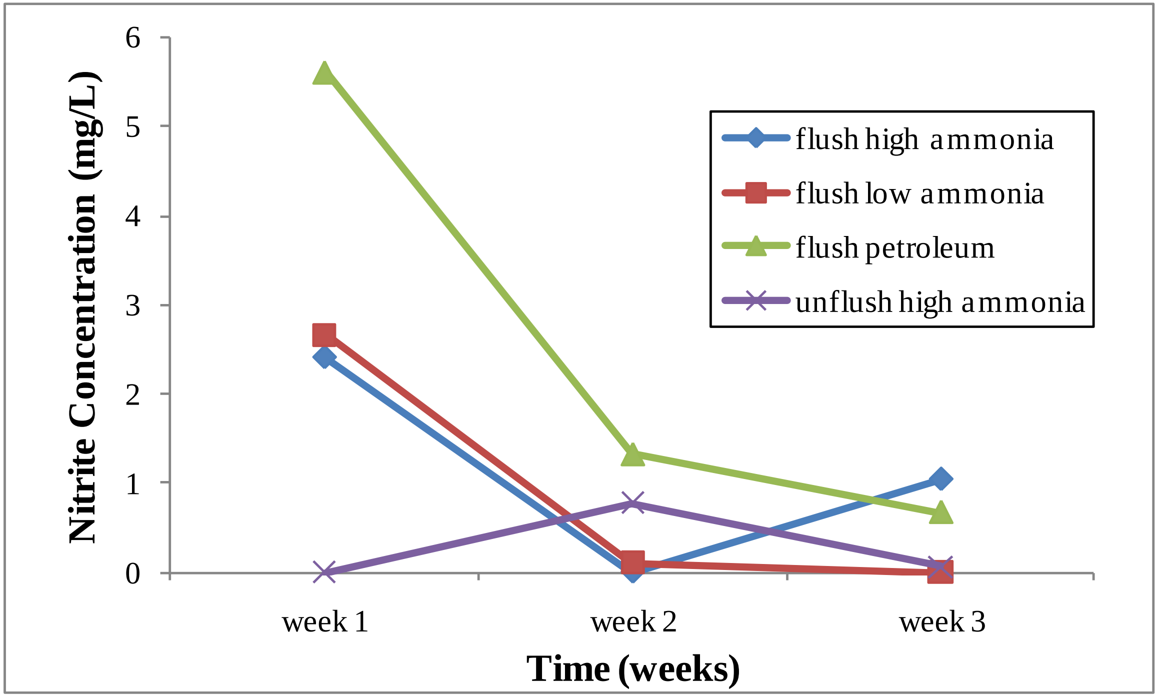

Figure 3-11. Nitrite concentrations in different pipe conditions over the first three weeks of water changes, after a three week stagnation period.

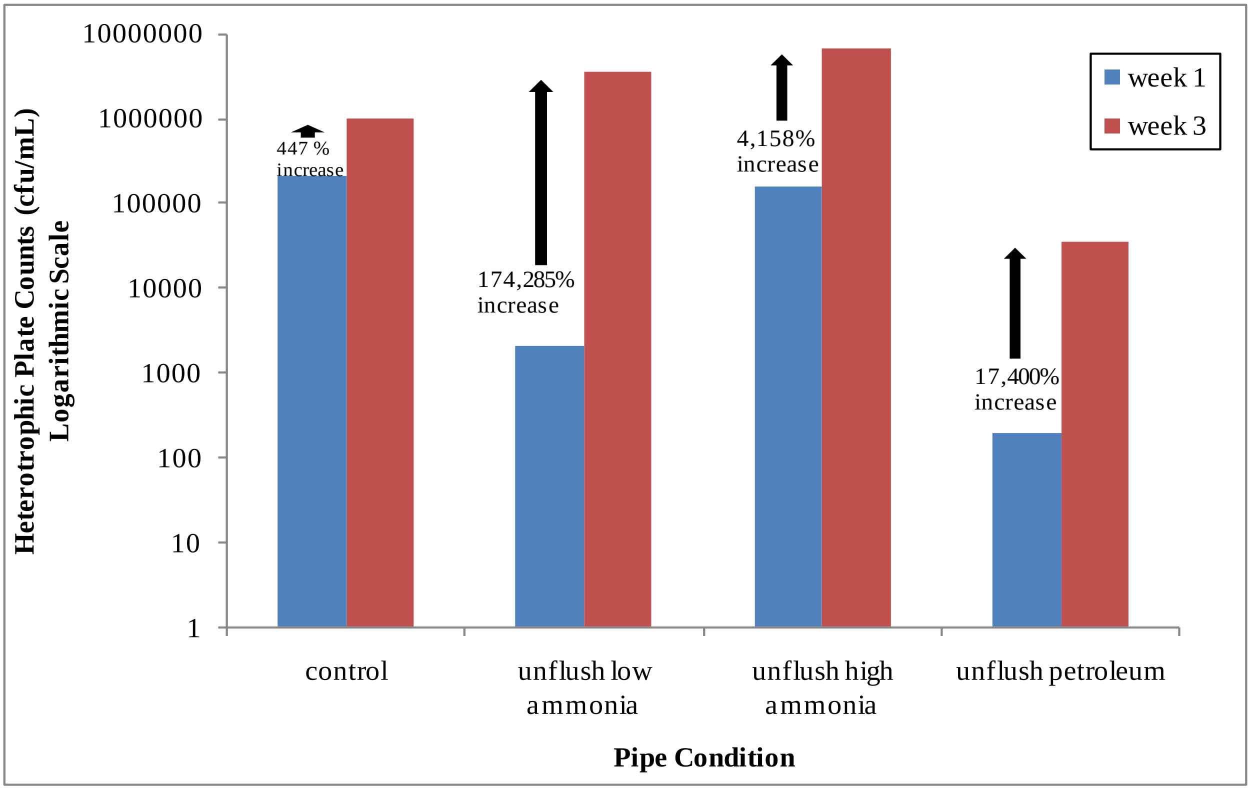

Figure 3-12. HPC's in unflushed copper pipes between week one and week three. The graph is presented using a logarithmic scale.

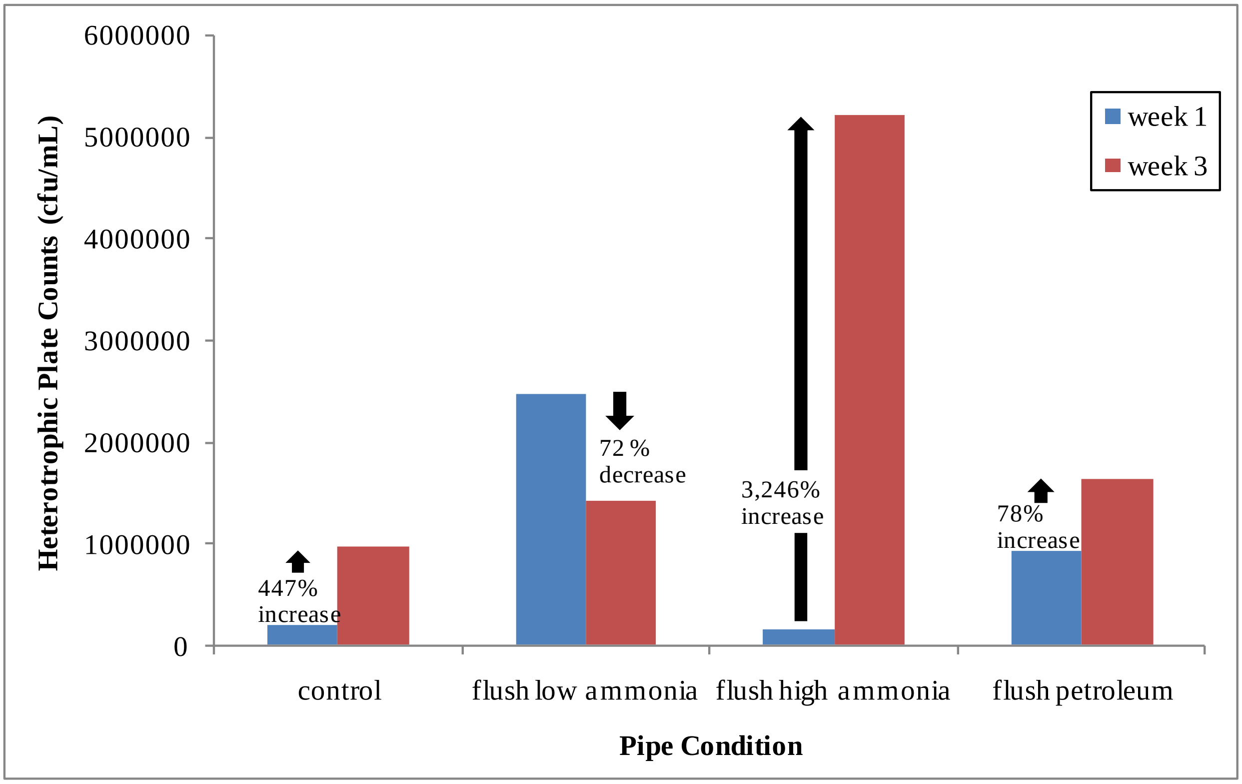

Figure 3-13. HPCs in flushed copper pipes between week 1 and week 3.

