

NEW INSIGHTS INTO LEAD AND COPPER CORROSION:
IMPACTS OF GALVANIC CORROSION, FLOW PATTERN,
POTENTIAL REVERSAL, AND NATURAL ORGANIC MATTER

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ABSTRACT

The EPA Lead and Copper Rule set Action Limits for lead and copper concentrations in potable water, but accelerated corrosion of lead in potable water systems due to a galvanic connection to copper remains a significant health risk to consumers. In addition to elevated lead release due to galvanic corrosion of lead-tin solder and leaded brass fixtures, partial lead service line replacements with copper pipe present long-term health concerns. Prior research has demonstrated that the effects of galvanic corrosion can be controlled by water chemistry, and the interplay between alkalinity, natural organic matter (NOM), and orthophosphate (added as corrosion inhibitor) may have a significant influence on corrosion of common lead plumbing materials. Results of bench-scale experiments demonstrate that in some waters galvanic corrosion can multiply lead release from lead pipe by up to 60 times, but other waters curtail the galvanic current and alleviate the effects of galvanic corrosion. Measurements of pH at the lead surface demonstrate that a corrosive micro-environment forms during stagnation in which the local pH drops to 3.0 or lower, demonstrating that the worst-case scenario for galvanic corrosion of lead occurs during long stagnation periods.

In addition to water chemistry, flow pattern also has an impact on galvanic corrosion of lead. Conventional wisdom regarding lead release indicates that continuous flow results in the greatest mass of lead release, but reports of anomalously high lead concentrations after long periods of stagnation point to the contrary. In this experiment, continuous flow of chlorinated water through a Pb-Cu galvanic couple promoted Pb(IV) formation and resulted in potential reversal that caused lead pipe to become cathodic to copper and minimized lead release to water. In contrast, intermittent flow resulted in sustained galvanic attack, and a mass balance of Pb release indicated that a greater total mass of lead was released with intermittent flow. These results have important implications for assessing lead risk at the tap, especially considering long stagnation periods at facilities such as schools and increasing efforts for water conservation.

Elevated copper release can be problematic in new plumbing systems prior to the formation of a protective scale layer on the pipe surface. While solubility in new copper pipes tends to be controlled by an amorphous solid of high solubility, over time, the natural copper aging process results in the formation of a protective scale of much lower solubility, but the transition can be inhibited in waters with high levels of NOM. Experiments demonstrated that GAC treatment to remove NOM accelerates the aging process to a protective scale that provides a long-term reduction in copper release even after GAC treatment is terminated. Therefore, compared to pH adjustment and orthophosphate addition, which must be continued perpetually, GAC treatment may be a more holistically pleasing method of copper corrosion control. This approach could be useful in the commissioning of new buildings to facilitate rapid aging and avoid potential long-term copper corrosion problems.

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AUTHOR'S PREFACE

This thesis has been written according to the guidelines of the Virginia Tech manuscript format, and each of the three chapters presented herein was written as a complete manuscript for publication, with supplementary information contained in an appendix. I served as first author for the three manuscripts contained in this thesis in collaboration with my advisor, and I am grateful for the dedicated assistance of undergraduate research assistants and other graduate students who contributed to the experimental work: Lars Peterson, Caitlin Grotke, Jaque Dalrymple, Meredith Raetz, and Allian Griffin. All photographs herein were taken by author. I plan to present the first chapter at the AWWA Annual Conference and Exposition in June, 2011, and the second chapter was selected for a special session on partial lead service line replacements at the AWWA Water Quality Technology Conference in November, 2011. I presented the third chapter at the AWWA Water Quality Technology Conference in November, 2010, and was awarded the Student Best Paper Award at the conference.

The first chapter examines the impacts of natural organic matter (NOM), alkalinity, and orthophosphate on galvanic corrosion, and the results broached several new questions about lead and copper corrosion addressed in the subsequent chapters. Chapter 2 focuses on the role of flow pattern on galvanic corrosion of lead, and Chapter 3 explores the role of NOM in copper corrosion problems in new construction.

In addition to the three chapters contained in this thesis, I served as second author for a manuscript titled "Effect of flow rate, lead/copper pipe sequence, and accelerated aging on galvanic & deposition corrosion of lead pipe" authored by Clément Cartier of École Polytechnique de Montréal, who worked in the laboratory at Virginia Tech for one semester to construct a pilot rig to study partial lead service line replacements. Following Clément Cartier's return to Montréal, I facilitated the experimental work at Virginia Tech for the pilot rig throughout the eight months of sampling. The resulting manuscript will be presented at the AWWA Annual Conference and Exposition in June, 2011 and submitted for publication in 2011.

Chapter 1: The Effects of Alkalinity, NOM, and Orthophosphate on Galvanic Corrosion of Lead

ABSTRACT

Previous work has demonstrated that alkalinity and natural organic matter (NOM) significantly influence lead corrosion in drinking water systems. Practical has shown that the addition of orthophosphate as a corrosion inhibitor tends to reduce the risk of lead contamination, but recent research has suggested that a higher dose of orthophosphate may be required for lead corrosion control in waters with high concentrations of NOM. Furthermore, galvanic corrosion has emerged as a significant health concern with unique corrosion behavior. A large test matrix was used to examine the interplay of alkalinity, NOM, and orthophosphate on lead release from five different configurations of plumbing materials commonly encountered in drinking water systems. The results indicated that NOM tends to increase lead release for most leaded materials and further suggested that a higher dose of orthophosphate is required for effective lead corrosion control in waters with a high level of NOM. The results also demonstrated that galvanic corrosion can be controlled by water chemistry; certain waters in the experimental matrix were identified in which galvanic corrosion increased lead release by up to 60 times, while in other waters, the detrimental impacts of galvanic corrosion were alleviated. Measurements of pH at the surface of the anode revealed a significant and persistent local pH drop during stagnation that may be mechanistically responsible for the drastic effects of galvanic corrosion on lead release.

Introduction

The important interplay between alkalinity, natural organic matter (NOM), and orthophosphate in controlling contamination of potable from leaded plumbing materials (brass, solder, and lead pipe) has been the subject of intensive research (Edwards and McNeill, 2002; Edwards et al, 1999; Korshin et al, 1999; Gregory, 1990; Schock et al, 1985). Prior work has demonstrated links between higher NOM and increased lead leaching (Hayes and Skubala, 2009; Korshin et al, 1999; Colling et al, 1992), and some practical research has suggested that increased dosing of phosphate inhibitors may be required to compensate for NOM in order to achieve the same degree of corrosion control (Hayes et al, 2010). Other recent research has demonstrated that in

some circumstances, addition of orthophosphate may actually increase corrosion of leaded solder galvanically connected to copper (Nguyen et al, 2011a). The practical importance of galvanic corrosion has been demonstrated by important long-term health concerns associated with partial replacement of lead services lines with copper and a few instances of elevated blood lead in children triggered by aggressive galvanic attack on old lead solder connected to copper joints (Triantafyllidou and Edwards, 2011; Nguyen et al, 2011b; Edwards & Triantafyllidou, 2009).

Galvanic corrosion can occur in potable water whenever two dissimilar pipe materials metals are brought into electrical contact. In the case of lead plumbing materials connected to copper, the overall corrosion rate of the leaded material is accelerated beyond the baseline rate, sometimes by orders of magnitude (Triantafyllidou & Edwards, 2011; Dudi, 2004). The rate of galvanic attack can be accelerated by high chloride-to-sulfate mass ratio (CSMR) (Nguyen et al, 2011b; Edwards & Triantafyllidou, 2007; Gregory, 1990). Localization of corrosion in galvanic conditions can drop the pH to 3.0 or lower at the surface of lead plumbing due to the release of Lewis acids Pb and Sn (Nguyen et al, 2010), and to maintain electro-neutrality, corrosive anions migrate to the lead surface, where chloride build-up can increase lead release via formation of soluble $PbCl^+$ complexes.

DeSantis et al (2009) analyzed pipe samples at galvanic joints from four utilities and observed greater lead scale buildup, lead pipe wall thinning, and different mineralogical deposits at the site of the Pb-Cu connection compared to pipe surfaces even a few inches away. Based on an analysis of minerals at the joints, the authors concluded that the local water chemistry at the site of the galvanic connection varied significantly from the bulk water, consistent with expectations based on the conclusions of Nguyen et al (2010) and Dudi (2004). DeSantis et al. (2009) further concluded that the extent of galvanic corrosion can be controlled by the water chemistry, consistent with the results of past research demonstrating a wide range of corrosion potential values in galvanic corrosion depending on water chemistry (Gregory, 1985).

Korshin et al (1999) theorized that the primary mechanisms by which NOM interacts with lead are complexation, which can increase the total soluble lead at equilibrium, and adsorption of NOM to crystalline lead corrosion by-products, which may alter the morphology of the lead corrosion scale. Their experiments indicated that NOM significantly increased lead release from brass, solder, and lead pipe without a galvanic connection to copper, but noted that effects of

NOM depend on other water quality parameters such as pH, corrosion inhibitor concentration, and anionic composition. For the case of lead pipe, Korshin et al (1999) found that NOM increased both soluble lead release and the fraction of soluble lead. Other research has also shown that addition of high levels of humic material increased lead release (Colling et al,). However, the impact of NOM on galvanic corrosion of lead has not been carefully studied, and its interaction with orthophosphate deserves further study.

The goal of the current research is to examine the impact of alkalinity, orthophosphate, and NOM on leaching of lead from brass, leaded solder, and lead pipe. In each case, the potential role of galvanically coupling the lead plumbing to copper pipe was also examined, and the impact of water chemistry on the galvanic corrosion current was quantified. The goal was to elucidate the possible role of water chemistry in mitigating or exacerbating galvanic corrosion and lead release to potable water under "worst-case" conditions induced by long stagnation times.

Methods and Materials

A set of bench-scale laboratory experiments were carried out to examine the effects of alkalinity, NOM, and orthophosphate on lead release from four different materials. For the lead pipe-copper pipe galvanic couple, a 1-foot section of $\frac{3}{4}$ -inch diameter copper pipe was attached to a 2-inch section of $\frac{1}{2}$ -inch inner diameter lead pipe. The two metals were separated by a $\frac{1}{16}$ -inch thick rubber dielectric washer and connected externally with copper wire to permit galvanic current measurements. For lead pipe without a galvanic connection, a 1-foot section of $\frac{3}{4}$ -inch diameter PVC pipe was attached to a 2-inch section of $\frac{1}{2}$ -inch inner diameter lead pipe to maintain the exact same ratio of water volume to lead surface area as the lead-copper couple. Differences in lead release between the two rigs can be attributed to galvanic and deposition corrosion effects (Triantafyllidou & Edwards, 2011). For conditions with leaded solder, a $\frac{3}{8}$ -inch diameter piece of 50-50 lead-tin solder wire was inserted through a hole drilled in a silicone stopper such that 2 inches of solder wire would protrude into the water along the central axis of a 1-foot section of $\frac{3}{4}$ -inch diameter copper pipe. Similarly, a section of $\frac{3}{8}$ -inch diameter brass wire containing 8% lead by weight was inserted through a silicone stopper so that a 2-inch length would be exposed to water, and the stopper was inserted into a 1-foot section of $\frac{3}{4}$ -inch diameter

copper pipe. The brass and solder wire were electrically connected externally to the copper pipe to permit galvanic current measurements.

An experimental matrix of water chemistry consisting of two levels of alkalinity, three concentrations of NOM, and four leaded materials resulted in a total of 24 test conditions. Each condition was tested in triplicate for a total of 72 pipes. To examine the impact of phosphate dosing, after establishing trends without phosphate, sodium orthophosphate (Na_3PO_4) was added first at a concentration of 1 mg/L as P and then at 2 mg/L as P.

Synthetic test waters were prepared from de-ionized water with pH 7.3, 0.5 mg/L free chlorine, and a CSMR of 2.5 (Table 1). Sodium bicarbonate stock solution was used to adjust the alkalinity to low and high levels of 12 mg/L and 250 mg/L as CaCO_3 , respectively. A stock solution of NOM comprised primarily of fulvic acids was isolated from soil was cleaned repeatedly in acid and caustic solutions, centrifuged, and filtered prior to being added to the water at concentrations of 0, 1, and 4 mg/L as TOC. Sodium hypochlorite solution (NaOCl , 6% w/w) was used to establish the target chlorine residual which was verified using HACH test kits. The pH of each solution was adjusted to 7.3 by bubbling with 99.9% pure CO_2 gas prior to filling the pipes.

Table 1-1. Summary of Synthetic Water Chemistry

Parameter	Value
pH	7.3
Chloride, Cl^- (mg/L)	50
Sulfate, SO_4^- (mg/L)	20
Nitrate, NO_3^- (mg/L)	3.0
Sodium, Na^+ (mg/L)	48
Silicon, Si^+ (mg/L)	2.7

All pipe sections were emptied and refilled with freshly prepared synthetic water every Monday, Wednesday, and Friday. Pipe sections were sealed with silicone stoppers and allowed to sit stagnant between water changes. The effluent of each pipe triplicate was retained as a weekly composite, but additional triplicate samples were taken periodically over one 48-hour stagnation period to determine trends with statistical confidence. All samples were acidified after collection with 2% by volume nitric acid (H_2NO_3) to dissolve any lead particulates. Water samples were

analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and the galvanic current was periodically measured with a Fluke zero-resistance ammeter. All results presented herein as significant exceed 95% confidence in ANOVA and t-tests. No attempt was made to quantify particulate lead apart from soluble lead, although it was clear from visual observations that sporadic release of lead particulates is a major contributor to variance in the data, as observed in previous research (Triantafyllidou et al, 2007; McNeill and Edwards, 2004).

Results and Discussion.

Lead Pipe connected to PVC.

For this particular water chemistry, higher alkalinity did not seem to markedly reduce lead release for lead pipe connected to PVC. The lowest lead concentrations tended to occur with 1 mg/L NOM, and lead release with 4 mg/L NOM was no worse than with zero NOM. Korshin et al (1999) evaluated the effects of NOM (extracted from a reservoir) in the range of 0 to 10 mg/L on lead release from lead pipe without a galvanic connection to copper, and the results indicated that higher levels of NOM increase soluble lead release as well as the percentage of soluble lead. In the experiments of Korshin et al (1999), with no NOM present, both the concentration and the fraction of soluble lead were quite low (> 5% soluble), but the total lead with no NOM was equivalent to that with higher doses of NOM. In fact, Korshin et al (1999) noted that considerable colloidal lead release occurred in the absence of NOM, and the addition of a small amount of NOM tended to stabilize the lead surface. Only total lead was measured in this experiment, but it seems likely that elevated lead release with no NOM was a result of particulate lead release which was minimized with a low dose of NOM (1 mg/L). With high alkalinity, the variability of lead release was quite high with no NOM, likely indicative of recurrent particulate release, but the variability with 1 mg/L was comparatively low (Figure 1). This theory may also explain the deviation of the results from field observations that colored waters have a greater risk of lead corrosion. Natural drinking water would not realistically be as void of organic matter as a synthetic water used in the laboratory, and low amounts of NOM remaining after treatment may serve to stabilize corrosion of leaded plumbing materials without a galvanic connection to copper. However, waters with higher levels of NOM would be expected to exacerbate lead release.

Consistent with expectations based on solubility models and utility experiences (Dodrill and Edwards et al., 1995; Cardew et al, 2002) addition of orthophosphate reduced lead release for all conditions with lead pipe attached to PVC. Furthermore, the results provided the first experimental confirmation of field observations that waters with high levels of organic matter required a higher dose of orthophosphate to yield achieve the same level of lead release compared to waters with less organic matter (as per Hayes et al, 2010). At both levels of alkalinity, the average lead concentration with 4 mg/L NOM and a 2 mg/L as P orthophosphate dose was still greater than that with 1 mg/L NOM and an orthophosphate dose of 1 mg/L as P, but higher phosphate did significantly reduce lead in waters with high NOM. Benefits of higher phosphate (2 mg/L vs. 1 mg/L as P) were not significant in waters with 0 or 1 mg/L NOM.