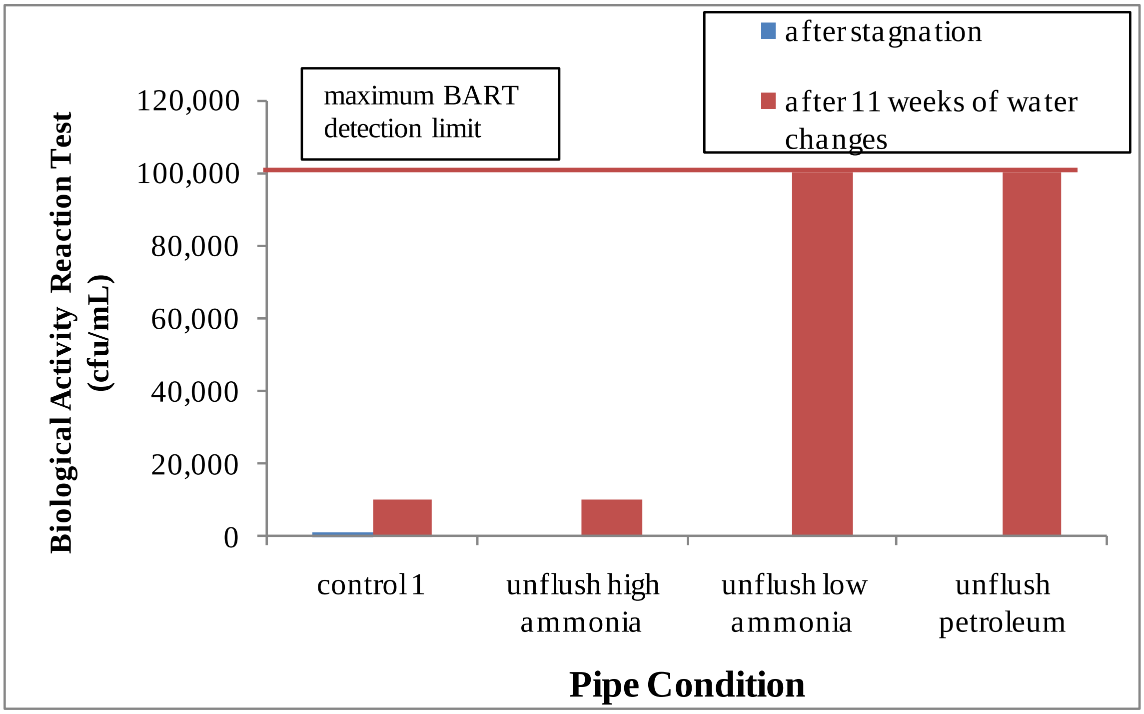

Figure 3-14. Nitrifier-Biological Activity Reaction Test results for unflushed flux pipes at three weeks and eleven weeks.

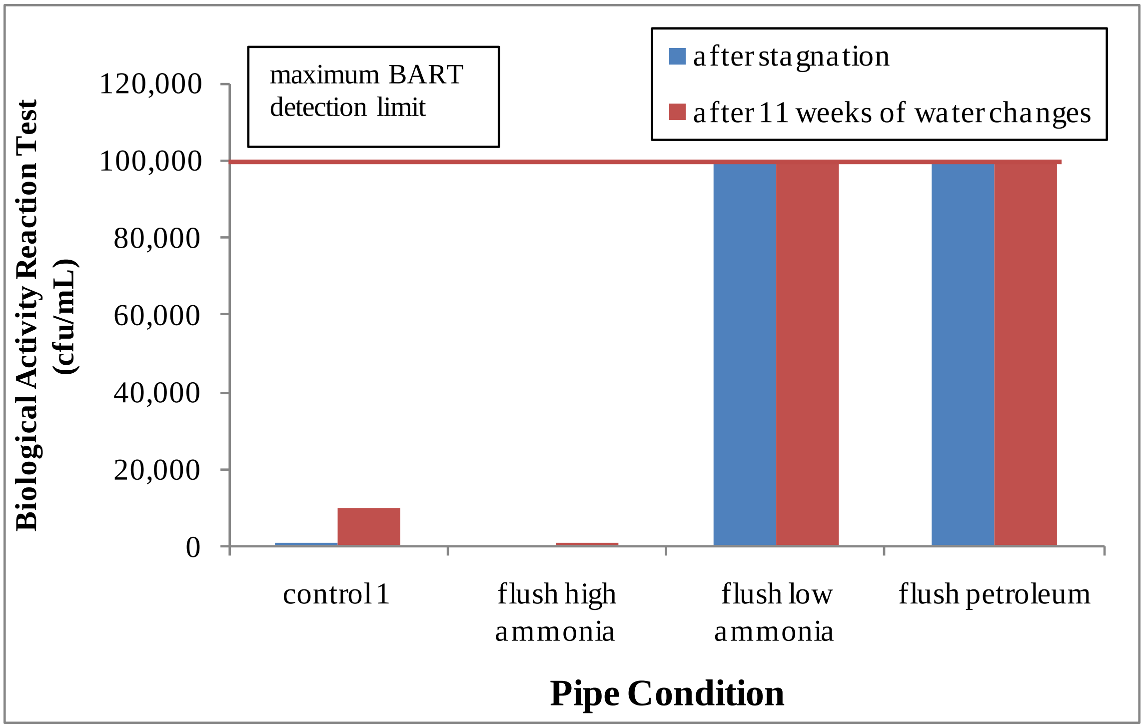

Figure 3-15. Nitrifier-Biological Activity Reaction Test results for flushed flux pipes at three weeks and three months.

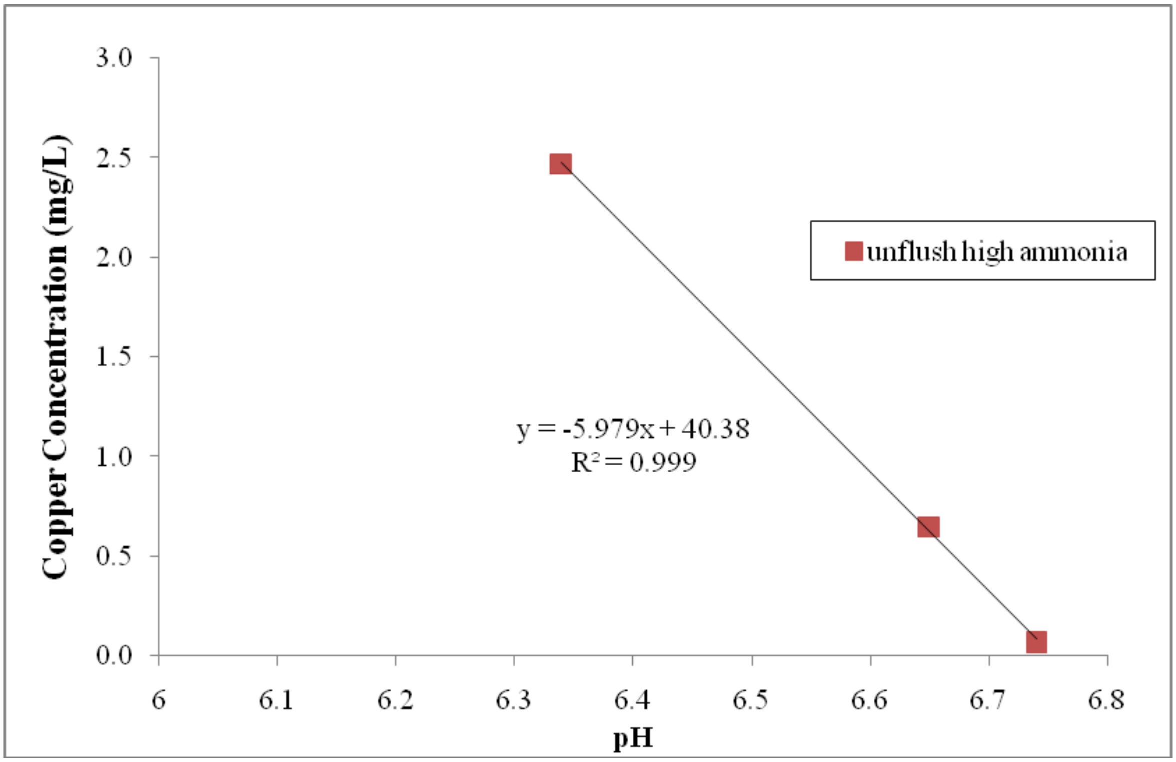

Figure 3-16. Copper concentration in copper pipe with unflushed high ammonia flux as a function of pH.

CHAPTER 4: EFFECTS OF ALKALINITY, PHOSPHATE, TEMPERATURE, AND VARIOUS MATERIALS ON THE STABILITY OF CHLORAMINE

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ABSTRACT

Chloramines have begun to replace chlorine as a leading disinfectant used in drinking water treatment processes due to their increased stability and fewer recognized disinfection by-products. Chloramine is a combination of chlorine and ammonia, and through auto-decomposition and other reactions it converts to chloride and free ammonia. Without a residual disinfectant in the water, rampant microbial growth can occur, especially in building plumbing systems, prompting an investigation of factors that promote chloramine decay in the presence of plastic piping.

INTRODUCTION

Chlorine has been the leading disinfectant used by wastewater and drinking water utilities for over 90 years and its use is largely responsible for eliminating waterborne diseases from drinking water [1]. Although chlorine is effective at deactivating disease causing pathogens and viruses, it can be dangerous because it is responsible for forming cancer-causing disinfectant byproducts (DBP's), such as trihalomethanes (THM) and haloacetic acids (HAA). The Environmental Protection Agency's (EPA) Safe Drinking Water Act has set a Maximum Residual Disinfectant Level (MRDL) for chlorine of 4 mg/L [2].

Recently, chloramines (in the form of monochloramine), have become a more desirable disinfectant because monochloramine produces fewer known disinfection byproducts. Although chloramine is not as strong of a disinfectant as chlorine, it has been shown to be more stable, which is desirable because presence of the disinfectant is believed important in maintaining safe water and preventing waterborne disease [2]. Another benefit of chloramine is that it does not react readily with organic compounds, resulting in a lower incidence of taste and odor issues [2]. When forming chloramines, a 4:1 ratio of chlorine to ammonia is generally used in order to get a stable chloramine solution [3].

Several experiments were conducted in order to evaluate the effects that both water quality and different materials have on chloramine decay. Cement, tygon tubing, and PVC pipes were amongst the materials tested along with several water chemistry parameters, including alkalinity, orthophosphate, and temperature. During the course of several experiments that evaluated corrosion of various materials, unusually high rates of chloramine decay were observed in some instances. Various follow-up experiments were conducted in an attempt to explain this phenomenon and this chapter is a preliminary report of those efforts.

MATERIALS AND METHODS

Effect of pH, orthophosphate and alkalinity on chloramine decay

Cement corrosion experiment

In a recent project for Water Research Foundation, our research team conducted bench-scale testing to provide insight into the mechanisms of phosphate and zinc interactions with cement while also considering the effects of temperature, pH and alkalinity [4]. Ten test rigs were constructed to simulate essential features of water hydraulics through a typical drinking water distribution system main (Figure 4-1). Ten cement coupons were inserted into Tygon tubing holders and were placed in series within the test rigs. Other materials present in the system were a polyethylene reservoir and PVC piping and valves.

Two different water quality conditions were evaluated, including a fairly aggressive condition with low alkalinity (20 mg/L as CaCO3) and low hardness (5 mg/L as Ca) and a relatively non-aggressive condition with high alkalinity (200 mg/L as CaCO3) and high hardness (120 mg/L as Ca). Five separate zinc and/or phosphate concentrations were tested for each alkalinity and hardness condition. These included no zinc or phosphate (control), 2 mg/L orthophosphate (as PO4), 0.25 mg/L zinc, 0.25 mg/L zinc plus 2 mg/L orthophosphate (as PO4), and 2 mg/L hexametaphosphate (as PO4). For all test conditions 4 mg/L chloramine was added prior to exposure to the cement coupons and test rig apparatus. Water was drained from the test rigs weekly and fresh water was added. Each condition was tested for either 6 or 12 weeks. Waters with pH 7 and pH 8.3 were tested. Many of the details of that study are expounded upon in the final project report [4]; however, chloramine decay was not a point of concern for that project. Chlorine and ammonia concentrations were measured during this study however, and results from chlorine and ammonia concentration testing are described herein.

Small glass bottle experiment.

To test the effect of various water qualities, 300 mL glass bottles were used since glass is considered a relatively inert material and would not likely affect the rate of chloramine decay. Fresh water was made prior to each water change and the water was changed bi-weekly on Monday’s and Thursday’s.

Three different water qualities were utilized to study the effects that different phosphate levels have on chloramine decay in glass bottles. Phosphorous levels of 0 mg/L P (control), 5 mg/L P, and 1000 mg/L P were used and chlorine and ammonia concentrations were measured at 30 minutes, 1 hour, 2 hours, 4 hours, and 24 hours. This was done to confirm a previous study performed by Nguyen et al. that found that the rate of chloramine decay was slowed when phosphate was added to the system [5].

A test was also conducted to analyze the effects that different alkalinity levels had on chloramine decay. Glass bottles were filled with water with 1000 mg/L P and different alkalinity levels including no alkalinity, low alkalinity (8 mg/L as CaCO3), and high alkalinity (95 mg/L as CaCO3). Chlorine and ammonia concentrations were measured at 30 minutes, 1 hours, 2 hours, 4 hours, and 24 hours.

PVC pipe experiment examining chloramine decay

One foot sections of PVC pipe were cut and triplicates were used for each water quality condition. For this study 8 mg/L chloramine was added to organic free water, filtered organic free water, nanopure water, control deionized water, and synthesized water. The organic free water contained negligible amounts of total organic carbon. The filtered organic free water was water containing negligible amounts of total organic carbon and had been filtered through a 0.45 micron filter in an attempt to further remove any trace amounts of organic matter. Nanopure water was filtered through a granular activated carbon filter to remove organic matter. The control water was deionized water which had all of the salt ions removed. The synthesized water contained the salt ions listed in Table 4-1.

Effect of different pipe materials on chloramine decay

This study was designed to test the effects of different water quality conditions, PVC pipe, and tygon tubing pipe materials on chloramine decay. The water was adjusted to pH 7 prior to each water change and a synthesized water recipe was used (Table 4-1). The pH was monitored by using a pH electrode according to Standard Method 4500-H^+ B [6]. Ammonia levels were measured on a Hach DR2000 spectrophotometer according to Standard Method 4500-NH_3 [4]. Total and free chlorine were also measured on a Hach DR 2000 spectrophotometer according to Standard Method 8167 [6].

Effect of tygon tubing on chloramine decay

Glass bottles were used to test the effects that old tygon, new tygon, and no tygon tubing had on chloramine decay. One inch sections of tygon tubing were cut and placed in the 300 mL glass bottles at the beginning of the experiment. New tygon tubing was purchased from a local hardware store and used for the "new tygon" glass bottle condition. A sample of tygon tubing was taken from a previous experiment which exhibited very rapid chloramine decay and was used for the "old tygon" glass bottle condition (cement corrosion experiment described previously). No tygon tubing was added to the "no tygon" glass bottle, which acted as a control condition. Chloramine (as measured by chlorine and ammonia concentrations) measurements were taken at 30 minutes, 1 hour, 2 hours, 4 hours, and 24 hours.

Effect of temperature on chloramine decay

Another study using 4 mg/L chloramine evaluated the role that temperature plays in chloramine decay. One set of pipes was held at room temperature (~22°C) and the other set of pipes was held in an incubator (~30°C). It was reported that increasing temperatures have been found to increase the rate of chloramine decay [5].

The effect of temperature on chloramine decay was also evaluated in the low alkalinity, low hardness water utilized in the cement corrosion experiment described previously. Three one liter polypropylene containers were filled with this water and total chlorine and ammonia concentrations were measured. One container was placed in a 10 °C constant temperature room, a second container was placed in a 37 °C constant temperature room, and the third was kept at room temperature. Total chlorine and ammonia concentrations were measured periodically for four days.

RESULTS AND DISCUSSION

Effects of water quality on rate of chloramine decay

In the cement corrosion study, the goal was to operate each test rig with 4 mg/L initial chloramine. However, on measuring chlorine (total and free) and ammonia after a few hours of operation a steady decrease in chloramine level was noticed for both the pH 7 and pH 8.3 waters.

Additionally, a very interesting trend was observed in all the test rigs during each run - the chloramine decay was lowest in the rigs without phosphate (i.e. the control (no inhibitor) and zinc chloride corrosion inhibitor conditions).

At pH 8.3, over 90% of the total chlorine disappeared within the first 24 hours of operation (Figure 4-2). The level of chlorine after 2 days was undetectable for all 10 water quality conditions. After forming, free ammonia was removed from the water a much slower rate (Figure 4-3). The ammonia loss in the control test rigs and the rigs containing only zinc chloride inhibitor approached 30 – 50% and appeared to stabilize. By day 5 the majority of ammonia had disappeared in all test rigs containing orthophosphate or polyphosphate for both low and high alkalinity test conditions. Results at pH 7 were similar, however the decay rate of ammonia was approximately half as fast as at pH 8.3 (data not shown).

At first nitrification was suspected to be the root cause for the steady decrease in ammonia concentration. In order to investigate further, ammonia, nitrite (using a Hach spectrophotometer) and nitrate (DIONEX DX-120 ion chromatograph) concentrations were measured and a total nitrogen balance was performed for each water quality condition (Figure 4-4). There was a steady decrease in the nitrogen level over the one week testing period between water changes. Very small concentrations of nitrite and nitrate were detected. This result suggested that denitrifying bacteria might be converting nitrate to nitrogen gas.

N-BART analyses indicated that only very low levels of nitrifiers were present in a few of the test conditions (including low alkalinity with zinc, high alkalinity control, high alkalinity with zinc, and high alkalinity with polyphosphate). Denitrifying BART analyses however, indicated that denitrifying bacteria were present in all water quality test conditions. However, overall, the results did not support the idea that chloramines disappearance was linked to the presence or activity of bacteria, prompting additional studies. Given that the pKa of ammonia is 9.3, we suspect that ammonia stripping may account for the quicker disappearance of ammonia at pH 8.3 as compared to pH 7.

Effect of orthophosphate on chloramine decay

Contrary to the results from the cement corrosion study, orthophosphate did not have a significant effect on the rate of chloramine decay in glass bottles. The pipes containing 5 mg/L P had a slightly higher rate of chlorine decay but after 4 hours the chlorine concentrations in all conditions had dropped to 0 mg/L (Figure 4-5). The ammonia did not decay significantly and after 24 hours its concentration had decreased by about 30-35% for all conditions (Figure 4-6).

Effect of alkalinity on chloramine decay

As in the case of orthophosphate, a change in the level of alkalinity did not result in a significant difference in the chloramine decay. The chlorine decayed slightly faster in the low alkalinity water but after 4 hours the chlorine decayed to 0 mg/L-Cl_2 for all three conditions (Figure 4-7). The ammonia decay followed a similar trend as in the phosphorous and tygon tubing experiments, showing only a slight decay over the 24 hour period (Figure 4-8).

Effect of temperature on rate of chloramine decay

Chloramine decay was strongly affected by temperature. Chlorine rapidly disappeared at higher temperatures (Figure 4-9). After 20 hours over 60% of the chlorine remained at 10 °C, while virtually no chlorine remained at 24 or 37 °C. Unlike chlorine, ammonia concentrations remained fairly stable throughout the four day test (Figure 4-10).

Another bench scale experiment was performed to further test the effects of temperature on chloramine decay dosed at 4 mg/L. The chlorine concentration decreased in both the PVC pipes held at room temperature and the PVC pipes placed in the incubator at 30 °C when compared to the glass bottle control. The chlorine in the pipes held at room temperature decreased by 81% over a 72 hour period and ammonia decreased by about 32% over a 72 hour period. The chlorine in the pipes held in the incubator decreased by 98% over a 72 hour period and the ammonia decreased by 93% over a 72 hour period (Figures 4-11 and 4-12).

Another study evaluated the effects that autoclaving had on chloramine decay. The water as well as the PVC pipes were autoclaved which exposes the water to a temperature of 121°C, effectively deactivating bacteria and sterilizing the equipment. Chloramine was added to the water after the water was autoclaved. Autoclaving the water did accelerate both chlorine and ammonia decay when compared to the control condition; however, the incubator condition still demonstrated the largest decrease in chloramine concentration.

This same study evaluated the effects that phosphate dosing had on chloramine decay. All of the synthesized waters contained 3 mg/L phosphate; however, in order to compare the effects that phosphate has on chloramine decay, one condition contained no phosphate and was termed “4 mg/L + no P.” The presence of phosphate in the water accelerated chloramine decay when compared to the “4 mg/L” condition.

Effect of different water’s on chloramine decay

The results from the study using 8 mg/L chloramine and different water qualities indicated that synthesized water caused the greatest chloramine decay when compared to any of the other conditions. There was not a notable difference in the chlorine or ammonia decay rates between the control water, the organic free water, the filtered organic free water, or the water from the nanopure column (Figures 4-13 and 4-14). Something in the synthesized water recipe accelerated chloramine decay, possibly the presence of phosphate at a concentration of 3 mg/L as PO_4.

Effect of pipe material on rate of chloramine decay

Tests were conducted in glass jars to study the effect of tygon tubing on chloramine decay. During the cement corrosion study it was suspected that the tygon rather than the cement surfaces was causing the chloramine decay. Low alkalinity, low hardness water was prepared as before with the addition of 4 mg/L chloramine (actual data showed that initial chlorine was 4.14 mg/L and initial ammonia was 0.80 mg/L). This water was divided into four parts and placed in glass containers. Nothing was added to the control. A 3” long piece of new Tygon tubing was placed in one container. A short piece of tubing was extracted from one of the test rigs to which orthophosphate had been added and had been experiencing rapid chloramine decay. This piece was cut into two and one half was chlorinated with 100 mg/L chlorine solution for 24 hours, rinsed, and then placed in one liter of the test water. The other half was added to a liter of the test water with no treatment.