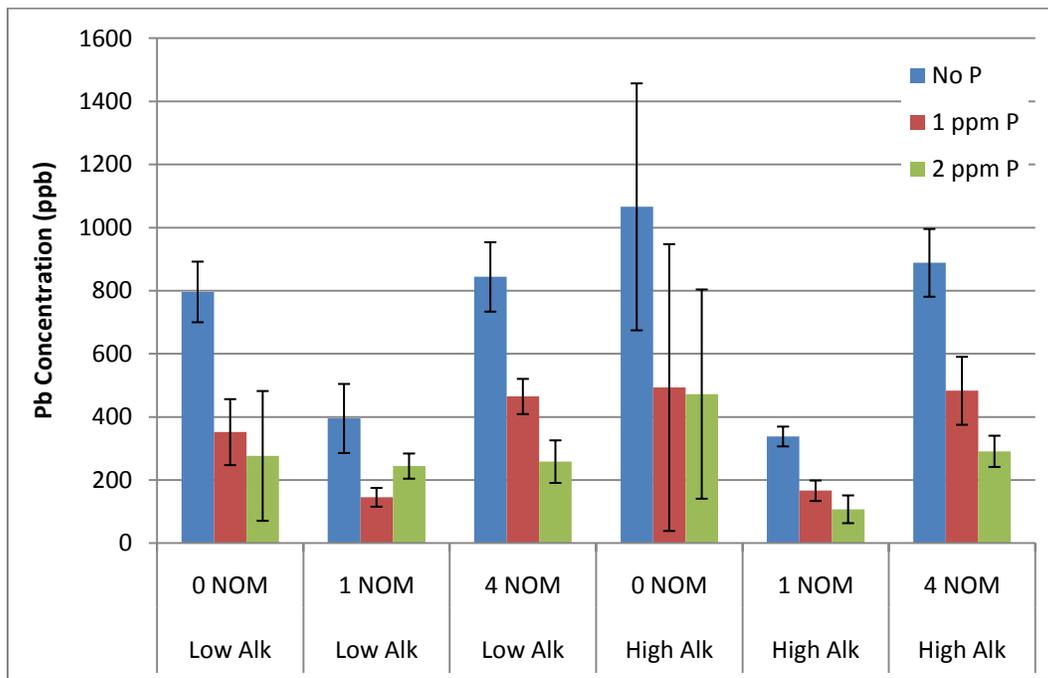


Figure 1-1. Average Lead Release from Lead Pipe attached to PVC (error bars represent 95% confidence intervals)

Lead Pipe Connected to Copper.

Connecting lead pipe to copper greatly increased lead release by nearly 10 times in the absence of orthophosphate, and the NOM concentration did not have a strong influence on the galvanic factor (Figure 2). With a galvanic connection, NOM had a diminished influence on lead release. Specifically, with high alkalinity, NOM had virtually no effect on lead release, and with low alkalinity, only the condition with 1 mg/L NOM had significantly lower lead release. Again, the

drop in total lead with a low dose of NOM may be due to stabilization of the lead surface and associated decreased particulate release. Prior to the addition of orthophosphate, the galvanic current remained very high (> 15 uA) for 3 months for all conditions tested. With low alkalinity, galvanic currents tended to be lower in waters with higher NOM, but with high alkalinity there was no strong trend between NOM and galvanic current (Figure 4).

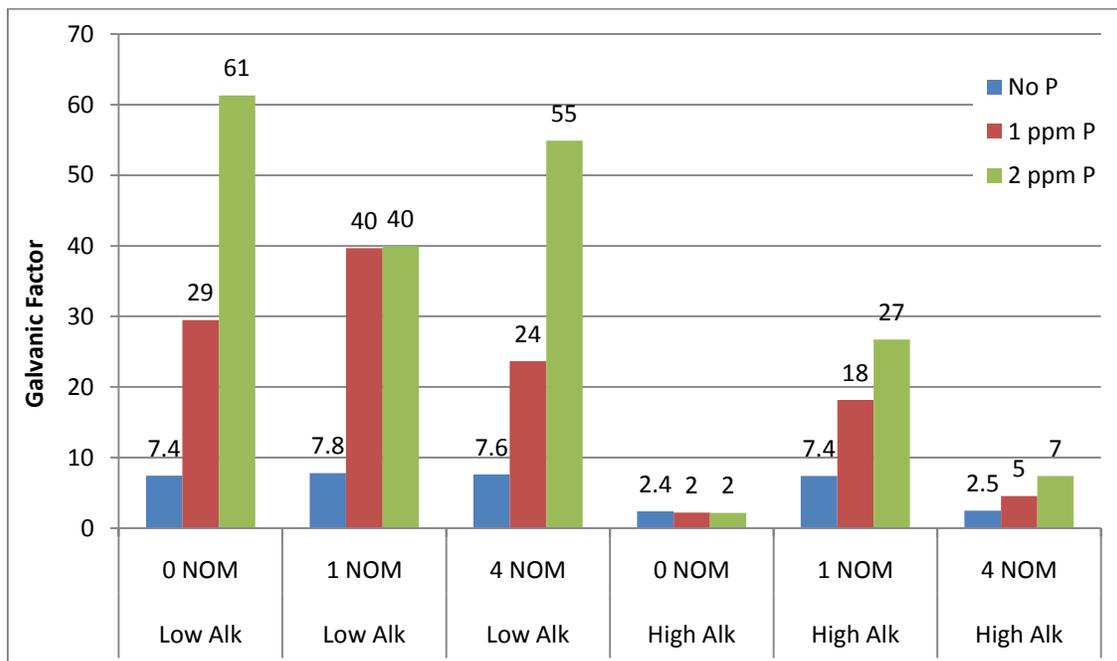


Figure 1-2. Impact of galvanic corrosion on lead release; Galvanic factor = (lead release when connected to copper)/(lead release connected to PVC)

The impact of galvanic corrosion (galvanic factor) tended to be higher with low alkalinity, consistent with prior research that demonstrated lower voltage potential between lead and copper in high alkalinity waters (Gregory, 1985). The addition of orthophosphate significantly mitigated galvanic corrosion for only one condition; with high alkalinity and no NOM, a dose of 2 mg/L as P dropped the current to 5 uA (Figure 4). This was also the only case in which higher orthophosphate reduced lead release, and lead release decreased by about 60% with 2 mg/L as P compared to no P (Figure 3). While the exact mechanisms by which the current was reduced are not fully understood, this result demonstrates that galvanic corrosion can be controlled by water chemistry and that galvanic corrosion may be mitigated by some waters. In all other high alkalinity waters, orthophosphate had no beneficial impact on lead release (Figure 3) and yielded only slight reductions in galvanic current (Figure 4).

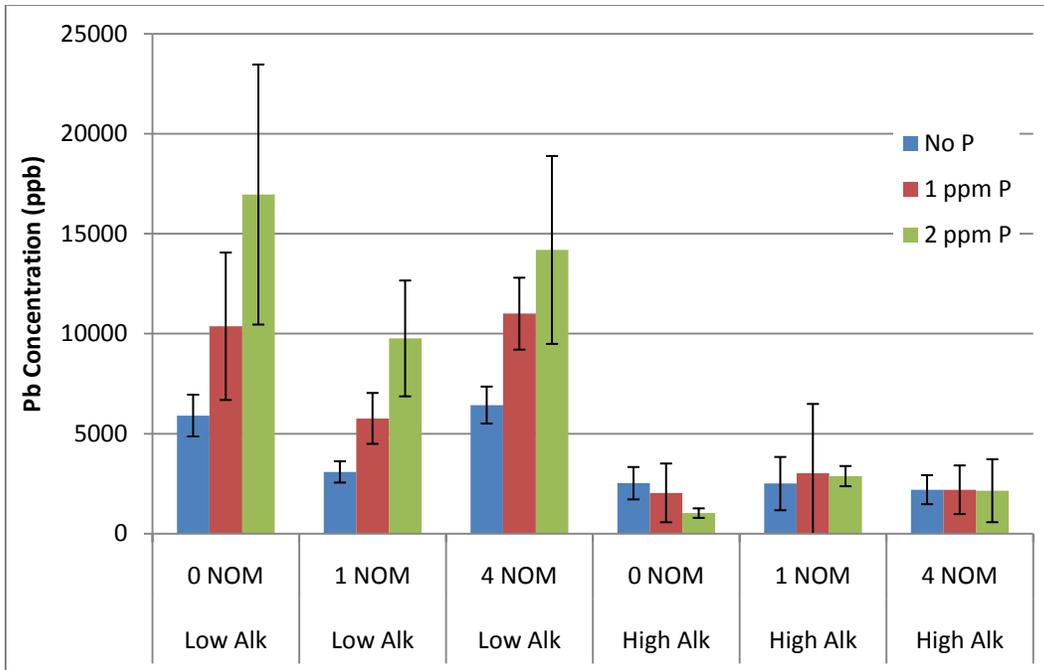


Figure 1-3. Average Lead Release from Pb Pipe attached to Cu (error bars represent 95% confidence intervals)

In low alkalinity waters, orthophosphate addition corresponded to a significant increase in galvanic current (Figure 4), and increasing the orthophosphate dose from 0 to 2 mg/L as P increased lead release by nearly 3 times. Nguyen et al (2011b) found that orthophosphate addition increased lead release from solder, and the results of this experiment confirm that the same behavior may occur for lead pipe galvanically connected to copper pipe in certain waters. The worst case impact of galvanic corrosion occurred in low alkalinity water without NOM and with 2 mg/L P, for which lead release increased 60 times (Figure 2). For some samples for this condition, lead release was over 100 times greater with a galvanic connection than without the galvanic connection. The galvanic current for this condition increased markedly with orthophosphate dosing, but not to the same extent as was observed for lead release. Therefore, other mechanisms are implicated for the spike in lead release, and, based on visual observations of white solids in the pipe effluent, particulate lead release induced by orthophosphate may have contributed. This experiment did not examine the long-term impacts of orthophosphate addition on galvanic corrosion, and a study on the topic with greater temporal length is recommended.

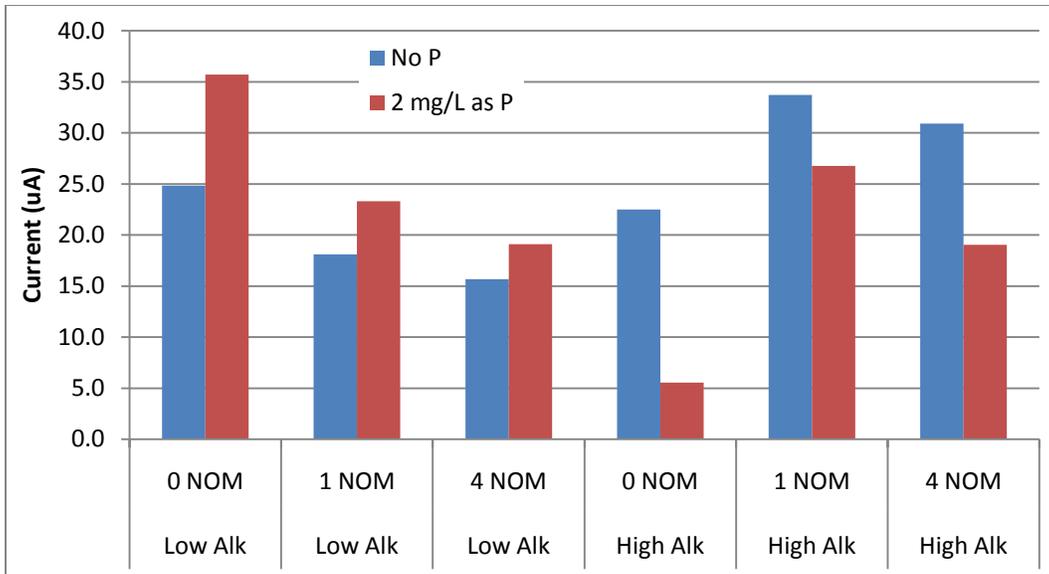


Figure 1-4. Impact of orthophosphate on galvanic current between lead pipe and copper

Solder connected to copper.

For 50-50 lead-tin solder connected to copper pipe, high alkalinity significantly increased lead release compared to low alkalinity (Figure 5). In the absence of orthophosphate, high levels of NOM also increased lead release, and its impact was more pronounced with low alkalinity.

Additionally, the NOM concentration influenced the impact of orthophosphate addition. Without NOM, orthophosphate greatly increased lead release from solder, but at higher concentrations of NOM orthophosphate had minimal effect (Figure 5). Addition of orthophosphate also increased the galvanic current for all water conditions in this experiment (Figure 6). The detrimental impact of orthophosphate persisted for the remainder of the experiment, but additional work should evaluate lead release and galvanic current over a longer time period. The results of this experiment agree with the findings Nguyen et al (2011a) for this particular water chemistry but further suggest that the concentration of NOM has an influence on the potential detrimental impacts of orthophosphate in certain waters.

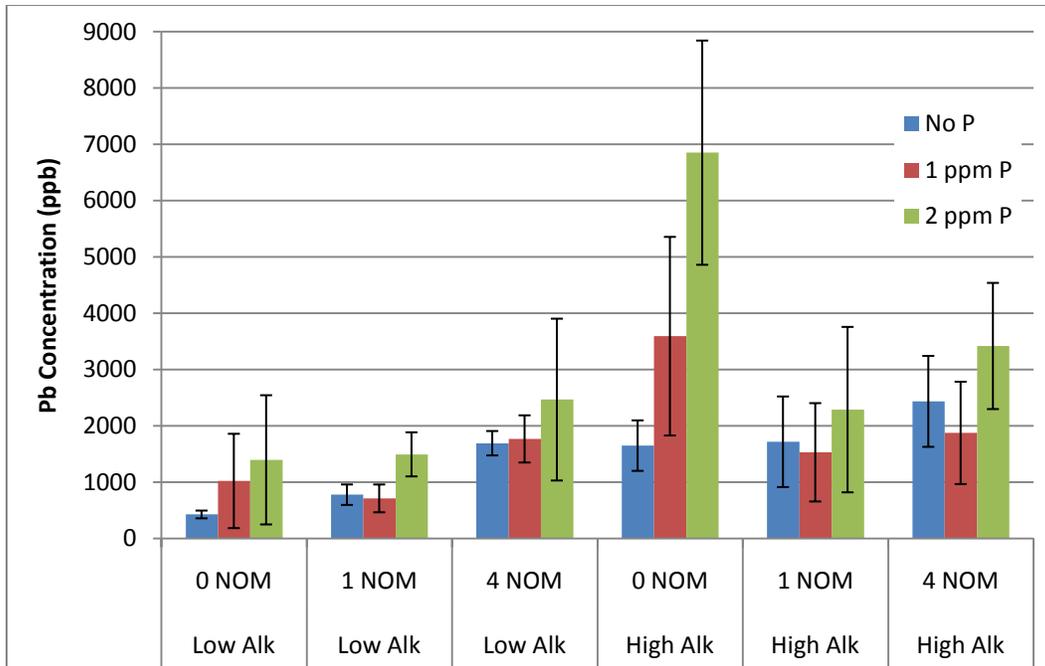


Figure 1-5. Average Lead Release from solder attached to copper (error bars represent 95% confidence intervals)

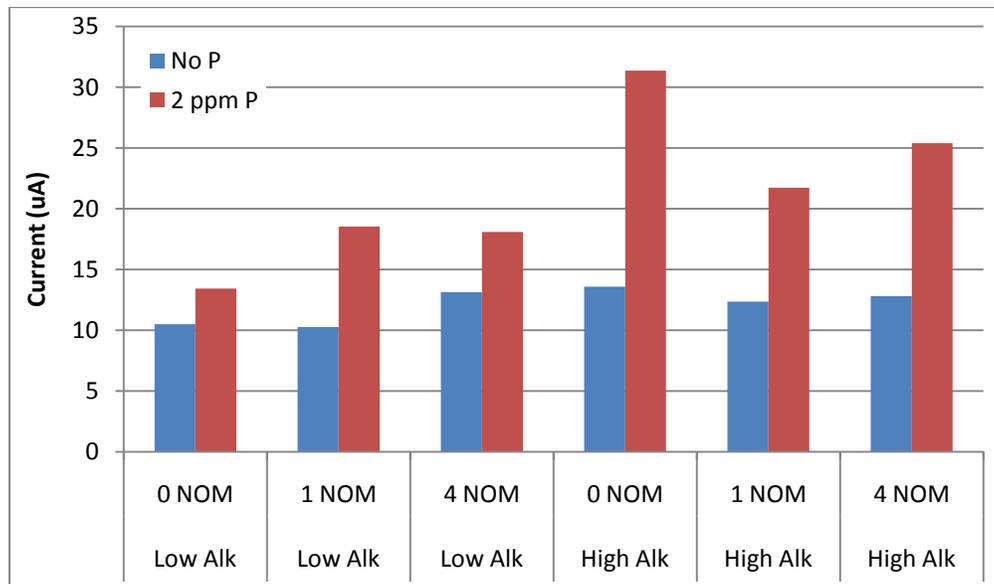


Figure 1-6. Impact of orthophosphate on galvanic current between solder and copper

Brass connected to Copper.