Chlorine decay was similar in the new tubing and chlorinated old tubing to the control water (Figure 4-15). The old tubing from the cement coupon corrosion test rig exhibited a dramatic decrease in chlorine concentration however. Likewise, ammonia decay was similar in the control, new tubing, and chlorinated old tubing tests (Figure 4-16). However, as in the case of chlorine, there was a significant decrease in ammonia from the outset of the test in the water exposed to the old piece of tubing. In fact, all of the ammonia was consumed after 120 hours. These results suggest that possibly a biofilm on the tubing that had been exposed to nutrient rich water was responsible for the ammonia decay.

Effects of aged tygon tubing on chloramine decay

After examining the results from the previous experiment and confirming that a component of the aged tygon material proved to have a significant effect on the rate of chloramine decay, an additional test was performed to further examine the effects that aged tygon tubing had on chloramine decay. The results agreed with the previous findings. The old tygon caused the chlorine to decrease to 0 mg/L within 4 hours. This rate was approximately 2.5 times faster than the bottle containing new tygon, and 2.75 times faster than the bottle containing no tygon (Figure 4-17). The ammonia in the chloramine did not decay at the same rate as the chlorine (Figure 4-18). The old tygon condition did cause the fastest ammonia decay compared to the other two conditions, however after 24 hours the ammonia concentration had only dropped about 30% (from 0.57 mg/L to 0.40 mg/L) whereas the chlorine had dropped 100% (from 2.5 mg/L to 0 mg/L) in 4 hours.

CONCLUSIONS

- The role of orthophosphate on chloramine decay is still unclear. Orthophosphate appeared to accelerate chloramine decay in the cement corrosion study and PVC pipe study, yet it did not appear to significantly affect the amount of chloramine decay in the glass bottle experiment.
- Ammonia disappeared more quickly at pH 8.3 than at pH 7, possibly indicating that ammonia stripping was occurring in the recirculating cement corrosion study.
- Alkalinity did not appear to affect the amount of chloramine decay.
- The aged tygon tubing dramatically increased chloramine decay, possibly due to biofilm.
- Chloramine decayed much faster at higher temperatures.
- For all conditions tested, the ammonia decay was much slower than the rate of chlorine decay.

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Table 4-1. Water quality concentrations.

Ingredients	Concentration
$MgSO_4$ as mg/L-Mg	40
$CaCl_2 \cdot 2H_2O$ as mg/L-Cl	8.8
$CaSO_4 \cdot 2H_2O$ as mg/L-SO_4	4.5
KNO_3 as mg/L-NO_3	0.2
K_2SO_4 as mg/L-K	0.6
Na_2SiO_3 as mg/L-Si	20
pH	7

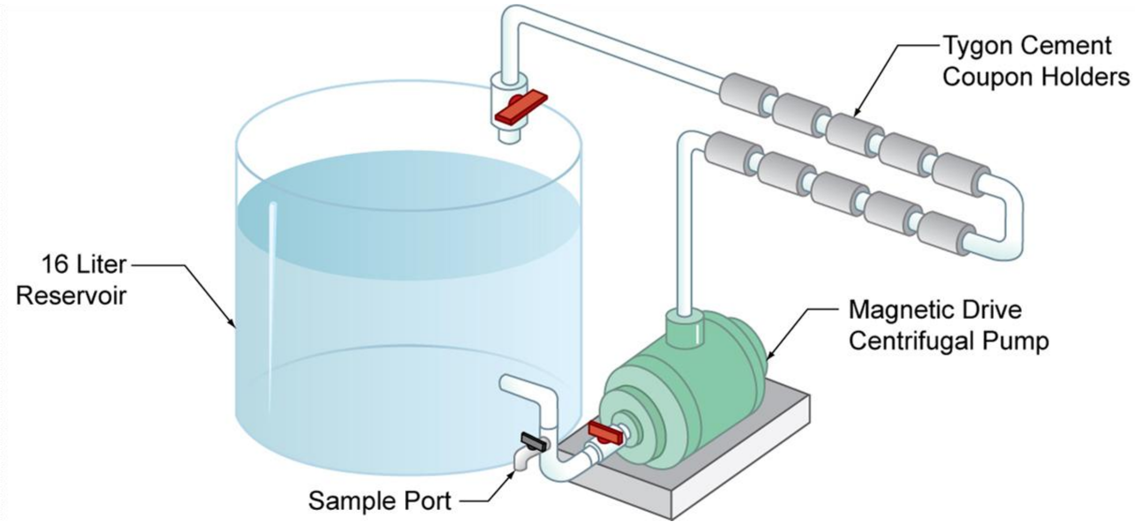

Figure 4-1. Test rig schematic for cement coupon corrosion study.

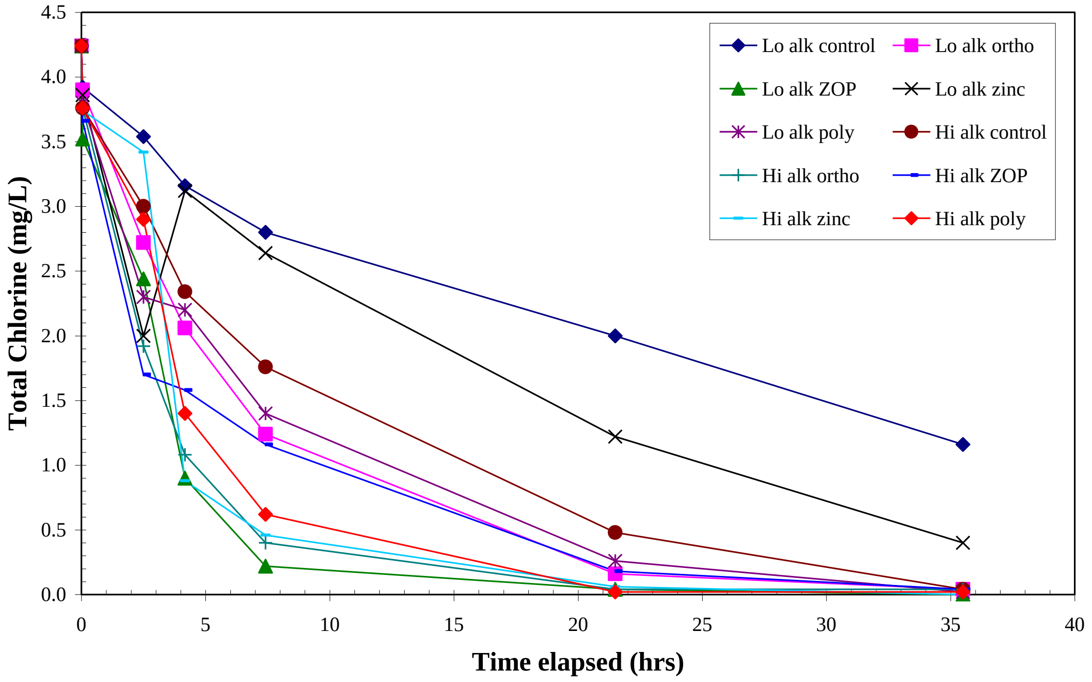

Figure 4-2. Total chlorine concentration versus time for cement coupon corrosion study. Operating conditions were pH 8.3 and 30 °C. Low alkalinity condition was 20 mg/L as CaCO3 with 5 mg/L calcium; high alkalinity condition was 200 mg/L as CaCO3 with 120 mg/L calcium. Orthophosphate concentration was 2 mg/L as PO4; zinc concentration was 0.25 mg/L; polyphosphate (hexametaphosphate) concentration was 2 mg/L as PO4.

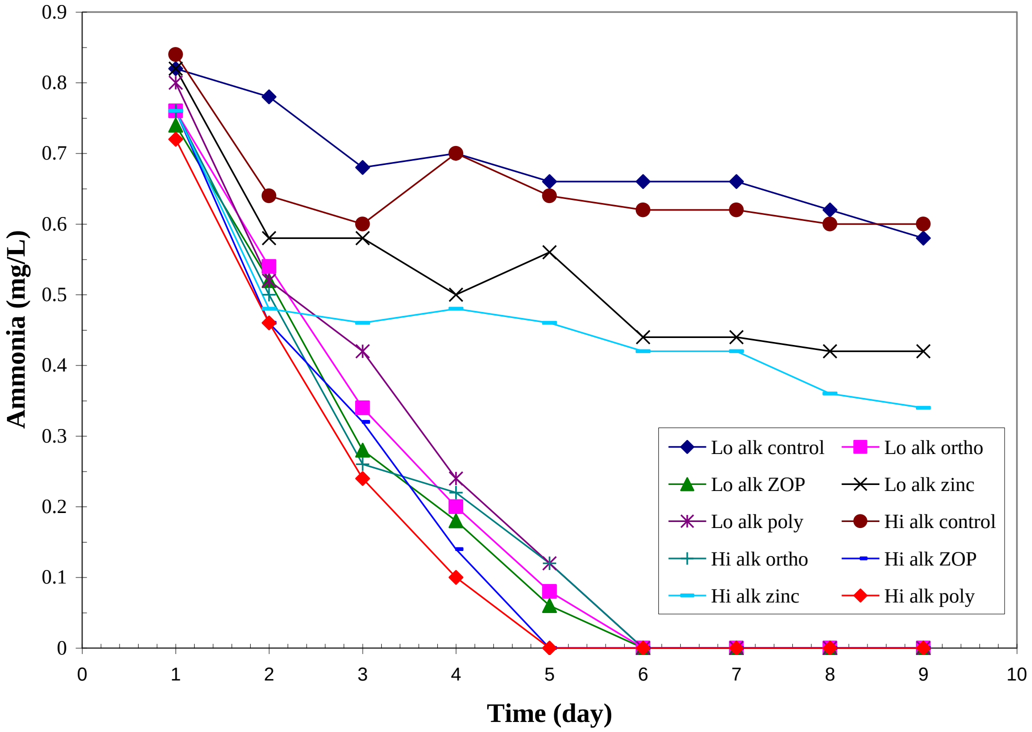

Figure 4-3. Ammonia concentration versus time for cement coupon corrosion study. Operating conditions were pH 8.3 and 30 °C. Low alkalinity condition was 20 mg/L as CaCO3 with 5 mg/L calcium; high alkalinity condition was 200 mg/L as CaCO3 with 120 mg/L calcium. Orthophosphate concentration was 2 mg/L as PO4; zinc concentration was 0.25 mg/L; polyphosphate (hexametaphosphate) concentration was 2 mg/L as PO4.