While alkalinity did not influence lead release from brass, NOM significantly increased lead release (Figure 7), consistent with previous research regarding the effect of NOM on brass without an external galvanic connection to copper (Korshin, et al, 1999). As brass contains copper, an external connection to copper pipe is not likely to have a drastic effect on lead release, and it is not surprising that a galvanic connection to copper did not alter lead release trends observed in the past for brass without a galvanic connection. Contrary to prior work (Korshin et al, 1999), higher concentrations of NOM increased Zn release from brass (Figure A-5).

Orthophosphate tended to reduce lead release in all conditions (Figure 7). At both levels of alkalinity with an orthophosphate dose of 2 mg/L as P, the average lead concentration with 4 mg/L NOM was higher than that with no NOM, indicating that a higher dose of orthophosphate would be required to reduce lead leaching from brass in highly organic waters.

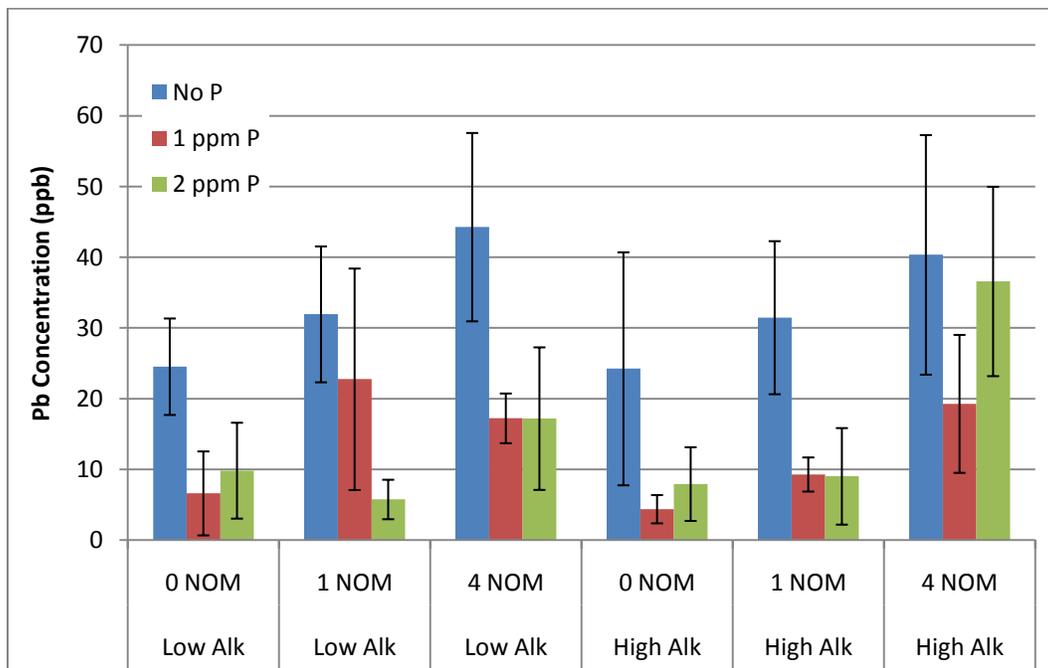


Figure 1-7. Lead Release from Brass attached to copper (error bars represent 95% confidence intervals)

Interestingly, galvanic current measurements demonstrated that an orthophosphate dose of 2 mg/L as P caused a potential reversal of brass versus copper, as the copper pipe became the anode and the brass became the cathode (Figure 8). Consistent with this observation, copper

release (data not shown) rose when orthophosphate was added. Orthophosphate was more effective with high alkalinity and caused the greatest reduction in galvanic current in conditions without NOM.

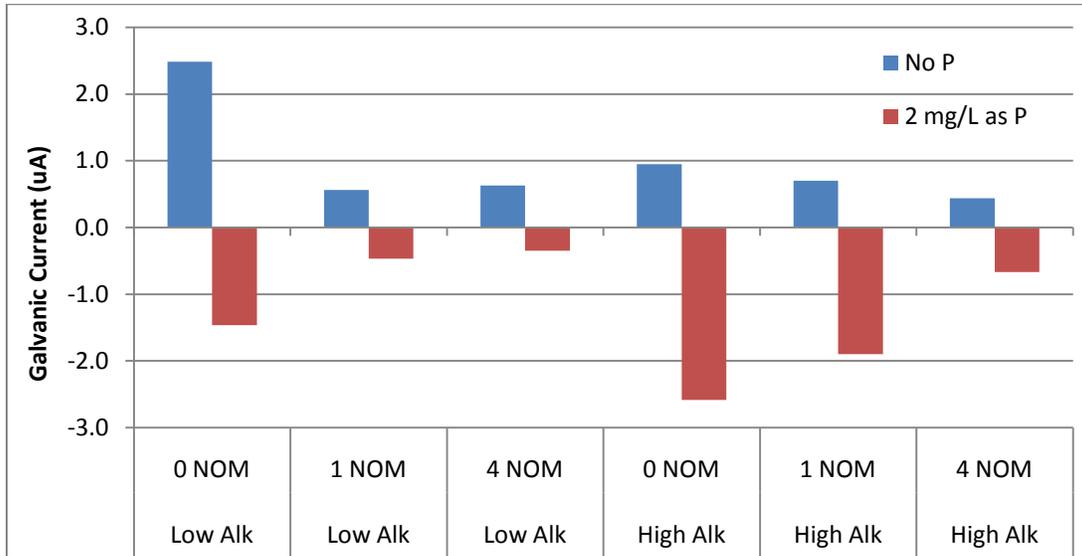


Figure 1-8. Impact of orthophosphate on galvanic current between brass and copper

Table 1-2. Summary of Lead Release Results

Material	Alkalinity	NOM	Phosphate
1. Lead pipe connected to PVC	•No significant Impact	•Low level of NOM has stabilizing effect •High levels of NOM exacerbate lead release	•Reduced lead release •Higher P dose required with NOM
2. Lead pipe connected to Copper	•High Alkalinity less corrosive	•No significant impact on lead release •Higher P dose required with NOM	•Increased lead release with low alkalinity
3. Solder connected to Copper	•High Alkalinity slightly more corrosive	•Higher NOM resulted in greater lead release	•Greatly increased lead release with high alkalinity and zero NOM •No benefit in other conditions
4. Brass Connected to copper	•No significant impact on lead release	•Higher NOM resulted in greater lead release •Higher P dose required with NOM	•Reduced lead release in all waters and reversed galvanic current

Micro-pH Measurements

To further elucidate the mechanisms involved with the localized galvanic attack, the pH of the microenvironment at the lead surface was measured for both lead-tin solder and lead pipe connected to copper. Previous research has examined the spatial variation of the pH-drop (Nguyen et al, 2010) but did not examine the temporal variation of the minimum pH during stagnation.

As expected, the magnitude of the pH drop was generally greater for lead-tin solder than for lead pipe connected to copper due to the additional dissolution of tin, a stronger Lewis-acid than lead. The minimum pH occurred just at the tip of the solder wire protruding into the water. The pH at the anode dropped rapidly, and a low-pH zone developed at the solder surface in as little as 1 minute after stagnation began and the persisted for the entire 24 hour period (Figure A-6, supplemental information). At both levels of alkalinity, the minimum and average pH at the solder surface increased at higher levels of NOM, with a difference of approximately 2 pH units between 0 and 4 mg/L NOM. A possible explanation is that NOM increased the complexation of dissolved Sn and Pb released at the anode surface, reducing their Lewis acidity and thus the pH drop in the microenvironment. The greatest detrimental impact of adding orthophosphate occurred in conditions with no NOM, and, accordingly, the lowest micro-pH values were measured in the same conditions.

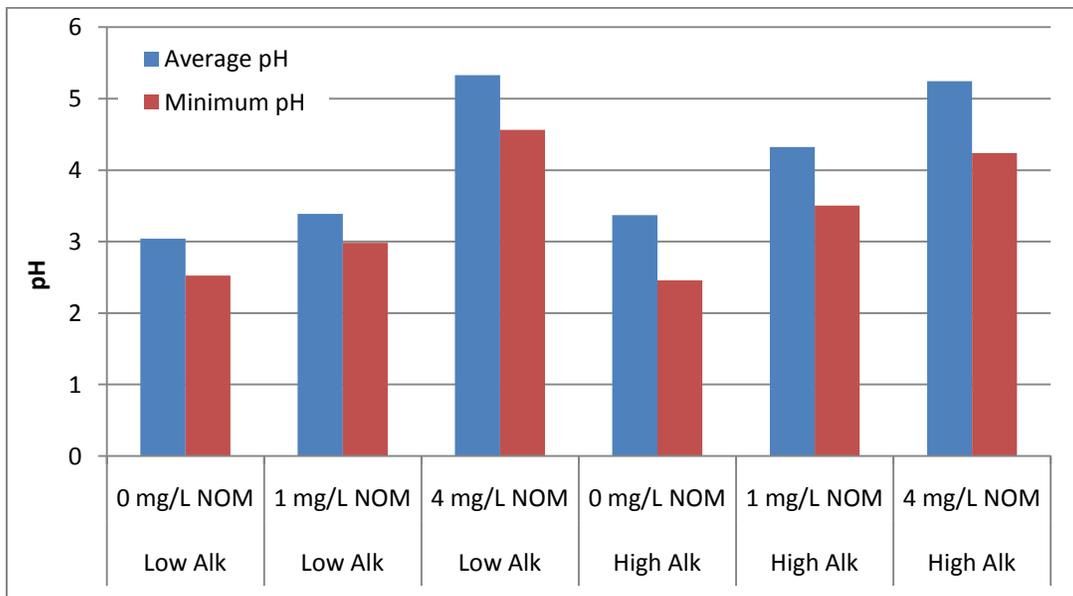


Figure 1-9. pH at Solder Surface during Stagnation (with 2 mg/L as P)

Significant pH drops were also observed for lead pipe connected to copper. The pH at the surface dropped rapidly upon filling the pipes, and the minimum pH was often measured within the first 15 minutes of stagnation (Figure A-7). The pH at the lead surface near the joint remained low for the entire 24 hour period. Unlike with solder, there was no clear correlation between the NOM concentration and the pH at the anode. To explain the discrepancy between solder and lead pipe, perhaps Sn, a stronger Lewis-acid than Pb, may more readily form complexes with NOM, and therefore, in the absence of Sn, NOM has a diminished impact on the pH at the lead surface. Additionally, the pH at the anode was significantly lower at the higher level alkalinity; this result contradicts model predictions in previous work that alkalinity would serve to buffer pH drop at the lead surface (Dudi, 2004). As discussed previously, the water with high alkalinity and no NOM was able to drop the galvanic current and reduce lead release compared to other conditions when orthophosphate was added. Accordingly, micro-pH measurements revealed that in this condition, the minimum pH was significantly higher than in conditions with high alkalinity and NOM.

Conclusions

The interplay between alkalinity, NOM, and orthophosphate is important, and the impacts of each cannot be fully understood in isolation (Table 2). High concentrations of organic matter in finished water can increase lead release from a variety of leaded materials and tends to increase the requisite dose of orthophosphate to achieve low lead levels. The variation of corrosion behaviors between different plumbing materials in the distribution system emphasizes the importance for utilities to be aware of the prevalent plumbing materials when considering the impacts of water chemistry alterations or corrosion inhibitor addition on lead compliance.

The observation that dosing of orthophosphate inhibitor can actually increase lead leaching from lead galvanically coupled to copper is of critical importance to water utilities, especially given newfound concern regarding potential long-term adverse health consequences arising from partial pipe replacements and isolated incidents of elevated blood lead in children from leaded solder. Based on the results of this experiment, a more thorough evaluation of the impacts of orthophosphate on galvanic corrosion is warranted, and the potential detrimental impacts should be examined further with larger sample sizes and longer time periods. Furthermore, the worst-

case impact of a partial replacement would occur if orthophosphate were added as a corrosion inhibitor, in which the results of this experiment demonstrated a 60-fold increase in lead release.

A galvanic connection between lead pipe and copper causes a significant galvanic current that initiate a low-pH microenvironment at the lead surface and multiplies total lead release to water by up to 60 times. The persistence of a low-pH microenvironment at the lead surface over a long stagnation period provides mechanistic insight about the “worst-case” scenario of long stagnation. However, galvanic corrosion between dissimilar metals in drinking water systems can be controlled by water chemistry, and certain waters may be able to minimize the effects of galvanic corrosion.

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APPENDIX A: Further Examination of Metals Release from Galvanic Conditions

During the experiment, the wires that externally connected lead pipe to copper pipe were disconnected for one week to determine if galvanic corrosion causes a lasting impact on lead corrosion after the galvanic current has terminated. Consistent with expectations based on the effect of galvanic current, with low alkalinity, lead release decreased substantially after lead pipe was disconnected from copper but did not fall as low as lead release from lead pipes never connected to copper (i.e. those connected to PVC). However, with high alkalinity, lead release spiked markedly after lead pipe was disconnected from copper, and became much higher than lead release from lead pipe never connected to copper (Figure A-1).

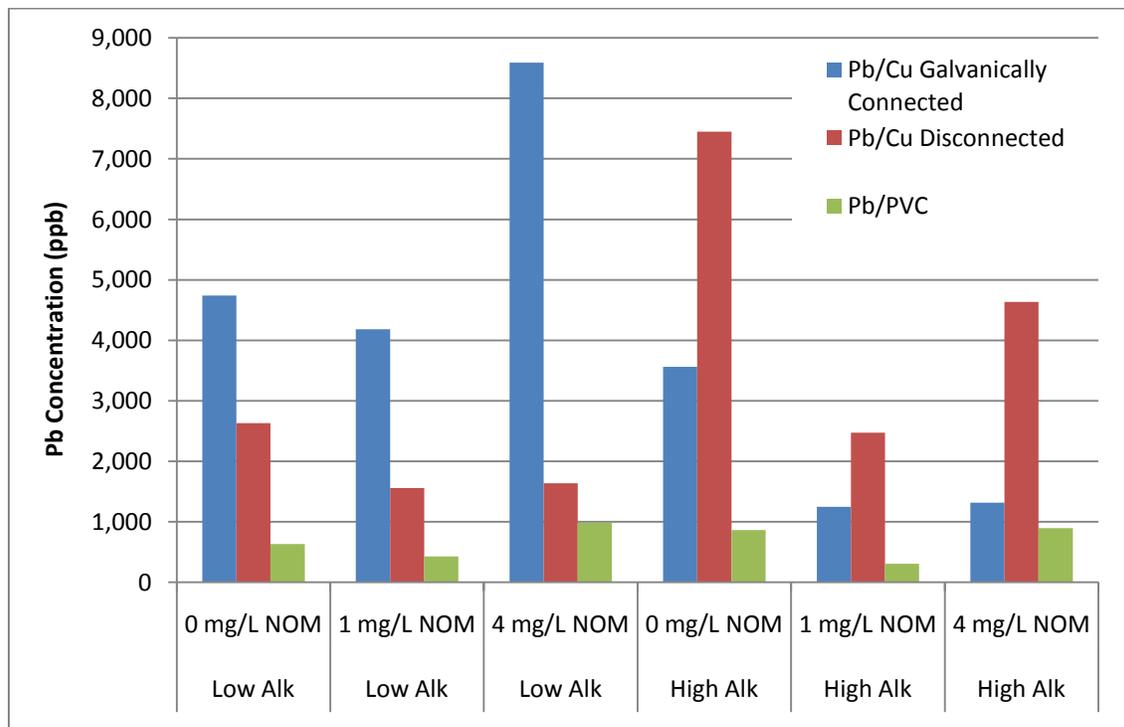


Figure A- 1. Summary of Galvanic Effect on Lead Release (Lead release data with galvanic connection and data for Pb connected to PVC taken from week prior to disconnection; disconnected lead release data taken from composite and triplicate samples during week of disconnection)

Disconnecting lead and copper pipe ended cathodic protection of the copper pipe, and as a result, copper concentrations spiked when lead and copper were disconnected and became equal to or higher than copper concentrations from copper pipe never connected to lead pipe (Figure A-2). The spike in copper concentrations upon disconnection may have increased the effects of deposition corrosion, which can occur when dissolved copper plating onto lead pipe creates an

abundance of local galvanic cells, and contributed to the lasting impact of galvanic corrosion at low alkalinity and the spike in lead concentrations at high alkalinity.