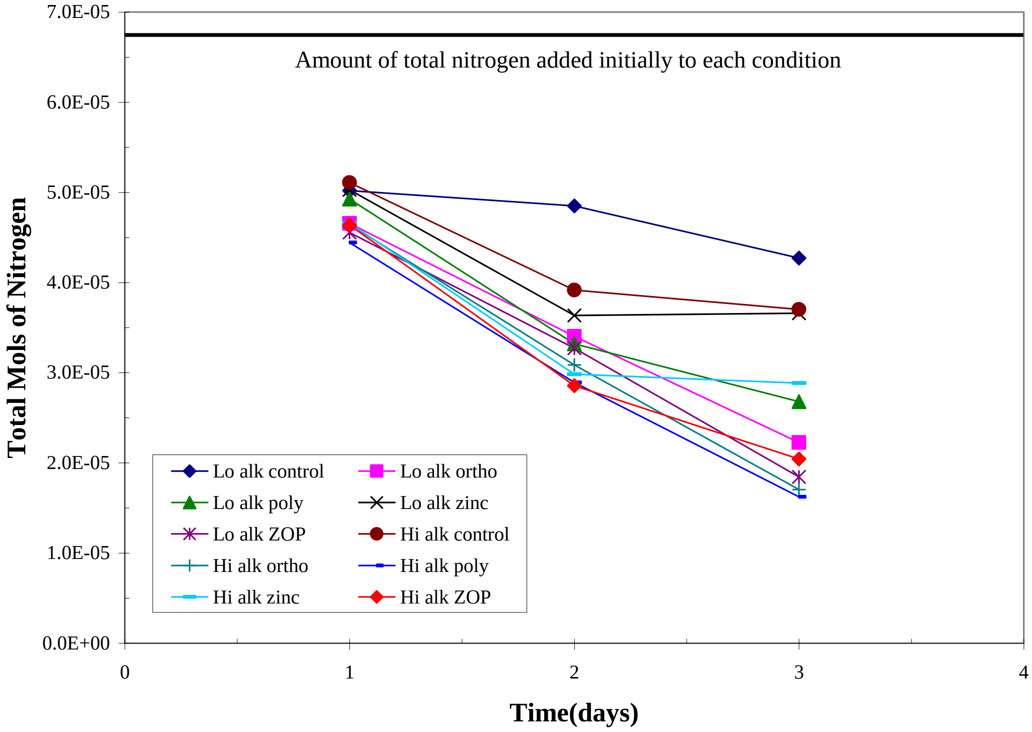

Figure 4-4. Moles of total nitrogen (ammonia + nitrate + nitrite) versus time for cement coupon corrosion study. Operating conditions were pH 8.3 and 30 °C. Low alkalinity condition was 20 mg/L as CaCO3 with 5 mg/L calcium; high alkalinity condition was 200 mg/L as CaCO3 with 120 mg/L calcium. Orthophosphate concentration was 2 mg/L as PO4; zinc concentration was 0.25 mg/L; polyphosphate (hexametaphosphate) concentration was 2 mg/L as PO4.

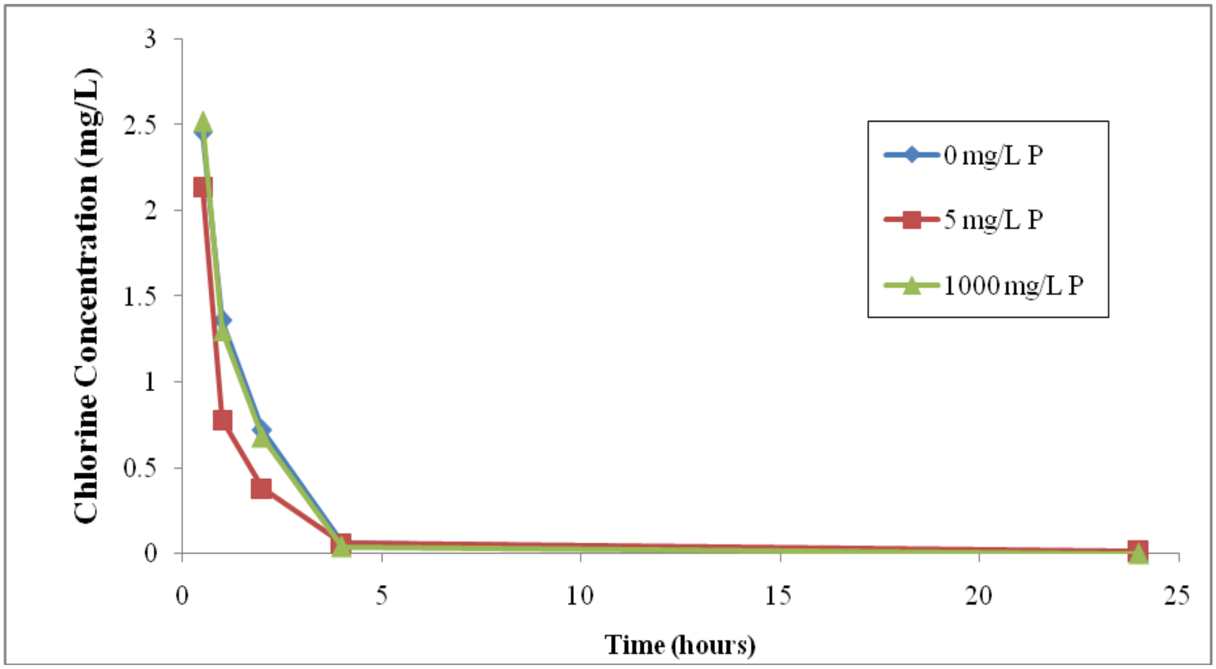

Figure 4-5. Chloramine decay (chlorine concentration) comparing the effects that different phosphate levels have in glass bottles over a 24 hour period.

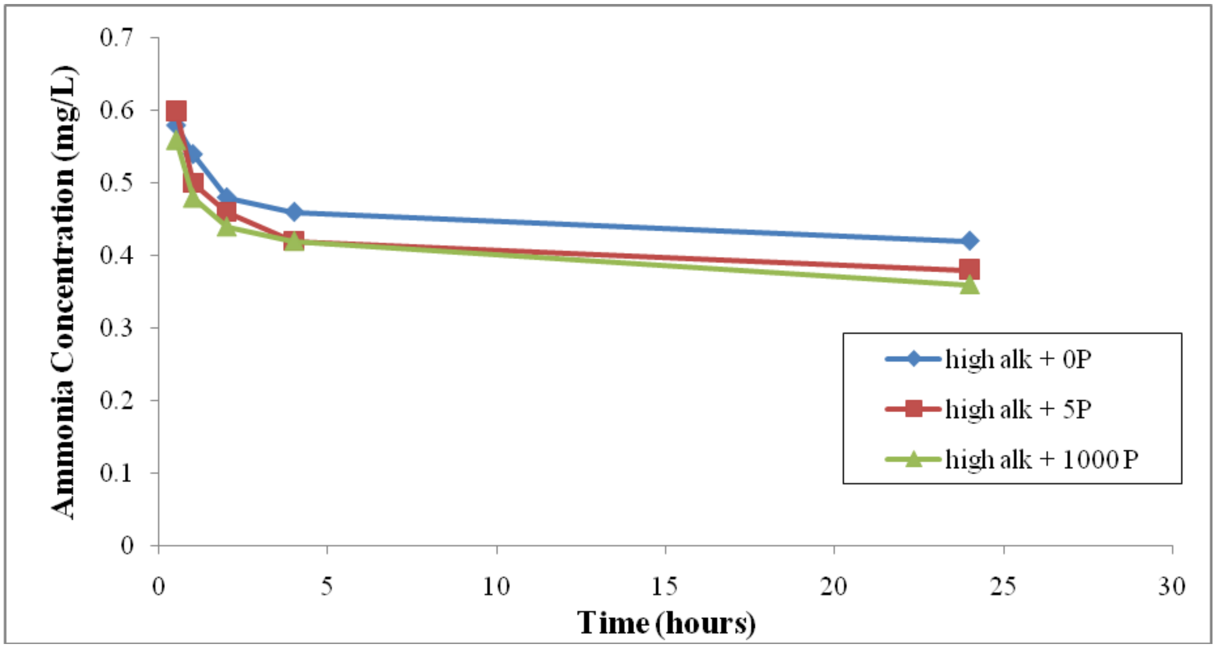

Figure 4-6. Chloramine decay (ammonia concentration) comparing the effects that different phosphate levels have in glass bottles over a 24 hour period.

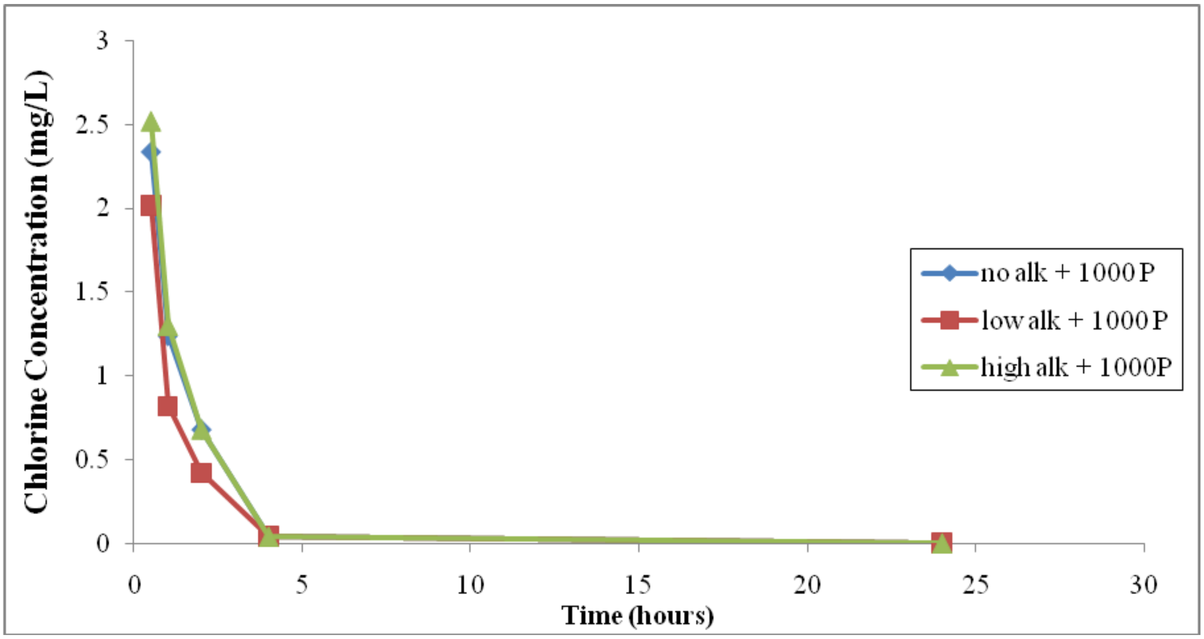

Figure 4-7. Effect of alkalinity on chloramine decay (chlorine concentration).