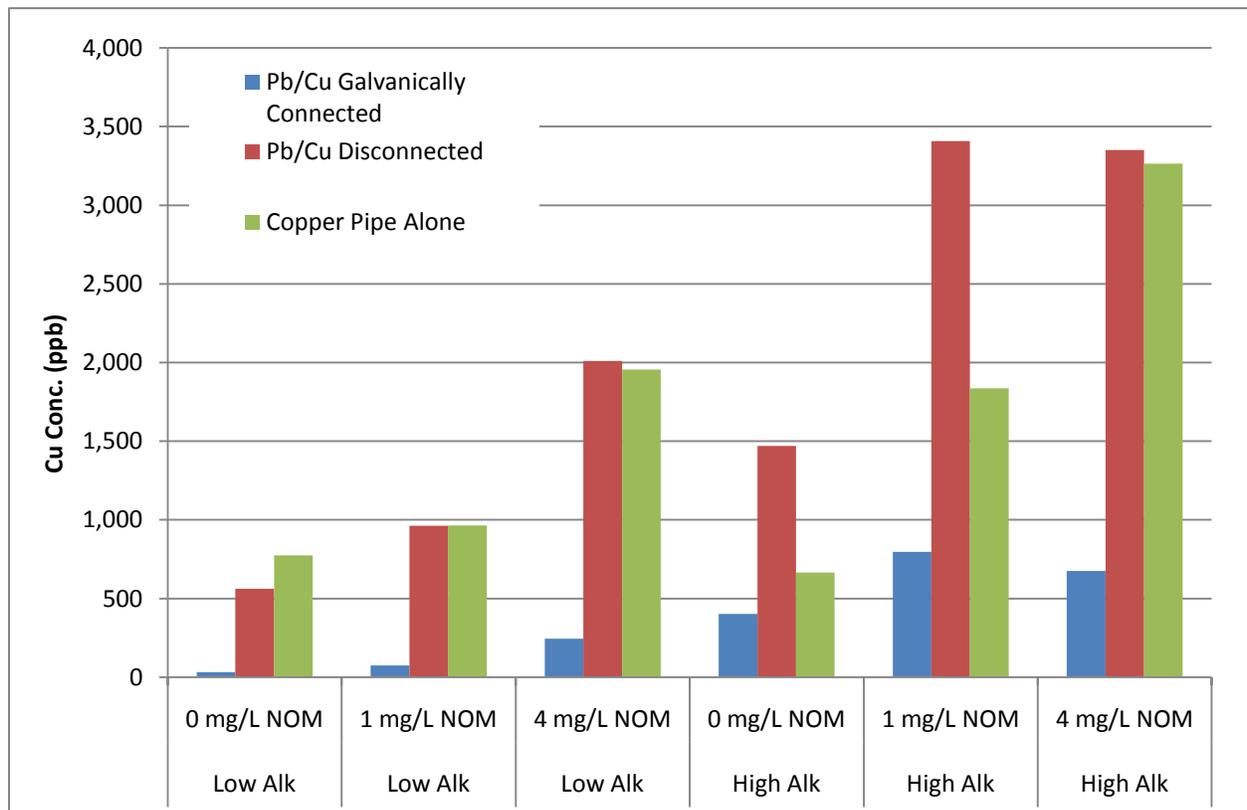


Figure A- 2. Summary of Galvanic Disconnection on Copper Release (Copper release data with galvanic connection taken from week prior to disconnection, disconnected copper release and copper pipe alone data taken from composite and triplicate samples during week of disconnection)

Ample previous research has demonstrated the detrimental effects of NOM on copper release from copper pipe without a galvanic connection; adsorption of NOM to crystalline copper corrosion by-products on the pipe surface interferes with the natural pipe aging process, preventing the formation of an insoluble protective scale such as malachite (Edwards and Sprague, 2001; Korshin et al, 1996; Edwards, Meyer, Rehring, 1996; Schock et al., 1995). In this experiment, a similar relationship between NOM and copper release was observed for copper pipe galvanically connected to Pb, but due to cathodic protection of copper pipe connected to lead pipe, copper release was approximately 70-90% lower from copper pipe with a galvanic connection compared to a control of copper pipe in isolation (Figure A-3). Rapid aging occurred for copper pipe without a galvanic connection in high alkalinity water with no NOM, resulting in a strong negative trend in copper release over time and the formation of a visible

blue scale on the internal copper surface. Interestingly, there was no evidence of aging on copper pipe with a galvanic connection to lead pipe in any waters.

Due to the increase in copper release in galvanic conditions at higher levels of NOM, deposition corrosion may have added further complexity to lead release results. Lead corrosion with a galvanic connection to copper was likely impacted by a combination of the effects of NOM and deposition corrosion, and the relative effects of each cannot be conclusively separated.

Nevertheless, the experiment constituted a relevant fundamental study of the effects of NOM on galvanic corrosion, as the impact of deposition corrosion on lead release is an important consideration for distribution and plumbing systems with elevated copper levels due to NOM.

Copper release from solder galvanically connected to copper was also considerably lower than the control. The reduction was likely due to cathodic protection of copper provided by a significant galvanic current of 10-20 μA . There was not a significant reduction in copper release compared to the control in the condition with high alkalinity and no NOM, in which aging occurred for copper pipe alone. As observed with Pb-Cu couples, the results indicate that the galvanic connection to solder inhibited copper pipe aging.

The connection of copper pipe to brass also caused a significant reduction in copper release compared to the control of copper pipe alone. While the galvanic current with brass was more than an order of magnitude lower than the galvanic current with lead pipe (0.5- 2.5 μA for brass vs. 15-35 μA for lead pipe), copper release with a galvanic connection to brass was 65-75% lower than from copper pipe in isolation (Figure A-3). Interestingly, the only instance in which copper release was equal between copper pipe alone and copper pipe with a galvanic connection to brass occurred with high alkalinity and no NOM. Copper release from copper pipe alone was minimized in this condition by rapid aging in the absence of NOM, but the results indicate that a galvanic connection to brass prevented aging of copper pipe.

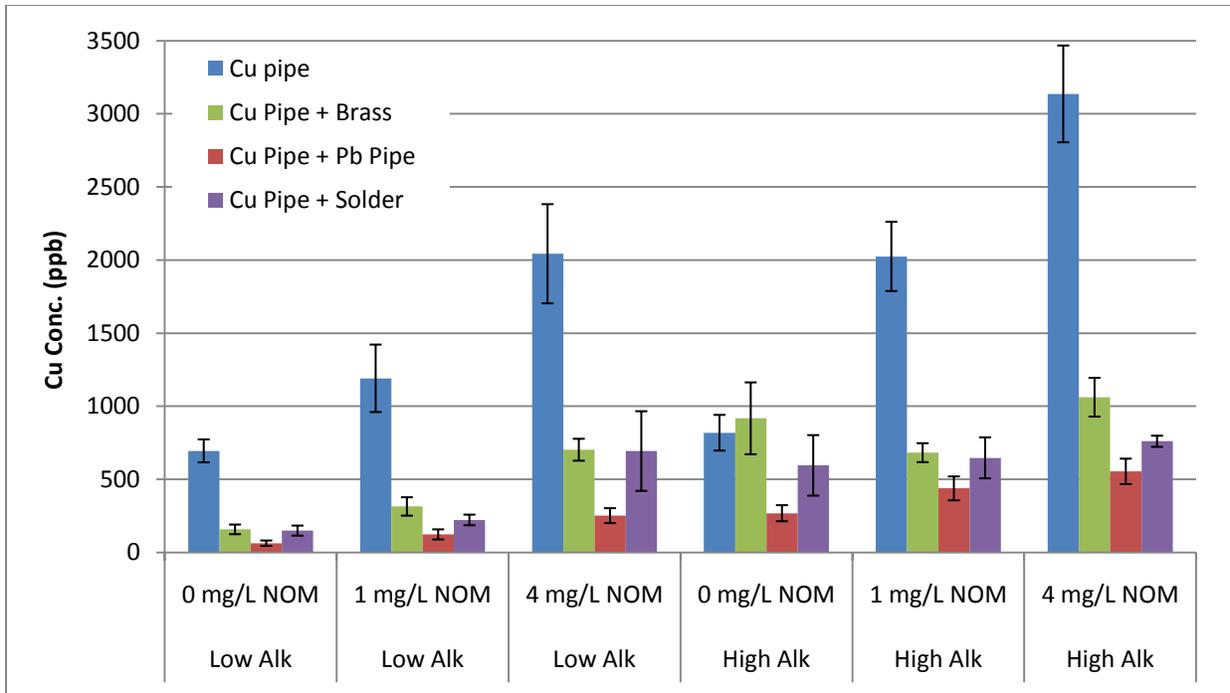


Figure A- 3. Analysis of cathodic protection from galvanic connection to lead pipe, brass, and solder (average copper concentrations; error bars represent 95% confidence intervals)

During the one-week galvanic disconnection, copper release rose slightly but remained lower than copper release from copper pipe alone (Figure A-4). Again, the only condition in which copper release was lower from copper pipe alone was with high alkalinity and no NOM, this further supports the conclusion that aging was prevented in the copper pipe connected to brass but occurred rapidly in copper pipe alone. Considering that the average galvanic current with high alkalinity and no NOM was only about 1 uA, cathodic protection from the connection to brass was not expected to be the sole cause of reduced copper release, and zinc in the water due to dezincification of brass may have also contributed to the reduction in copper release. As the copper release during the galvanic disconnection was still considerably lower than the control, the results demonstrate that cathodic protection of copper pipe was not the primary mechanism responsible for the reduction in copper release compared to the control.

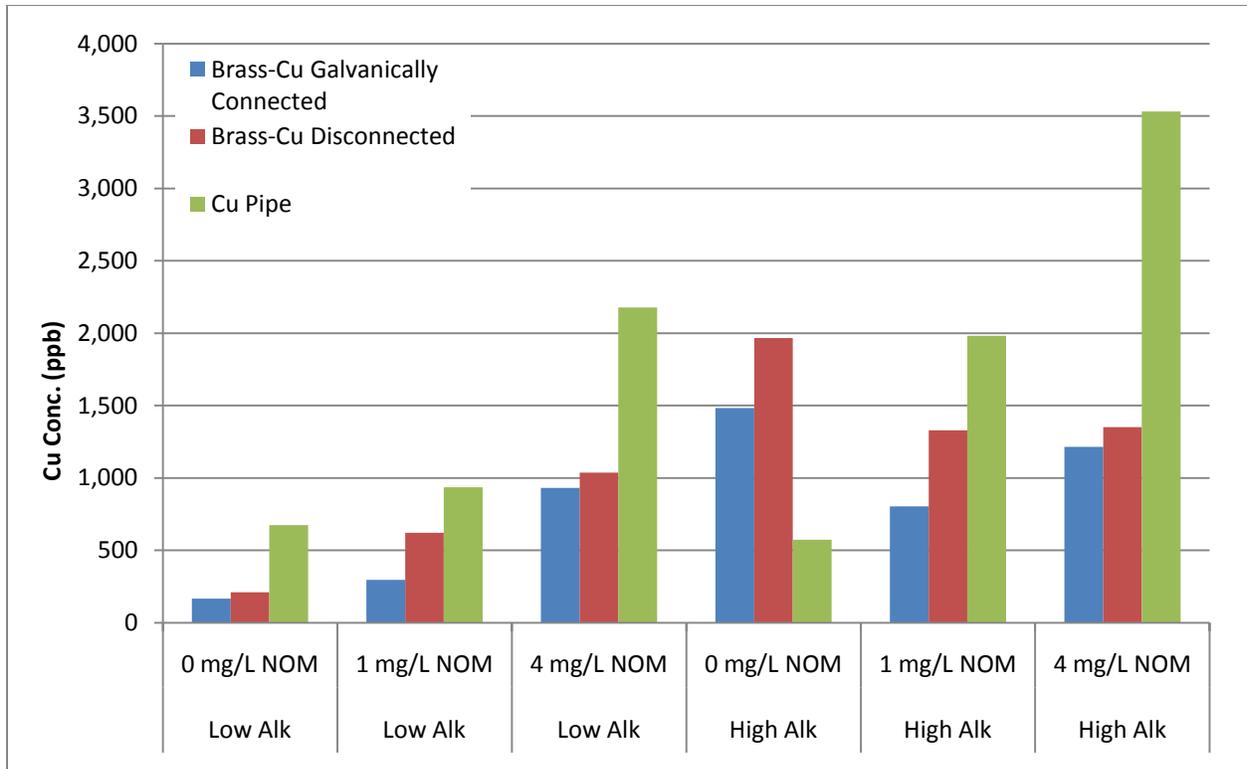


Figure A- 4. Effect of galvanic disconnection on copper release from Cu-Brass couple. (Copper release data with galvanic connection taken from week prior to disconnection, disconnected copper release and copper pipe alone data taken from composite and triplicate samples during week of disconnection)

Zinc release from the brass also dropped significantly during the disconnection (Figure A-5), which would have served to decrease any potential corrosion inhibition by zinc. Therefore, it is not possible to conclusively separate the relative contributions of cathodic protection and zinc inhibition of copper corrosion, but a combination of the two likely caused the reduction in copper release. Further experimentation is recommended to evaluate the potential impacts of zinc on copper corrosion. Zinc release data (Figure A-5) shows that when brass was galvanically connected to copper, higher levels of NOM increased dezincification of the brass (in addition to increasing lead release, as discussed previously).

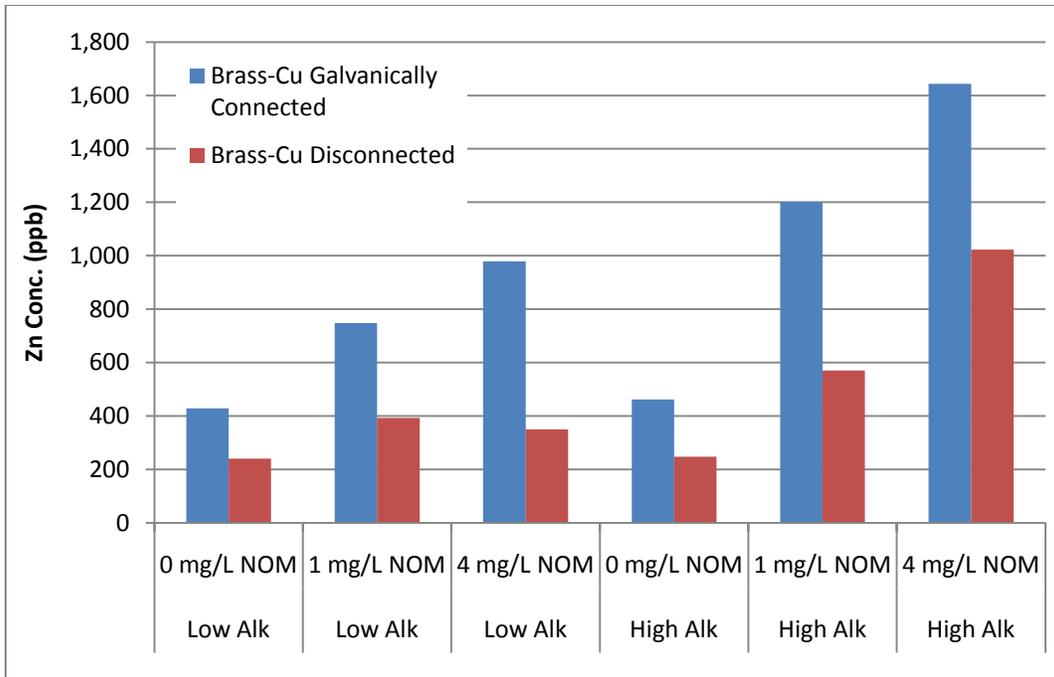


Figure A- 5. Effect of galvanic disconnection on zinc release from brass connected to copper pipe.
 (Zinc release data with galvanic connection taken from week prior to disconnection, disconnected zinc release taken from composite samples during week of disconnection)

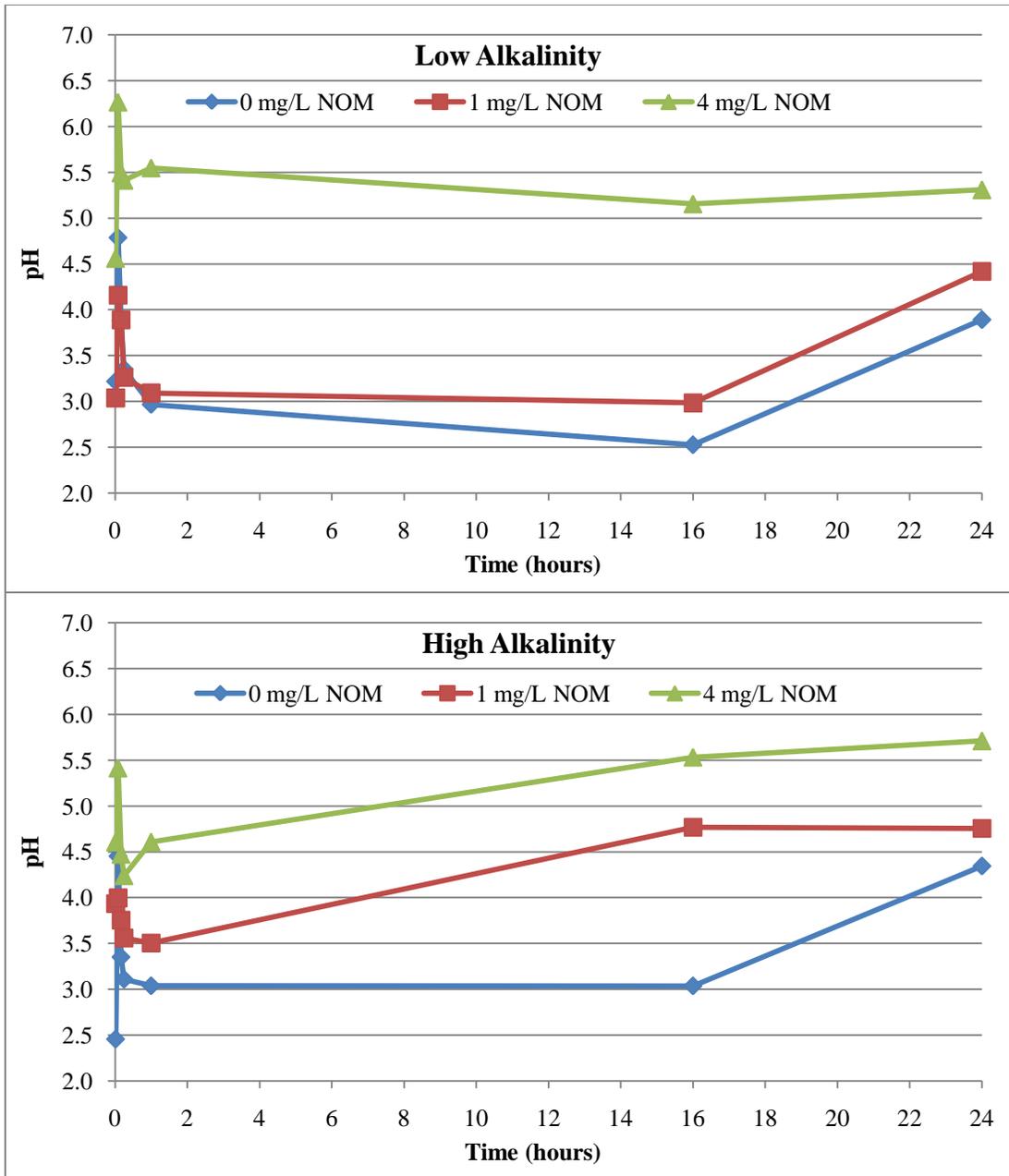


Figure A- 6. Profiles of micro-pH at the tip of the solder (connected to copper pipe with low alkalinity (top) and high alkalinity (bottom)). The pH dropped rapidly and remained low for the entire 24-hour stagnation period. A lesser pH drop occurred with high levels of NOM, and the pH at the solder surface reached as low as 2.5 in the absence of NOM).

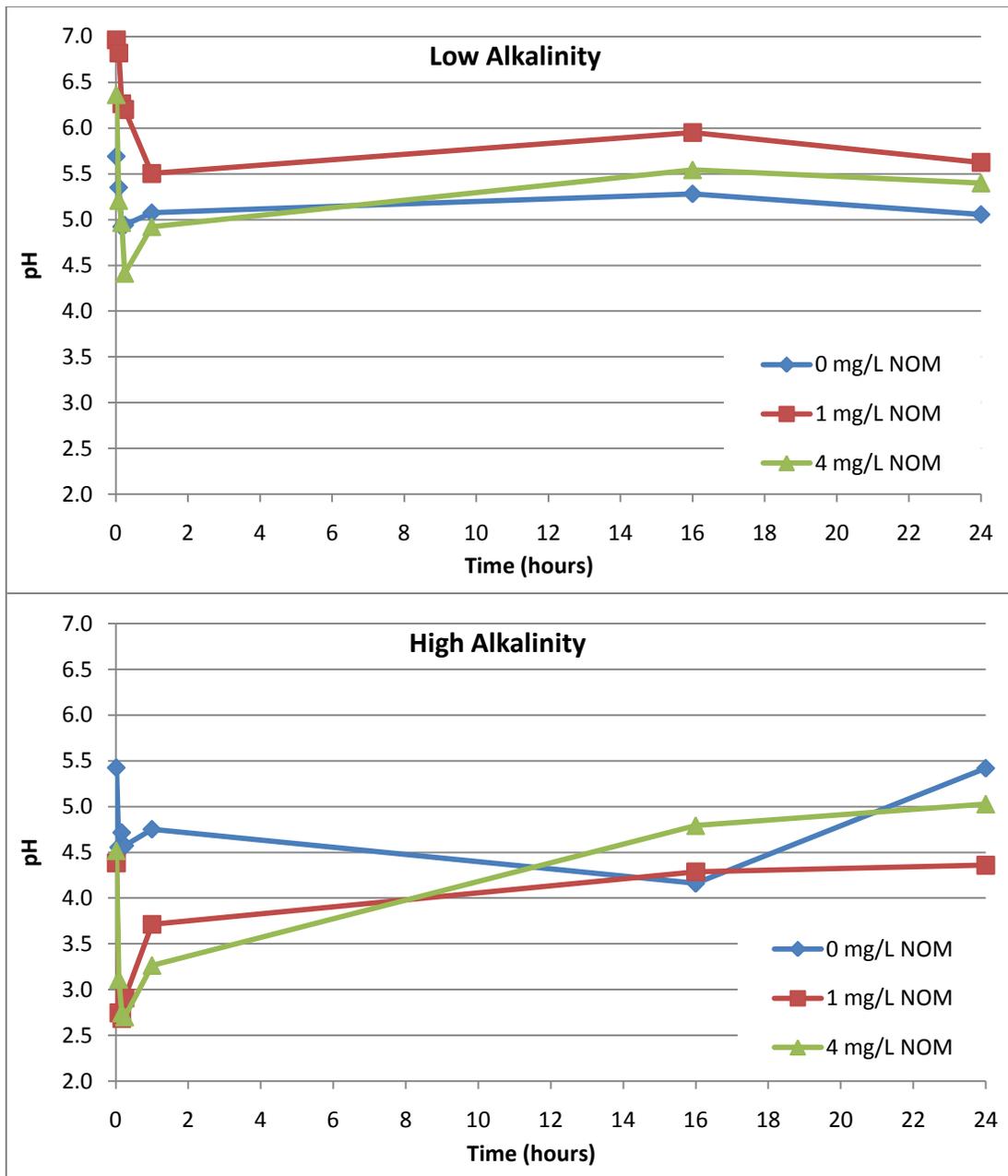


Figure A- 7. Profiles of micro-pH at the surface of the lead pipe (near the junction with copper pipe with low alkalinity (top) and high alkalinity (bottom). The pH dropped rapidly and remained low for the entire 24-hour stagnation period. Lower micro-pH was measured with high alkalinity, and no strong correlation between NOM and micro-pH was observed.)

Chapter 2: Impacts of Flow Pattern and Disinfectant on Galvanic Corrosion of Lead

ABSTRACT

Simplistic conventional models of soluble lead release invariably predict a greater mass of lead release from pipes to drinking water at higher velocity and flow duration. In some cases, however, formation of corrosive microenvironments at Pb-Cu galvanic couples during stagnation and reduced formation of Pb(IV) scale can result in a greater mass of lead release with reduced flow duration, increasing the risk of elevated lead in water of homes with lower water use. Furthermore, with high flow duration in the presence of free chlorine, potential reversal of galvanic corrosion between lead and copper pipe occurs due to the formation of Pb(IV), resulting in galvanic protection of the lead pipe via the connection to copper and reduced lead in water. Potential reversal did not occur with chloramine oxidant, with intermittent flow, or if orthophosphate was added to water with free chlorine. For both disinfectants, electrochemical measurements supported a mass balance of lead release demonstrating that a greater total mass of lead release occurred with intermittent flow than with continuous flow.

Introduction

Infinitely variable water usage habits that affect flow velocity, duration, and stagnation patterns can impact corrosion of premise plumbing systems and water quality in buildings (NRC, 2006; Zhang, et al, 2009, Schock et al, 1985). Especially considering increasing efforts for water conservation, the potential impacts of reduced water usage patterns on the risk of lead contamination of potable water deserve further examination. Conceptual and numerical mass-transfer models of soluble lead release from lead service lines have been useful in understanding certain trends in potable water lead concentrations as a function of hydraulic conditions (Kuch and Wagner, 1983; Cardew, 2006), but they neglect the important effects of stagnation on galvanic corrosion and invariably predict that a greater mass of lead will be released to water at higher velocities and flow duration. Likewise, simplistic conceptualizations of particulate lead release from service lines by scouring and erosion corrosion (Britton and Richards, 1981), would also predict increased mass of lead release to water with higher velocities and flow duration.

In addition to the well-established knowledge that long stagnation periods result in higher lead concentrations (Schock et al, 1985; Britton and Richards, 1981), recent observations of anomalously high lead concentrations in situations with low water usage (Elfland et al., 2010; Triantafyllidou and Edwards, 2011; Lambrinidou et al, 2010; Nguyen et al, 2010) gave rise to concerns that the conventional wisdom regarding the relationship between flow and mass of lead release to water is not always valid. Although field observations are hopelessly complicated by variations in plumbing from site to site and cannot provide proof of cause and effect, especially when considering dilution effects (i.e., the same mass of lead released to much lower volume of water results in higher concentration), it appeared that a greater mass of lead might actually be released to water in situations with lower water use and longer stagnation times. In many such cases, the leaded plumbing material was galvanically connected to copper pipe.

In parallel with the field observations, recent research on galvanic corrosion (Edwards and Triantafyllidou, 2007; Nguyen et al, 2011; Triantafyllidou and Edwards, 2011) developed a logical model for reduced mass of lead release to water at higher flow rates and greater flow frequency. Specifically, during stagnation, a highly corrosive micro-environment characterized by a high chloride concentration and very low pH (< pH 3.0) can form at the surface of lead plumbing galvanically connected to copper (Nguyen et al, 2010). Higher flow duration and velocity can be expected to minimize microenvironment formation due to dispersion and increase the likelihood of forming a passivated scale layer.

The choice of disinfectant may also play a role lead corrosion (Edwards and Dudi, 2004), and according to other research, use of free chlorine as a disinfectant increases the effects of galvanic corrosion compared to the use of chloramine (Reiber and Dufresne, 2006; Reiber, 1991). Moreover, it was recently revealed that Pb(IV) can form on lead pipe surfaces if free chlorine causes the lead surface potential to rise to approximately 1000 mV versus about -400 mV for Pb metal, and its formation has been observed in chlorinated drinking water systems (Wang et al, 2010; DeSantis et al, 2009; Switzer et al, 2006; Lytle & Schock, 2005). The presence of Pb(IV) can greatly reduce lead release due to the extremely low solubility of Pb(IV) compared to Pb(II) solids traditionally assumed to control lead solubility (Lytle & Schock, 2005; Schock et al, 1985). Continuous flow through lead pipe should accelerate Pb(IV) formation by sustaining the free chlorine concentration at the lead surface, which would tend to drop during stagnation.

Recent field observations by researchers at the US EPA (DeSantis et al, 2009) also provided mineralogical evidence of galvanic corrosion in the presence of free chlorine, in which the identity of minerals formed at the junction of two dissimilar metals differed from those formed away from the joint. Moreover, in other cases, the copper alloy was clearly being sacrificed by the galvanic connection to lead pipe (DeSantis et al., 2009). Such a reversal of the standard electrochemical series of metals is termed "potential reversal" and has been documented for couples between galvanized iron and zinc in hot water applications due to the formation of a passivated surface scale on zinc (Schikorr, 1939).

In retrospect, the discovery that Pb(IV) can form on lead pipe surfaces in systems with free chlorine creates the expectation that "potential reversal" should occur for Pb-Cu galvanic couples in situations promoting the formation of Pb(IV) surface scales. Pb(IV) formation is favored by any circumstances that increase transport of free chlorine to lead surfaces, including higher Cl₂ concentration, flow rate, and flow duration (Lytle & Schock, 2005). Other factors can hinder the formation of Pb(IV), including the presence of orthophosphate (Lytle et al, 2009) or natural organic matter (Lin and Valentine, 2009; Dryer and Korshin, 2007), and lower pH (Lytle & Schock, 2005). Pb(IV) formation is reversible, and reductive dissolution of lead oxide can occur when the oxidation-reduction potential is not kept sufficiently high by free chlorine (Xie and Giammar, 2007; Switzer et al, 2006; Lytle & Schock, 2005), raising the possibility of oscillating galvanic currents between Pb-Cu couples in systems with free chlorine.

This research aimed to provide a better understanding of the role water use patterns and disinfectant on the potential for lead contamination of potable water from Pb-Cu galvanic couples. The possible electrochemical reversal of Pb-Cu galvanic couples and the practical impact of reduced formation of corrosive micro-environments at lead surfaces was a special focus of the evaluation.

Experimental Methods

A set of re-circulating pipe-loop experiments was designed to quantify the impact of hydraulic flow patterns on lead release to water, galvanic currents between Pb-Cu couples, and electrochemical potential (E_{corr}) of pipe surfaces. Two types of disinfectants were tested including free chlorine and chloramine. Three flow durations were tested, including continuous

flow, two flow events per day (4 minutes of flow after 11 hours and 56 minutes of stagnation) and 8 flow events per day (1 minute of flow after 2 hours and 59 minutes of stagnation). The intermittent flow conditions were achieved by using a centrifugal pump controlled by a programmable timer, with total flow of 260 L/day which is typical for a home. In addition to the six pipe loops described above, continuous flow testing with chlorine and chloramine was also conducted in the presence of orthophosphate (2 mg/L as P) for a total 8 test conditions.