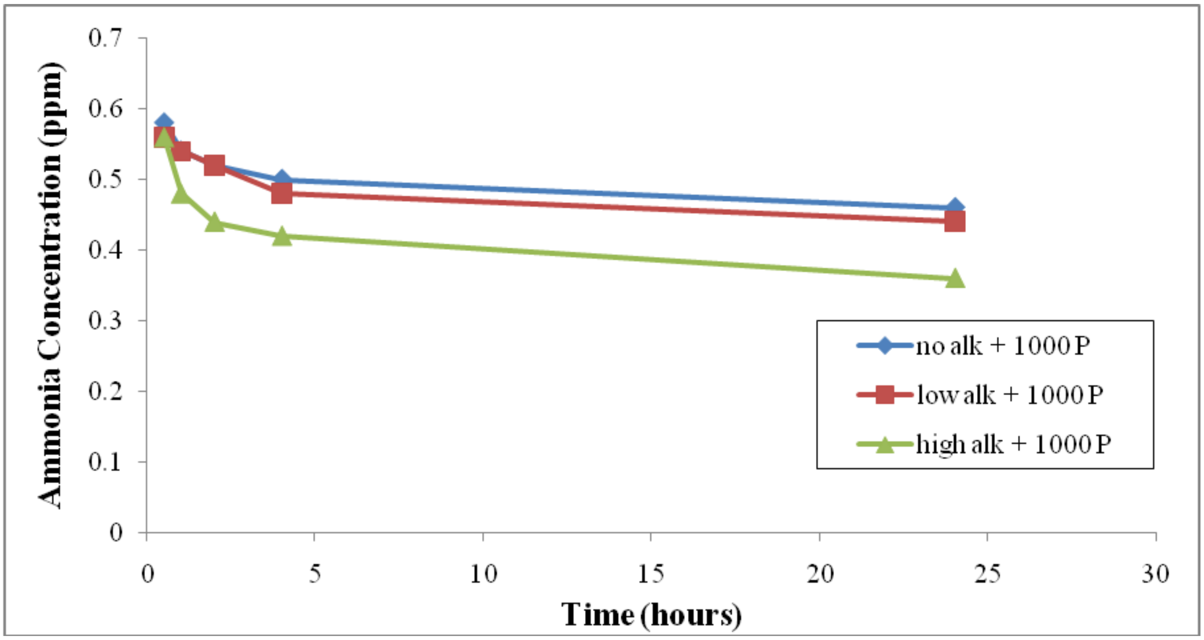

Figure 4-8. Effect of alkalinity on chloramine decay (ammonia concentration).

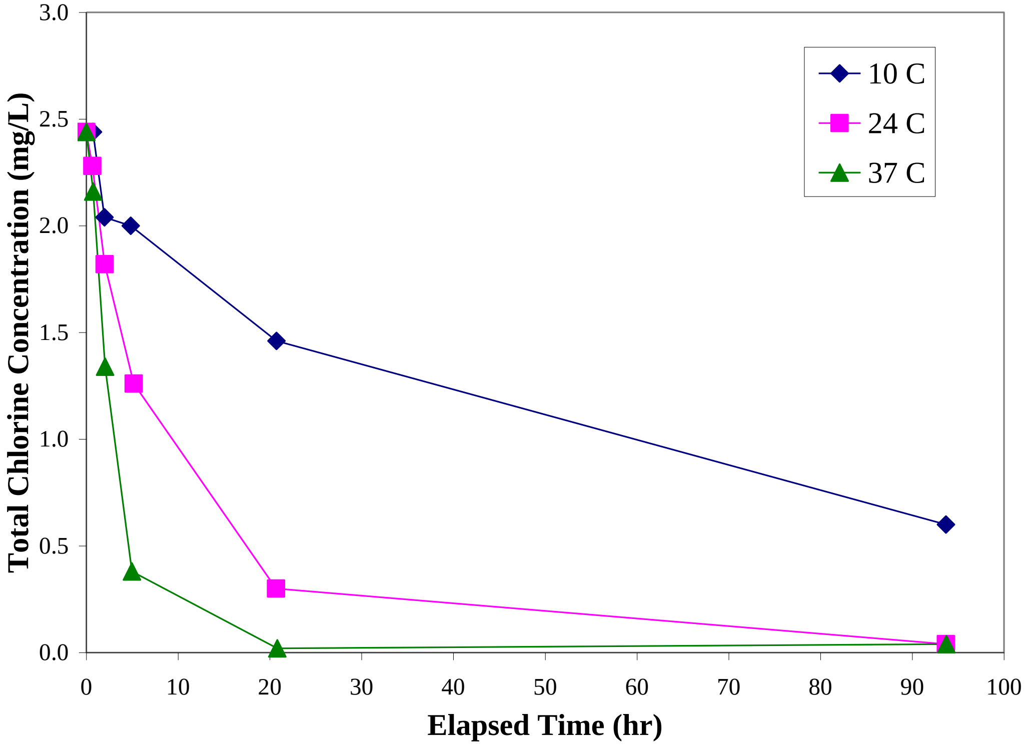

Figure 4-9. Effect of temperature on chlorine concentration.

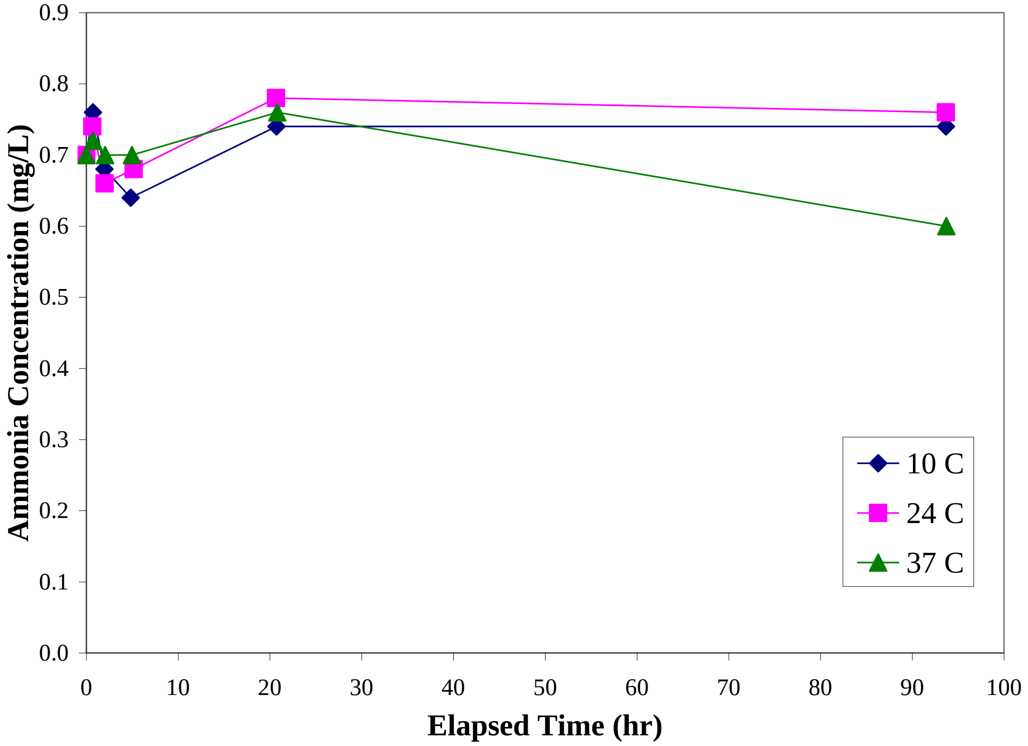

Figure 4-10. Effect of temperature on ammonia concentration.

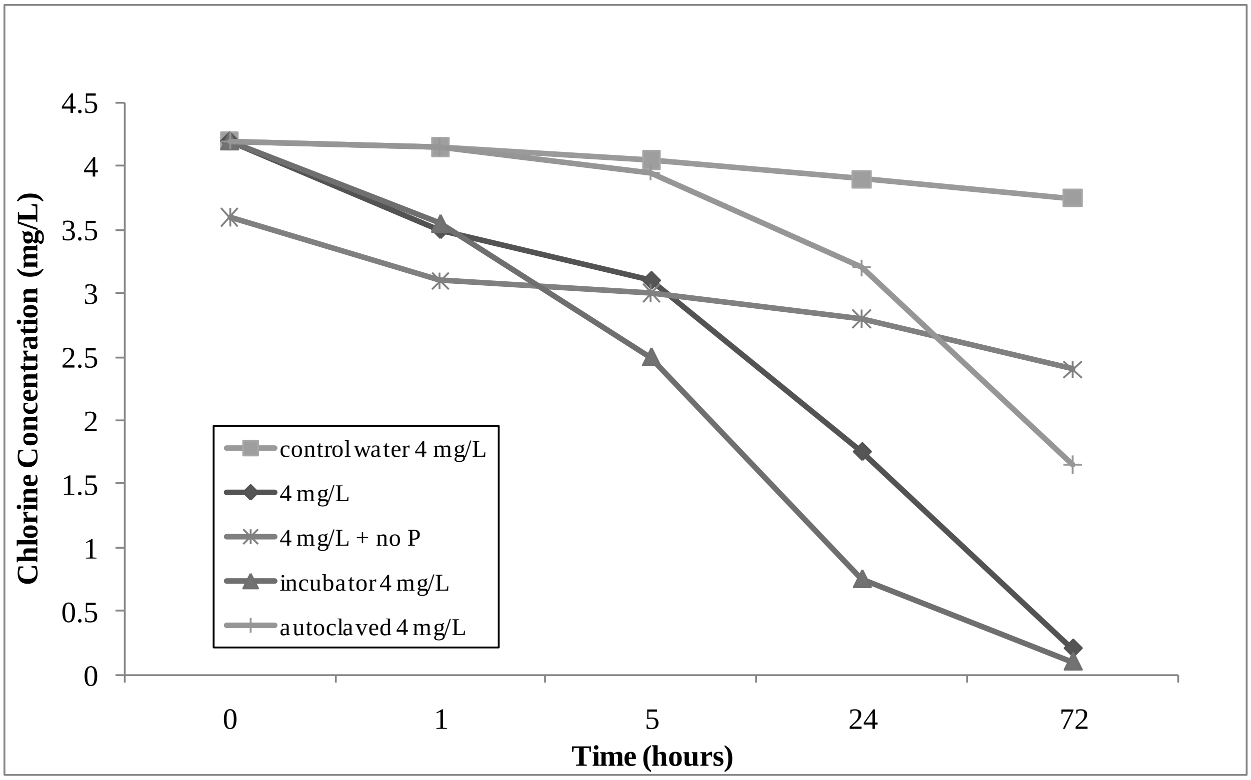

Figure 4-11. Chloramine decay (chlorine concentration) comparing temperature and autoclaving effects.