In each pipe rig, a lead-copper galvanic couple was assembled with new 2-inch long sections of 3/4-inch diameter copper and lead pipe. The pipes were electrically separated by a 1/16-inch thick rubber dielectric washer and connected externally with a grounding strap to facilitate measurement of the galvanic current. A large ratio of reservoir water volume to pipe surface area was desirable to minimize disinfectant dissipation and maintain target water chemistry of pH and other constituents during the experiment. For each pipe rig, a plastic basin (90 L) was used as reservoir for the re-circulating apparatus, and a floating plastic-coated foam insulation cover minimized the air-water interface sufficiently to reduce CO₂ influx but maintain O₂ saturation of the water. The lead-copper couple was connected to the pump with tygon tubing, and an air gap was strategically placed in the tubing loop to prevent movement of water through the pipe sections due to thermal or other convection currents during stagnation.

The target water chemistry (Table 1) was pH 9.2, alkalinity of 15 mg/L as CaCO₃, high CSMR (~2.5), and 4 mg/L of chlorine or chloramines (synthesized with a 4:1 mass ratio of Cl₂ to N). The chlorine and pH were adjusted daily to target values but varied diurnally between 3.5-4.0 mg/L and 8.8-9.2, respectively. Sodium hypochlorite stock solution (NaOCl, 6% w/w) was used to establish chlorine residual, and free and total chlorine and total ammonia-N concentrations were verified by Hach Colorimetry. A 1 M solution of NaOH was used to raise the pH back to the target value of 9.2. Sodium orthophosphate was added to two basins at a concentration of 2 mg/L as P. The water in all eight basins was changed every 2 weeks to maintain Cl⁻ to within 25% of the initial value and limit the buildup of Pb and Cu.

Table 2-1. Summary of Water Chemistry Parameters

Parameter	Value
pH	9.2
Alkalinity (mg/L as CaCO ₃)	15
Chloride, Cl ⁻ (mg/L)	50
Sulfate, SO ₄ ⁻ (mg/L)	20
Nitrate, NO ₃ ⁻ (mg/L)	3.0
Sodium, Na ⁺ (mg/L)	48
Silicon, Si ⁺ (mg/L)	2.7

The lead and copper pipes were connected to a Gamry potentiostat operated in zero resistance ammeter (ZRA) mode to permit continuous galvanic current measurements for all eight conditions. Three times per week, the Gamry was disconnected, and a Fluke ZRA ammeter was used to measure the corrosion cell voltage between lead and copper pipe, and electrochemical potential (E_{corr}) of each metal was measured by comparison to an Ag-AgCl reference electrode. Measured E_{corr} values were adjusted to standard hydrogen electrode (SHE) throughout this paper.

Samples were collected periodically from the reservoirs to track Pb and Cu concentrations during the two-week water change cycles, but the last sample from the end of the two-week cycle was used to assess average concentration throughout the experiment and compute the total mass of lead release. However, the earlier measurements were imperfect due to settling of particulates in the bottom of the reservoir and sorption to the apparatus. To address that limitation, during the second half of the experiment, each basin was decanted to a volume of 15L at the end of each 2 week cycle and acidified with 1% nitric acid (HNO₃) for 2 hours to dissolve particulate lead on the bottom and sides of the reservoir and complete a rigorous mass balance. It was later determined that even this approach was inadequate to completely recover Pb(IV) particulates formed in the presence of chlorine, so during the last 2 weeks of testing, in addition to strong acid (1% HNO₃), hydroxylamine was also added, which visually removed all Pb(IV) presumably by reduction to soluble Pb(II). All samples were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

After terminating the re-circulating flow experiments, all eight lead-copper couples were sealed at each end with silicone stoppers and filled with their respective target water chemistries. Pipes were allowed to sit stagnant for 1-week intervals, and water from the pipe was collected and

acidified with 2% nitric acid for at least 24 hours to dissolve all visible particles. Following the long stagnation phase, the corrosion scale layer in each lead coupon was carefully removed and weighed in order to attempt a mass balance of lead release.

Results and Discussion

Electrochemical Results: Chloramine.

With chloramines, the E_{corr} of the lead pipe with continuous flow never rose dramatically and remained between -250 to -150 mV vs. SHE for the duration of the experiment (Figure B-1). This was expected based on prior work that suggested that Pb(IV) did not form in the presence of chloramines. The voltage potential driving galvanic corrosion between the lead and copper pipes also remained fairly constant throughout the experiment, in the range of 400-500 mV.

Galvanic current data for conditions with chloramines revealed that a clear trend in corrosion rates developed by the end of the experiment (Figure 1). The galvanic current with chloramine and continuous flow eventually declined to nearly half that measured in intermittent flow conditions, suggesting that some passivation occurred in the Pb-Cu galvanic couple by the end of the experiment. With intermittent flow, the average galvanic current did not decrease with time; in fact, the galvanic current in the condition with a flow event every 3 hours increased slightly over the duration of the experiment and was higher than the condition with a flow event every 12 hours.

Examination of current profiles during flow events reveals a spike in current at the beginning of flow (Figure B-4). At the beginning of the experiment, the peak currents from both flow frequencies were approximately equal, so the condition with more frequent spikes had a higher average current. As the experiment progressed, the peak current often became higher in the condition with more frequent flow events, increasing the difference in the average currents between the two flow frequencies. Interestingly, the duration of the flow event did not seem to have a major impact on the duration of the current spike, as the spike durations were approximately equivalent for flow times of 1 minute and 4 minutes. The galvanic current data suggests that more galvanic corrosion occurred with intermittent flow and that orthophosphate would reduce galvanic corrosion in waters with chloramine.

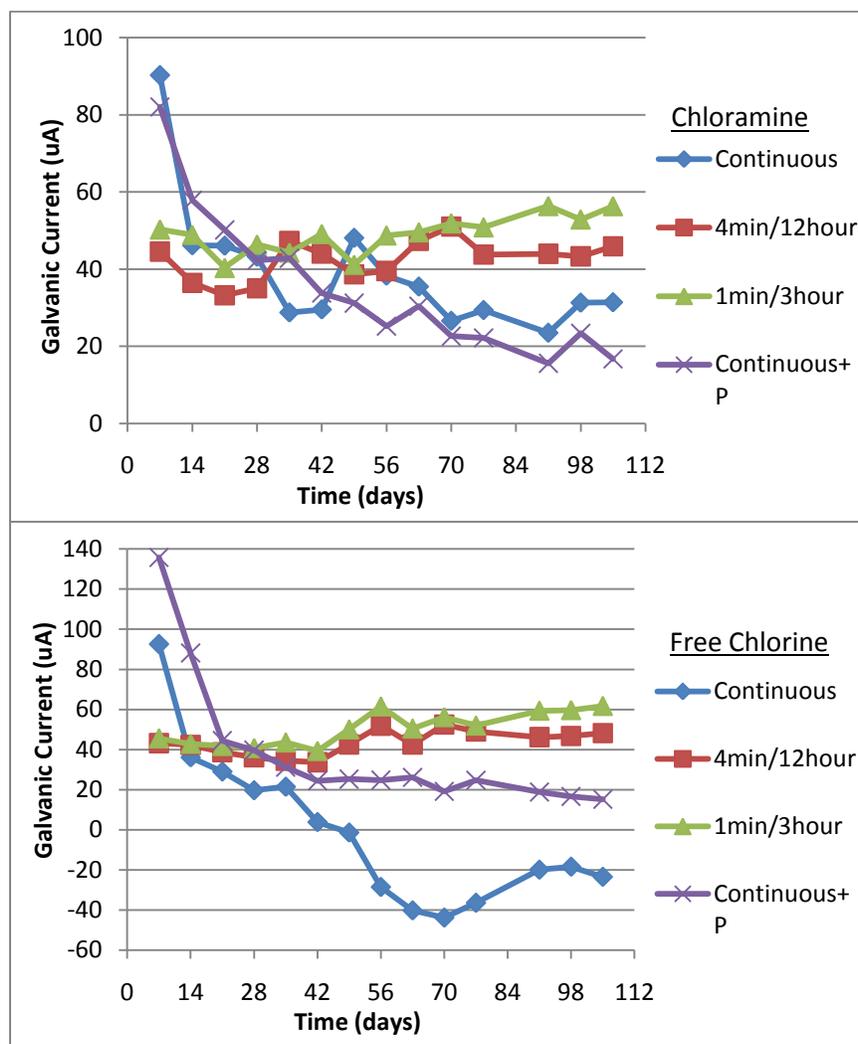


Figure 2-1. Galvanic Current with chloramine (top), and free chlorine (bottom). A positive current indicates that Pb was anodic.

Electrochemical Results: Chlorine.

The E_{corr} of the lead coupons was monitored throughout the experiment to track the progression to conditions consistent with formation of Pb(IV) surface scales. At the beginning of the experiment, the E_{corr} values of the lead coupons in all eight conditions were approximately equivalent at about -200 mV SHE, and, consistent with expectations based on the galvanic series, the lead was anodic to the copper with a potential of 450-500 mV. During the second week, however, the E_{corr} of the lead coupon subjected to continuous flow and free chlorine began to rise markedly compared to other conditions (Figure 2). E_{corr} of the copper pipe in the continuous flow chlorinated condition also rose but not nearly to the same extent as the lead, such that the

lead achieved electrochemical reversal to the copper by day 45 (Figure B-2). In other words, in contrast to all other conditions in which the lead was anodic to copper, in this case, the copper was being sacrificed to galvanically protect the lead.

Pipe couples exposed to free chlorine and intermittent flow never exhibited a similar E_{corr} rise, indicating that Pb(IV) did not form with intermittent flow in the time-frame of this experiment, although it should be noted that Pb(IV) formation with frequent flow events over a much longer period of time (i.e., years) is possible and expected (Lytle & Schock, 2005).

There was no significant difference in the average galvanic current between free chlorine and chloramines at either intermittent flow frequency; in fact, by the end of the experiment, the galvanic currents between the two disinfectants were nearly identical in all conditions except continuous flow (Figure 1), suggesting that chloramines do not significantly increase galvanic corrosion except by hindering the formation of Pb(IV).

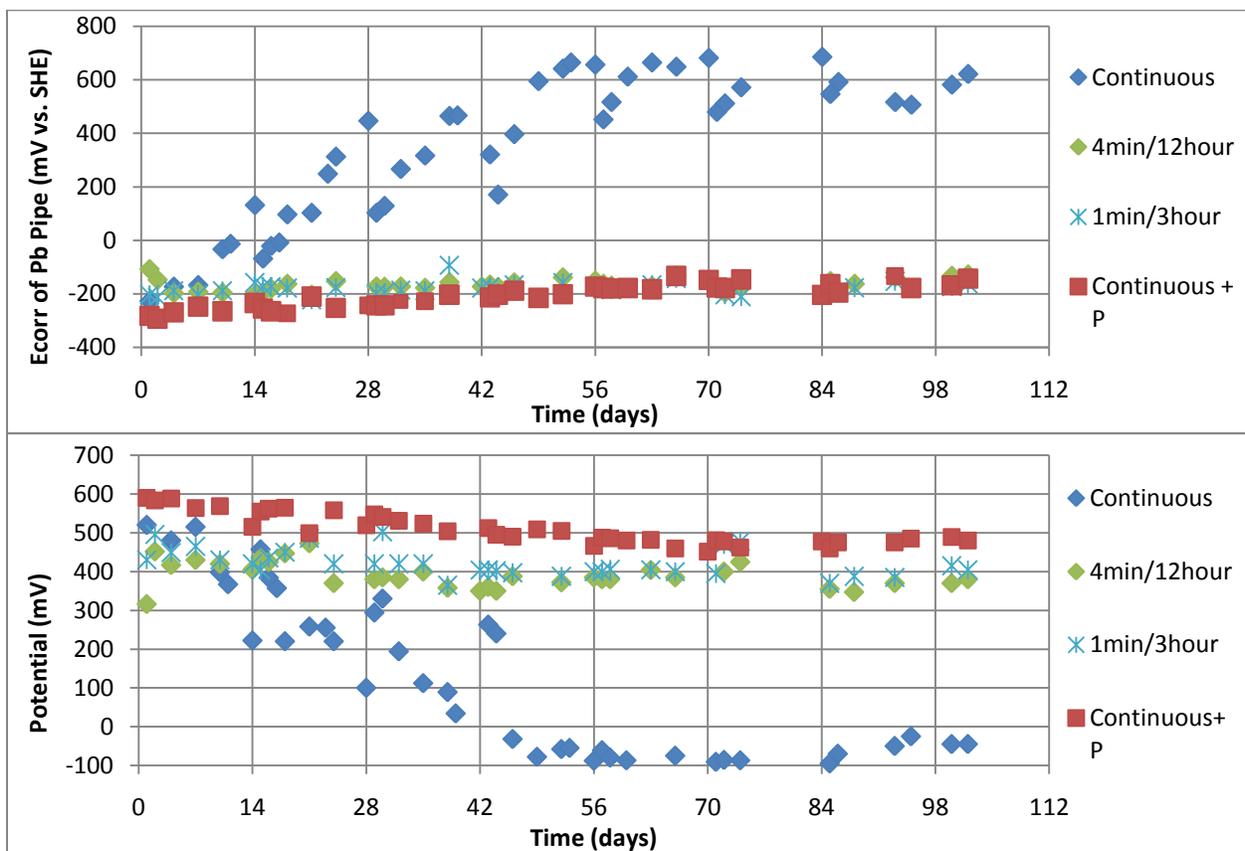


Figure 2-2. Corrosion potential (E_{corr}) of lead pipe (top) and potential between copper and lead (bottom) in the presence of free chlorine

Galvanic current data (Figure 2) also reflected the potential reversal between lead and copper with free chlorine and continuous flow. The current, sacrificing the copper and protecting the lead from corrosion, reached as high as $-50 \mu\text{A}$ or $-7.6 \mu\text{A}/\text{cm}^2$. In contrast, the copper was protected by the connection to lead in all other circumstances. Visual observations of the copper pipe at the end of the experiment (Figure B-6) revealed a severe corrosive attack of the copper connected to the lead pipe, consistent with observations of DeSantis et al (2009) for copper alloys connected to lead over decades of service in the presence of free chlorine. A much lower extent of attack on the copper occurred at intermittent flow and continuous flow with orthophosphate present, confirming that the copper was acting as a sacrificial anode in the continuous flow condition with chlorine no phosphate. Additionally, an accumulation of dark-brown rust characteristic of Pb(IV) was observed on the exposed surfaces of the basin only in the condition with free chlorine and continuous flow, and a dense dark-brown scale formed uniformly over the length of the lead coupon, with minimal accumulation of scale at the joint with copper. A white solid formed on all other lead coupons, with the greatest accumulation of scale directly adjacent to the joint, indicative of galvanic corrosion (Triantafyllidou and Edwards, 2011; DeSantis et al, 2009).

In chlorinated waters, the current with orthophosphate and continuous flow was initially the highest but eventually fell below the currents with intermittent flow (Figure 1). The current with orthophosphate and continuous flow remained positive, likely because orthophosphate inhibits the formation of Pb(IV) as per prior experimental results (Lytle et al, 2009). Under intermittent flow conditions, the average galvanic current was higher in the condition with a flow event every 3 hours than with a flow event every 12 hours (Figure 1). As with chloramine, the current spiked at the initiation of flow, and the peak current was often higher in the condition with more frequent flow events. Overall, the galvanic current data suggests that more lead corrosion would occur with intermittent flow than with continuous flow and that orthophosphate would increase lead corrosion in chlorinated water.

Lead Release Results.

At the beginning of the first two-week cycle, extensive corrosion occurred in the system with chlorine and continuous flow. The average lead concentration in the basin reached a peak of 40 ppb in 4 days but declined for the rest of the cycle, signaling the rapid formation of a passive and

protective lead scale layer on the pipe. Conversely, at day 4, the average lead concentration in the basin with chloramines and continuous flow was 17 ppb, but the lead concentration continued to build-up for the remainder of the 2-week cycle. During subsequent 2-week cycles, the average lead concentration in the basin with continuous flow and free chlorine remained below 1.5 ppb (Figure B-3), demonstrating the extremely low solubility of the PbO_2 scale (Lytle & Schock, 2005). In contrast, the average lead concentration in the basin with continuous flow and chloramines, which did not promote $Pb(IV)$ formation, was nearly 40 ppb (Figure 3).

Although the measured lead release to water only ranged from 5-15% of the theoretical total amount of lead oxidized by the galvanic current, the trends in average lead concentrations correlated well with those from galvanic current measurements. For both disinfectants, continuous flow resulted in less lead release to the bulk water than intermittent flow, (Figure 3). Greater lead release also occurred when the same volume of flow was passed through the pipe with more frequent flow events. This is consistent with galvanic current data indicating a higher average current with 1 minute of flow per 3 hours compared to 4 minutes of flow per 12 hours. Other data (not shown) demonstrated that the pH at the lead surface near the copper joint remains low throughout the stagnation period, but the minimum micro-pH usually occurs within the first few minutes of stagnation. Therefore, the condition with 1 minute of flow per 3 hours may have had more frequent drops to minimum pH than did the corresponding condition with 12 hours stagnation. Orthophosphate increased lead release in chlorinated waters, as orthophosphate hindered potential reversal presumably due to inhibition of $Pb(IV)$ formation, but reduced lead release with chloramine.

Lead corrosion in chlorinated water with continuous flow occurred rapidly in the beginning of the experiment, consistent with results in short-term experiments that the use of chlorine increases the effects of galvanic corrosion (Reiber and Dufresne, 2006). After the potential reversal, however, lower lead release occurred with chlorine than with chloramines. In conditions with chlorine when electrochemical reversal did not occur, there was not a significant difference in the average concentrations of lead between the two disinfectants at the same flow pattern. This is consistent with previous research (Edwards and Dudi, 2004) which found that chloramines did not significantly increase lead release from new lead pipe without a galvanic connection. Despite the galvanic connection in this experiment, the same behavior was observed

for new lead pipe with intermittent flow but not continuous flow. Therefore, the primary negative impact of chloramines must be its failure to promote formation of protective PbO_2 layers and cause potential reversal.

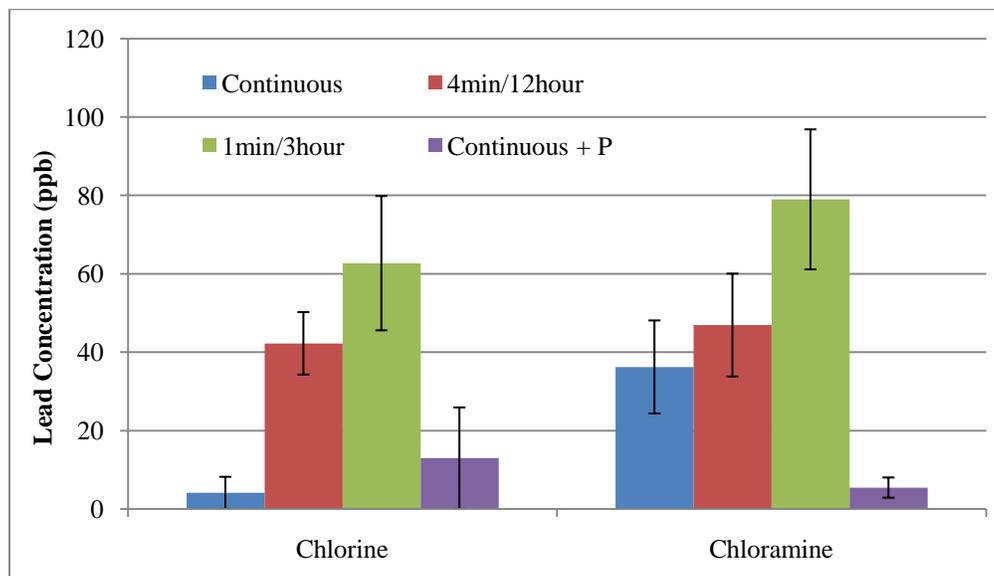


Figure 2-3. Average Lead Concentration in bulk water at end of water-change cycles throughout experiment. (Error bars represent 95% confidence intervals)

Throughout the experiment, significantly higher concentrations of lead were measured in the bottom of the basins than in the bulk water following decantation, indicating the presence of particulate lead that had settled to the bottom. In fact, 40-85% of the total mass of lead in the basin was found in bottom of the basin, consistent with prior research showing that particulate lead can be an important source of lead exposure at the tap (Deshommes, 2010; Triantafyllidou, 2007; Hulsmann, 1990). Therefore, results based solely on average lead concentrations in the bulk water would be incomplete. However, due to a gradual formation of a black coating on some basins and tubing, the original release time of the lead measured in the bottom of the basins could not be conclusively linked to a specific water change cycle. In order to compare the total mass of lead released in each condition, lead in all basins was thoroughly dissolved in the prior to the last 2 weeks of the experiment in order to eliminate any particulate lead accumulation from previous water change cycles.

Even before the more reliable mass balances at the end of the experiment, the lead release trends observed with bulk water concentrations were confirmed by total mass of lead measurements

after thorough acid dissolution, and a greater total mass of lead was released in conditions with intermittent flow compared to continuous flow (Figure 4). This result reinforces the impact of the corrosive micro-environment that forms at the lead surface during stagnant conditions and the improved passivation of lead surfaces during flow. According to conventional theory, the effects of mass transfer and increased scour during flow should cause greater overall lead release, but the opposite trend was observed in this experiment. A further reduction in lead release due to continuous flow will occur in highly chlorinated systems if potential reversal between Pb and Cu occurs, although significant particulate lead release comparable to other conditions still occurred from the pipe with presumed PbO₂ formation. Consistent with previous work regarding health concerns due to the sporadic release of lead particulates (Triantafyllidou and Edwards, 2007), a massive and seemingly random lead release occurred in one condition (Figure 4) during the final two weeks of the experiment that was not necessarily representative of average lead release throughout the experiment.

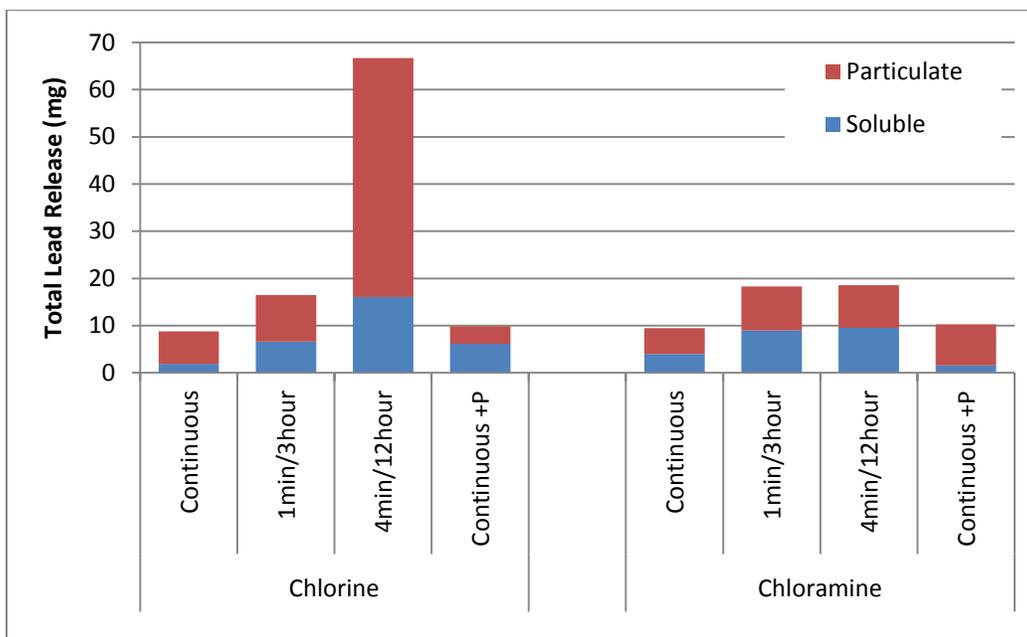


Figure 2-4. Total mass of lead released during final two weeks of the experiment. The blue fraction represents soluble lead, and the red fraction above represents particulate lead

Effect of Long Stagnation.

Following the termination of re-circulating flow conditions, all eight lead-copper couples were subjected to stagnant conditions with the same water chemistry and disinfectant dose. Upon the

onset of stagnation when filling the Pb-Cu couple exposed to free chlorine and continuous flow, the lead pipe was cathodic to copper with a galvanic current of -26 μA . However, after 4 days, the current reversed, causing the lead to once again become anodic with a current of 12 μA (Figure B-7). During stagnation, free chlorine was consumed in the corrosion process, and when the chlorine residual disappeared, the ORP of the water dropped below the threshold required for stabilization of Pb(IV), and reductive dissolution of the Pb(IV) scale could begin. After the first week of stagnation, refilling the couple with fresh chlorinated water did not cause electrochemical reversal, as the current sacrificing the lead was maintained at 14 μA .

The destabilization of the Pb(IV) scale resulted in a massive release of accumulated scale that had formed during continuous flow with free chlorine. Over the four 1-week water change cycles after imposing stagnant conditions, the average lead concentration in the water contacting the pipes was about 130 mg/L, which was more than 4 times higher than the average lead concentration in other condition during long-stagnation (Figure B-8). Moreover, the total mass of lead release during the 4-week long stagnation phase was over 55 times higher than the mass of lead released to the bulk water from this condition during four weeks of continuous flow. Thus, re-establishment of lead pipe as an anode during prolonged stagnation and resulting destabilization of Pb(IV) during extended stagnation in a galvanic couple can be an additional risk factor causing mobilization of Pb(IV), along with a switch from chlorine to chloramine and presence of reductive constituents such as NOM (Xie et al, 2010; Lin & Valentine, 2009; Dryer & Korshin, 2007). This may present significant implications for chlorinated water systems in which Pb(IV) formation is expected; during a long period of no water usage, reductive dissolution in the absence of a significant free chlorine residual may result in a massive lead release into drinking water.

Furthermore, the trends in galvanic current observed during flowing conditions were upheld after the switch to stagnation (Figure B-7); as pipes were exposed to identical water chemistry, the flow pattern had a lasting effect on the galvanic current. With both disinfectants, the galvanic current after the switch to stagnation was higher in the pipes previously exposed to frequent flow events and lowest in the pipes previously exposed to continuous flow.

Mass Balance.

Finally, a mass balance of lead release across the experiment was performed (Table 2), and the total mass of measured lead was compared to the predicted mass of lead corroded by the galvanic current, obtained by integrating the current data recorded by the Gamry potentiostat throughout the experiment. The total mass of lead measured was the sum of lead measured in the bulk water, in the bottom of the basins, and in the scale, and the lead in scale was the total mass of scale removed from lead pipe, copper pipe, and the tygon connector (Table B-1). Scale mass measurements confirmed visual observations that a greater mass of scale buildup occurred on pipes subjected to intermittent flow (Figure B-9), and a higher percentage of the total measured lead was found in the scale on pipes with intermittent flow.

Table 2-2. Summary of Pb Mass Balance (mass in mg)

Flow Pattern	Disinfectant	Mass in Scale	Mass in Water	Mass in Basin Bottom	Total Mass Measured	Mass Predicted	% of Predicted Pb Measured	% of Measured Pb in Scale
Continuous	CA	36.0	31.6	284	351	373	94%	10.24%
Continuous	Cl	54.7	5.0	494	554	132	417%	9.88%
Continuous	Cl+P	81.4	9.7	136	227	362	63%	35.78%
Continuous	CA+P	25.1	4.7	77	107	335	32%	23.53%
4min/12hour	CA	142.1	35.3	284	462	415	111%	30.78%
4min/12hour	Cl	157.9	32.9	311	502	427	118%	31.47%
1min/3hour	Cl	173.6	44.5	620	838	494	170%	20.71%
1min/3hour	CA	166.0	67.3	234	467	473	99%	35.52%

For all conditions without orthophosphate, approximately 100% or more of the lead predicted to be corroded by the galvanic current was measured in the experiment, and higher values beyond the 100% value can be attributed to non-galvanic lead corrosion processes. Overall, for these conditions, the results indicate that a majority of the measured lead was likely associated with the galvanic corrosion due to the connection to copper. Furthermore, the overall weight loss of the lead coupons from the beginning of the experiment to after the removal of scale was also calculated. In general, weight loss corresponded well to the total mass of lead measured in the experiment (Figure B-10); the mass of measured lead tended to be higher than the overall weight loss, perhaps due to external corrosion of lead coupons in air.

The mass balance also indicates that far more lead than predicted based on galvanic current alone was measured in the condition with continuous flow and free chlorine in which Pb(IV) formed. This is expected because the net galvanic corrosion was low due to the potential reversal, and Pb

corrosion was occurring due to reactions on the lead surface, as per lead pipe alone. While a minimal amount of dissolved lead release and some sporadic particulate release continued to occur while the galvanic current was negative, the majority of the lead measured in this condition was likely derived from the beginning of the experiment prior to Pb(IV) formation, when lead corrosion proceeded rapidly with a galvanic current exceeding 100 uA. The total mass of lead measured was less than the overall weight loss (Figure B-1) only in this condition, suggesting that a significant amount of lead may have been lost in the beginning of the experiment when the basin was not acidified with nitric acid. This is not inconsistent with the disparate corrosion behaviors before and after the potential reversal.

In conditions with orthophosphate, significantly less than 100% of the predicted lead was measured during the experiment. This is a perplexing result that defied explanation based on attempts to improve recovery and account for the lead that was "missing." However, it was discovered that the lead scale formed in the presence of the phosphate was extremely recalcitrant; specifically, samples of scale collected from each lead pipe with phosphate were acidified in a solution of 1% nitric acid. Only 10-20% of the lead present was recovered after 2 hours in a 1% nitric acid solution, whereas lead scale from pipes without phosphate completely dissolved in the same time. Recovery of the scale from lead phosphate system increased to 70-80% after 16 hours in a 1% nitric acid solution. Thus, the two hours dissolution in 1% nitric used to recover lead during the experiment likely underestimated the total lead released to the basin in conditions with orthophosphate. Future work would be needed to determine if this fully explains the discrepancy and to identify the exact lead species present in these conditions.

Other researchers have reported formation of lead phosphate solid phases that are extremely insoluble in acid (e.g., hydroxypyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{OH}$) or lead orthophosphate ($\text{Pb}_3(\text{PO}_4)_2$ Lytle et al, 2009; Schock et al, 1985). However, incongruously, far less than the stoichiometry expected amounts of phosphate were recovered after strong acidification from these samples, so the exact identity of the lead solid phase remains unclear. The results do have obvious practical implications for lead monitoring at the tap for drinking water systems with orthophosphate; a very aggressive preservation and digestion protocol might be required to fully detect the actual concentration of lead in such samples if recalcitrant particulates are present (Triantafyllidou et al, 2007).

Practical Implications.

In drinking water systems with free chlorine disinfection, potential reversal can occur for lead pipe and copper couples due to Pb(IV) formation and is accelerated by increased flow. The net result of potential reversal is to essentially eliminate galvanic corrosion of lead and to electrochemically protect lead from corrosion. Contrary to simplistic expectations based on conventional models of lead release, in systems with galvanic corrosion, a greater mass of lead can be released to water in situations with lower flow duration, presumably due to enhanced formation of micro-corrosive environments during stagnation events and improved passivation of Pb-Cu couples with continuous flow.

Even when electrochemical reversal does not occur, continuous flow pipe-loop experiments can produce drastically different results than experiments conducted under stagnant conditions; in addition to water chemistry, flow pattern must be considered when comparing experimental results. In re-circulating tests, sorption and settling of particulates in the reservoir can create great difficulties in conducting rigorous mass balances. Particulate lead can account for a majority of the total mass of lead release and other issues including highly recalcitrant solids formed in the presence of phosphate interfered with definitive closure of mass balances.

In systems in which electrochemical reversal has occurred and lead is protected from corrosion by galvanic connection to copper, prolonged stagnation events (> 4 days) can reverse the protective galvanic effect and create conditions that could induce highly toxic lead levels in potable water. To the extent such problems occur in practice, appropriate flushing of lead service lines after long stagnation events might mitigate public health concerns and could potentially assist in re-establishing the potential reversal and its benefits for controlling lead in water.

Homes with low flow patterns and infrequent water use or prolonged stagnation may represent an additional risk factor for lead release. It has long been understood that schools and homes with low water use may have higher first and second draw lead concentrations, but the possibility that a greater mass of lead may also be released in such circumstances deserves increased scrutiny. As consumers respond to efforts for water conservation and new water sources such as rainwater are used to flush toilets, it is important to know if reduced flow volumes can markedly increase risk from lead in drinking water.