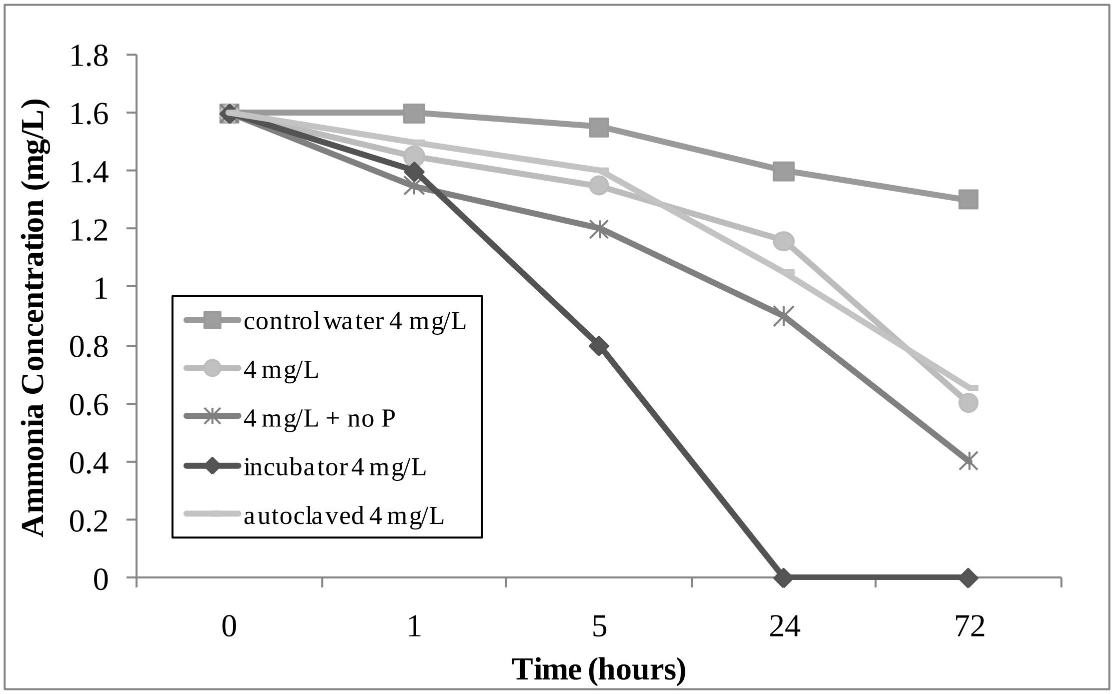

Figure 4-12. Chloramine decay (ammonia concentration) comparing temperature and autoclaving effects.

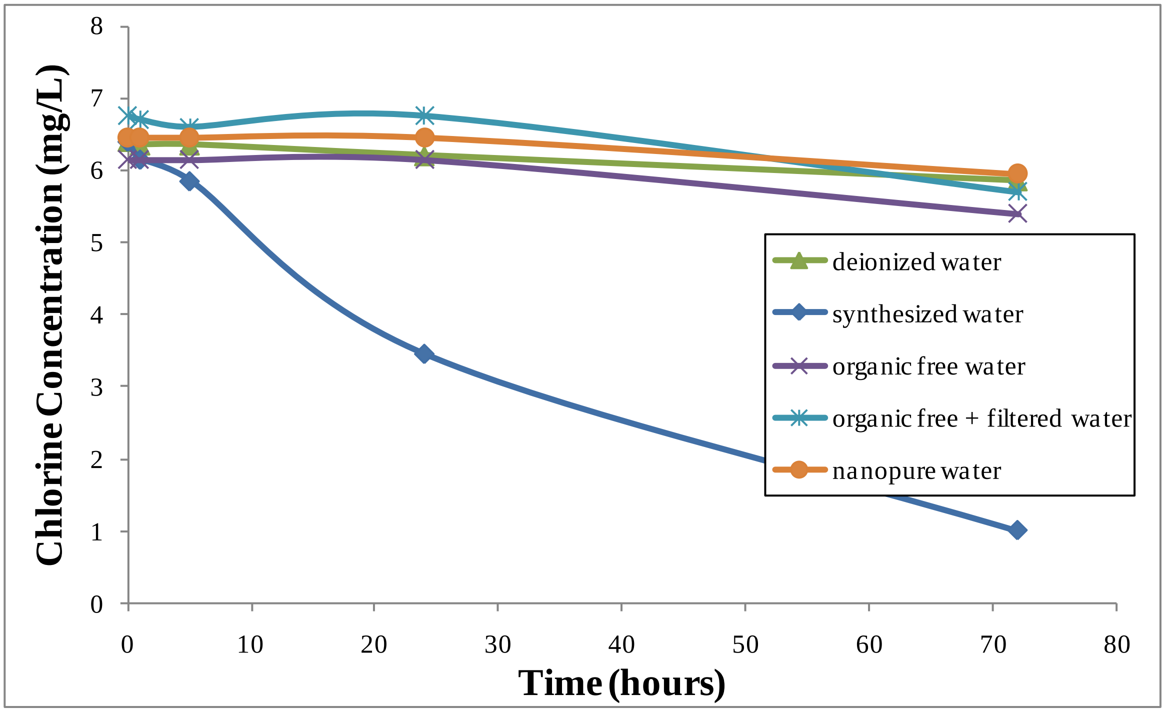

Figure 4-13. Chloramine decay (chlorine concentration) comparing PVC pipes exposed to different waters with 8 mg/L chloramine.

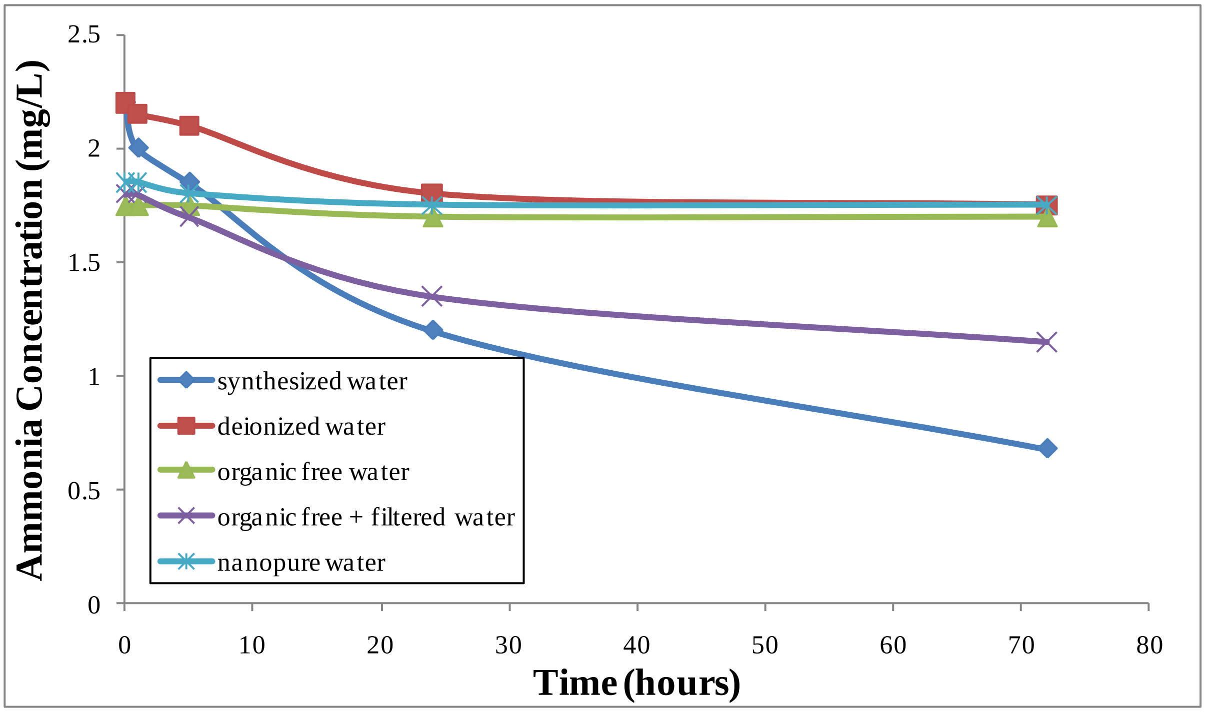

Figure 4-14. Chloramine decay (ammonia concentration) comparing PVC pipes exposed to different water with 8 mg/L chloramine.

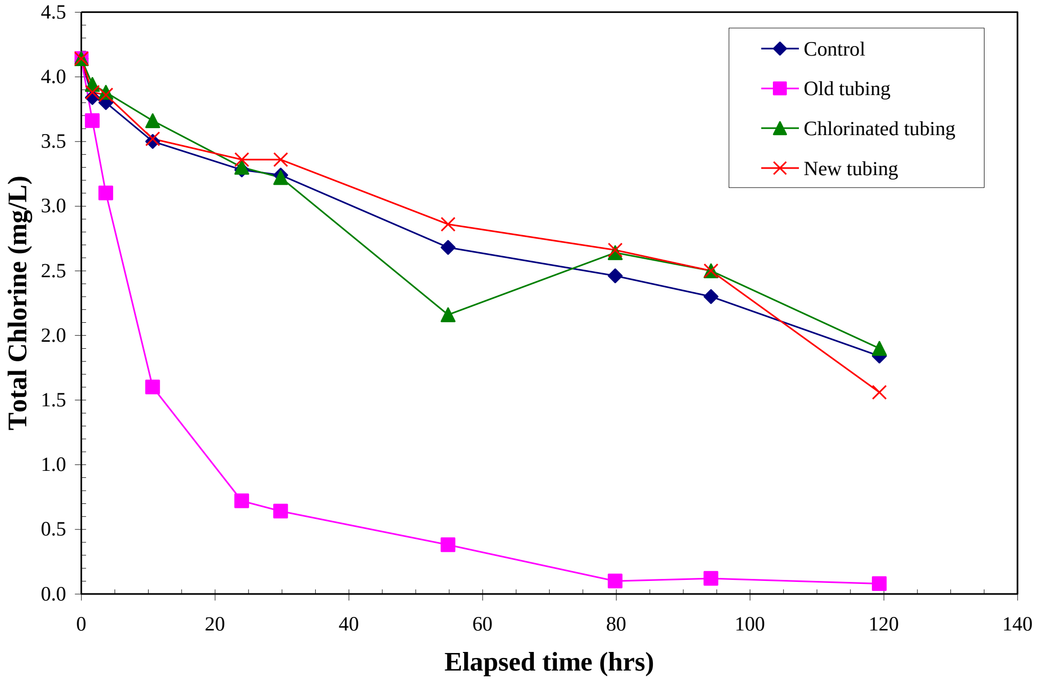

Figure 4-15. Total chlorine concentration versus time for glass jar test. Old tubing which had been exposed to conditions conducive to chloramine decay during the cement coupon corrosion testing exhibited a large chlorine demand compared to new tubing and tubing which had been pre-chlorinated.

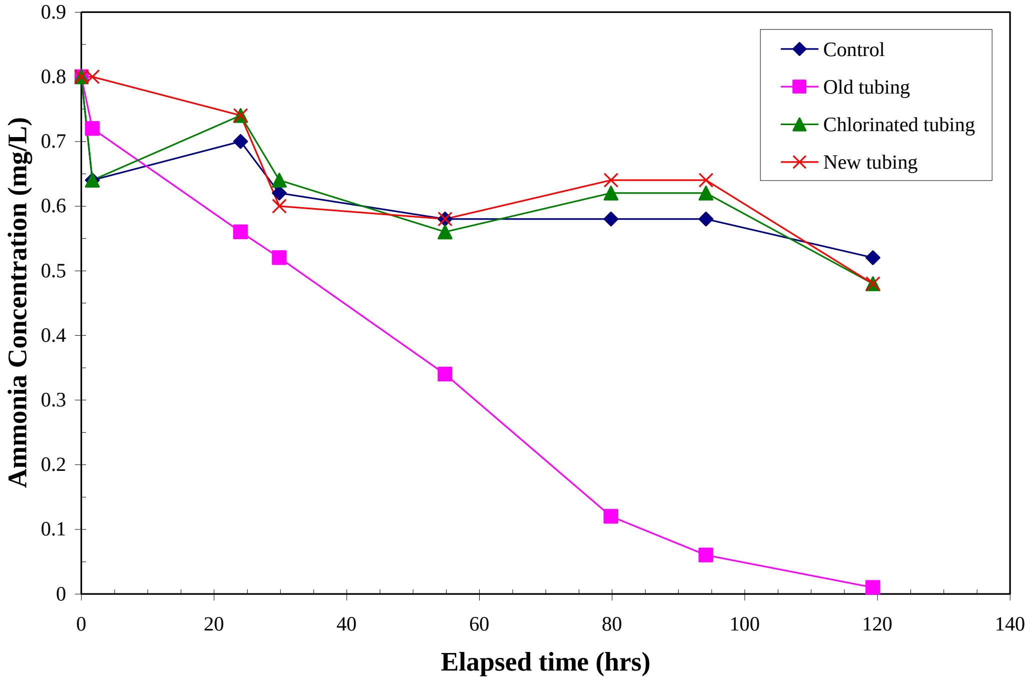

Figure 4-16. Ammonia concentration versus time for glass jar test. Old tubing which had been exposed to conditions conducive to chloramine decay during the cement coupon corrosion testing exhibited a large chlorine demand compared to new tubing and tubing which had been pre-chlorinated.

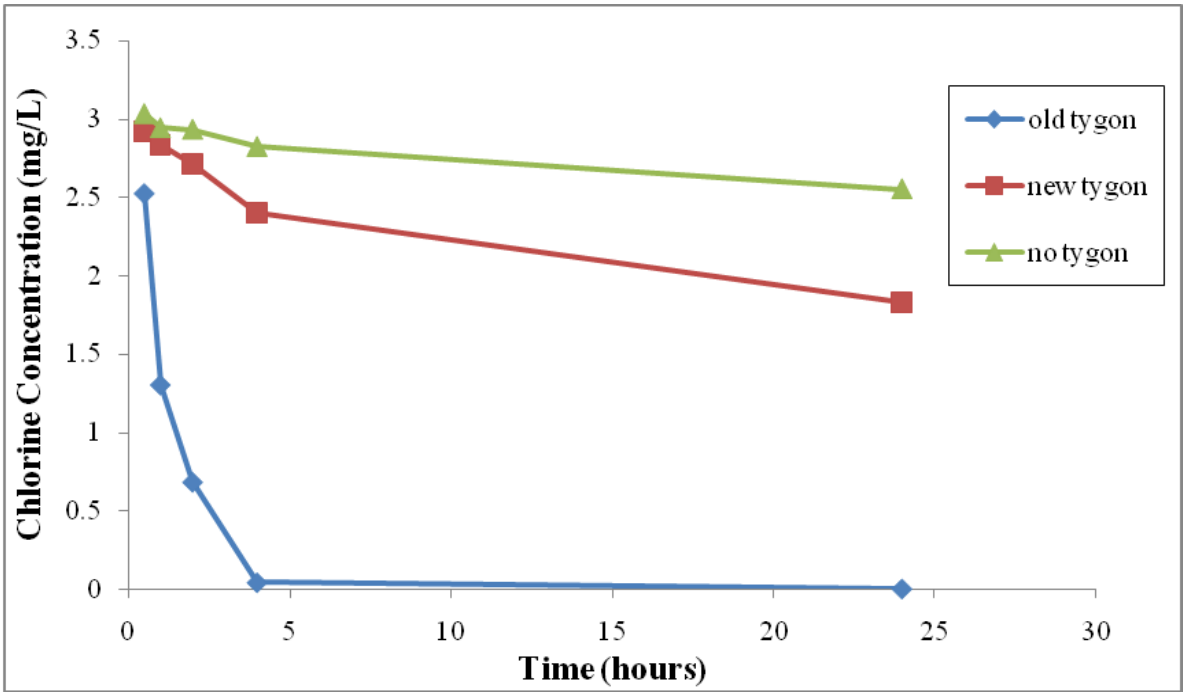

Figure 4-17. Chloramine decay (chlorine concentration) comparing old tygon tubing, new tygon tubing, and a control without tygon tubing over a 24 hour period.

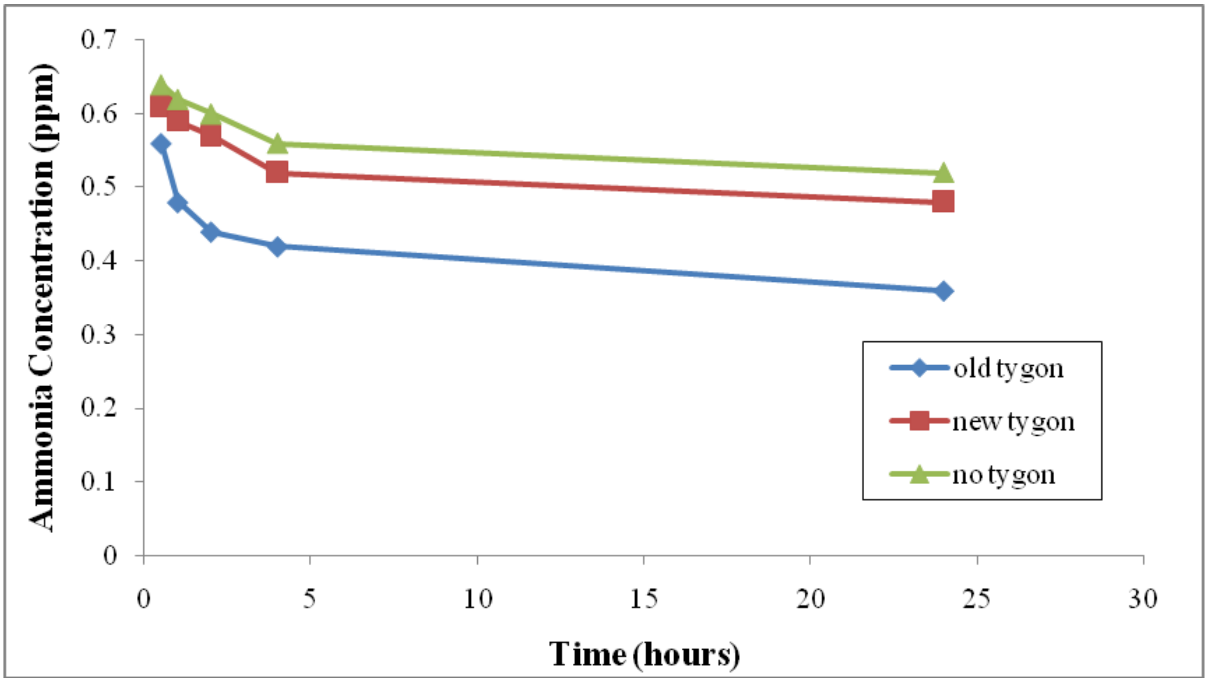

Figure 4-18.Chloramine decay (ammonia concentration) comparing old tygon tubing, new tygon tubing, and a control without tygon tubing over a 24 hour period.

APPENDIX A

Nitrification in Premise Plumbing: Role of Phosphate, pH and Pipe Corrosion
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APPENDIX B

Lead Contamination of Potable Water Due to Nitrification
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