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APPENDIX B: SUPPLEMENTAL INFORMATION

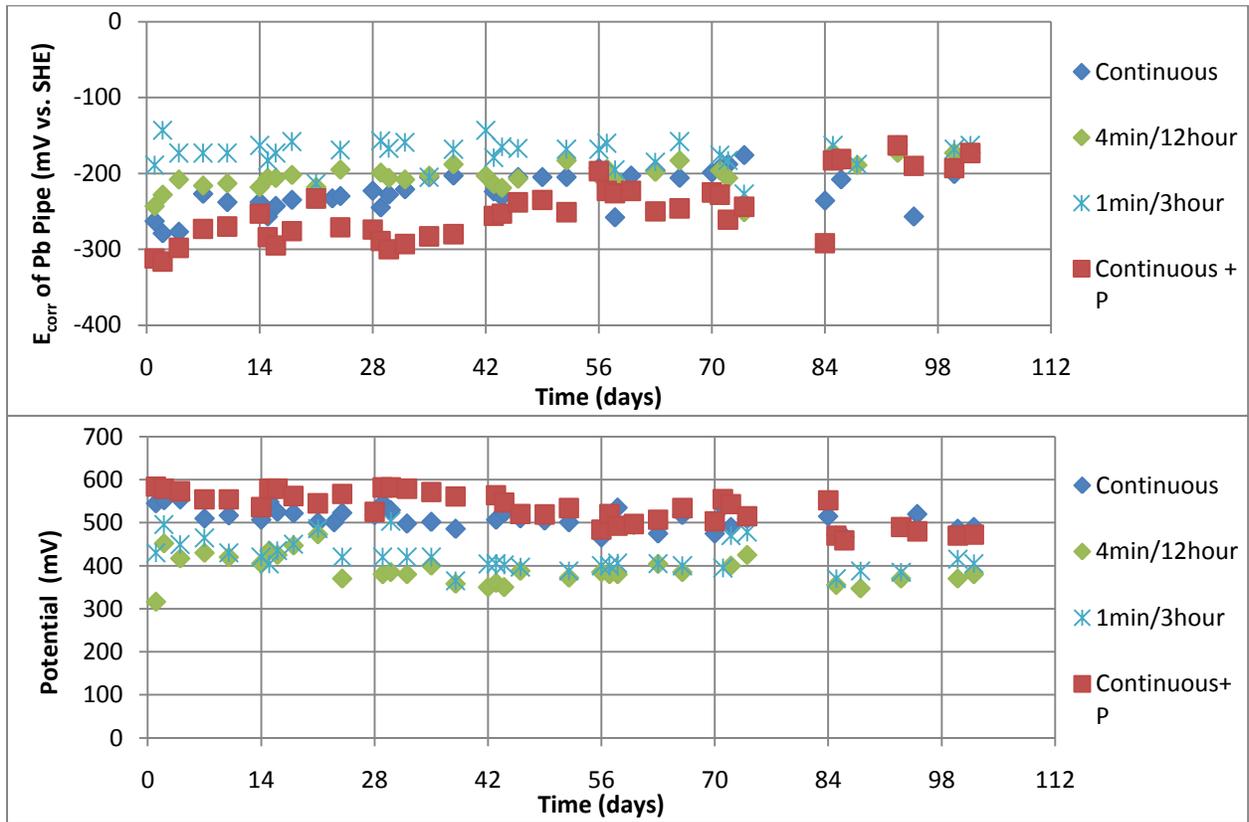


Figure B- 1. Corrosion potential of lead pipe (top) and potential (bottom) with chloramines. No significant trend in ORP of lead pipes was observed over time with chloramines.

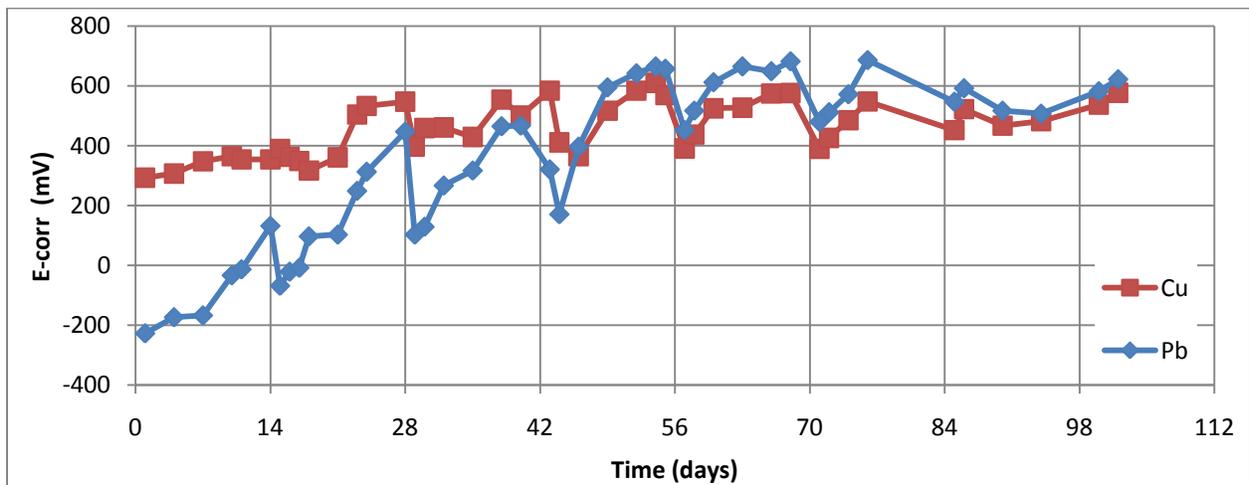


Figure B- 2. Corrosion potential (E_{corr}) of Pb and Cu pipes with continuous flow and free chlorine. Data reveal that Cu became anodic at day 45.

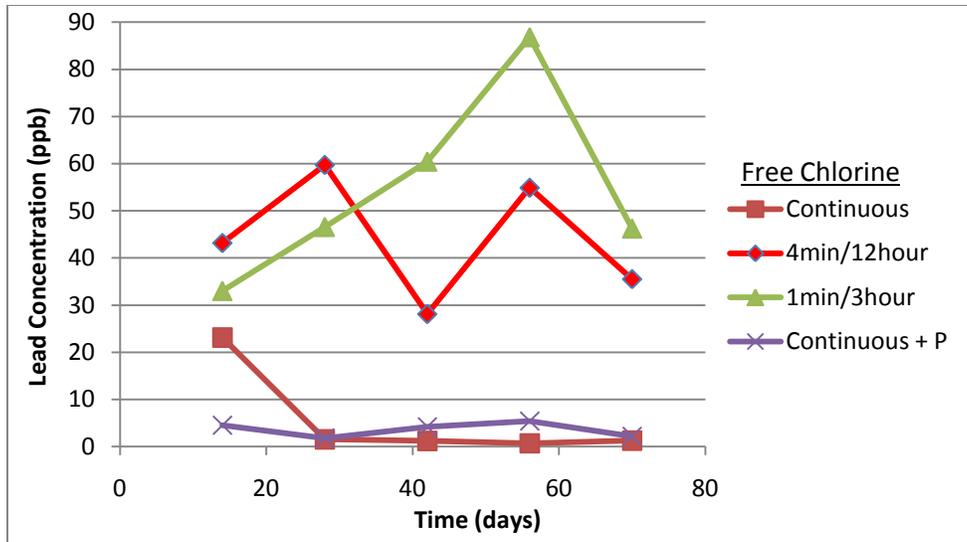


Figure B- 3. Lead Concentrations with Free Chlorine after 2-week cycles. Lead release with continuous flow declined at the beginning of the experiment as Pb(IV) formation minimized soluble Pb release. Lead release from conditions with intermittent flow remained high throughout the experiment.

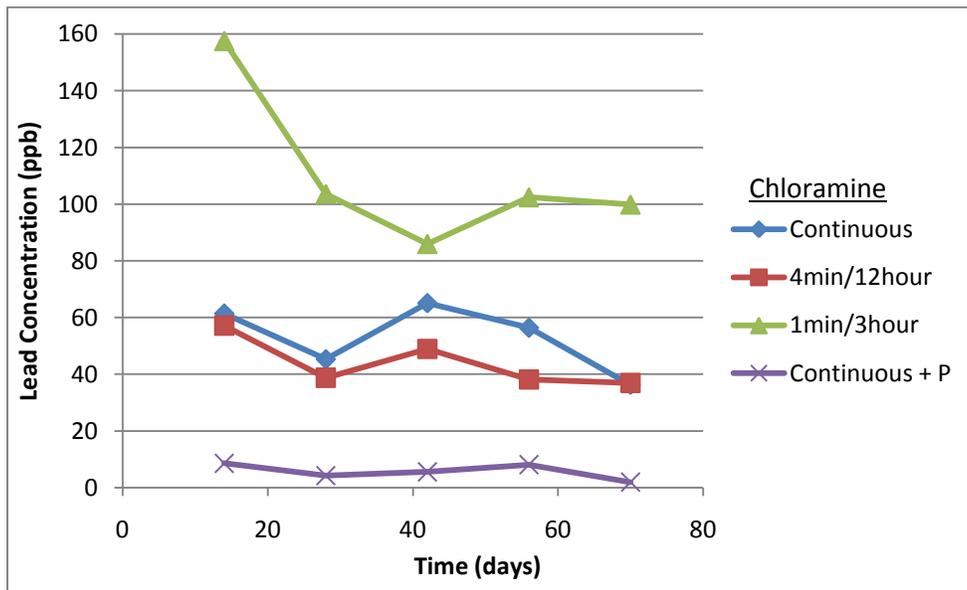


Figure B- 4. Lead Concentration with Chloramines after 2-week cycles. Throughout the experiment, lead release from conditions with intermittent flow was higher than lead release with continuous flow. Orthophosphate addition yielded a significant reduction in lead release compared to continuous flow without P.

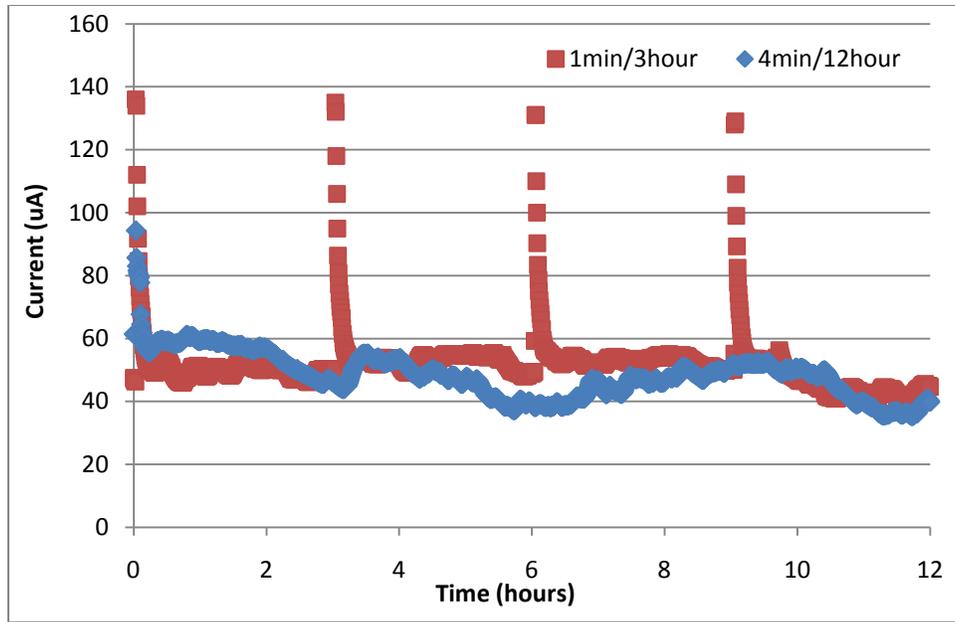


Figure B- 5. Typical Current profiles with chlorine and intermittent flow. More frequent current spikes with 1 minute of flow per 3 hours caused greater average current than with 4 minutes of flow per 12 hours. The magnitude of current spikes with 1 minute of flow per 3 hours was often greater as well.



Figure B- 6. Photographs of copper pipes with free chlorine (left) and chloramine (right) under continuous flow conditions. The side of the copper pipe adjoined to lead pipe is at the bottom of the photo. The photograph indicates a severe galvanic attack on the copper pipe exposed to chlorine that acted as the anode, especially on the side of the pipe adjoining Pb. The copper pipe exposed to chloramine (right) shows no similar visual signs of anodic activity or galvanic attack at the site of connection to Pb.

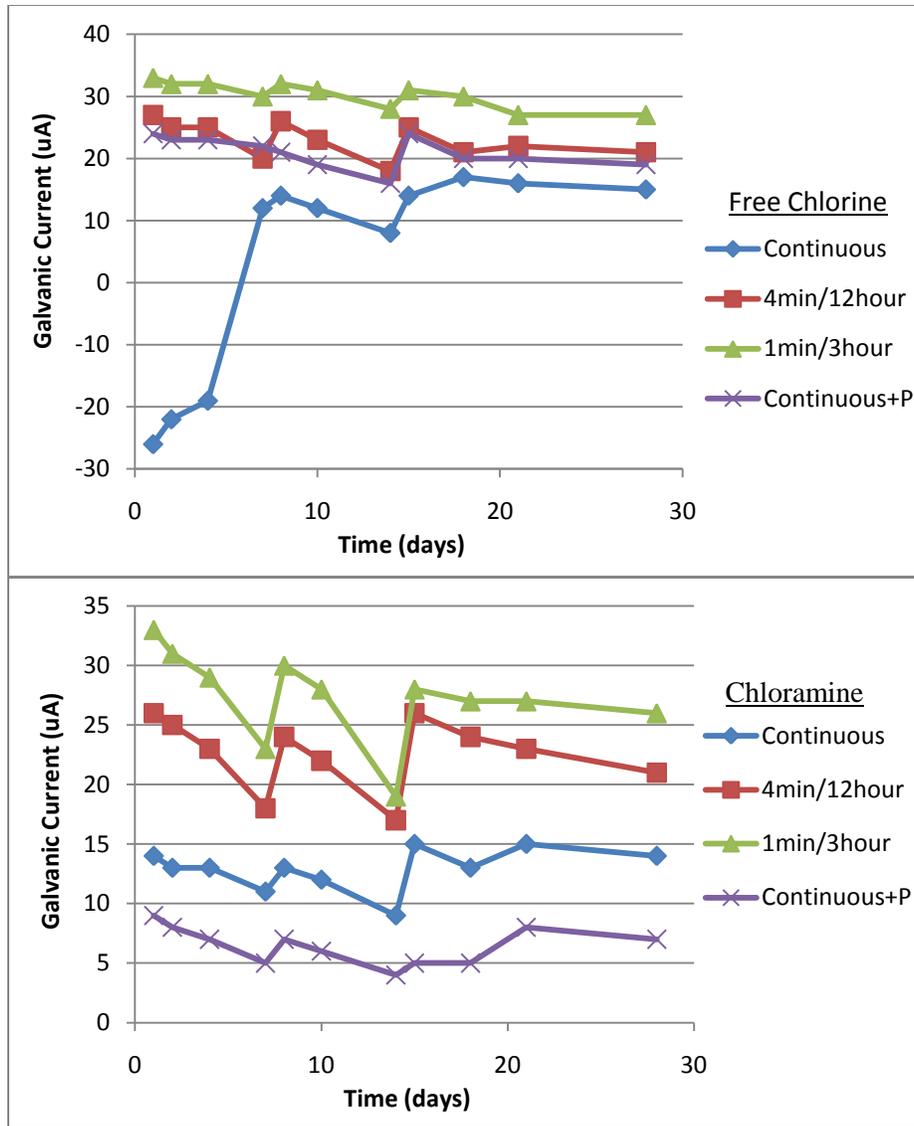


Figure B- 7. Galvanic current during four 1-week stagnation periods with chlorine (top) and chloramines (bottom). Note that the current data for both disinfectants during long-stagnation exhibits the same the trend that was observed during re-circulating conditions. Conditioning due to flow pattern alone caused a lasting impact on the galvanic current after switching to long-stagnation.

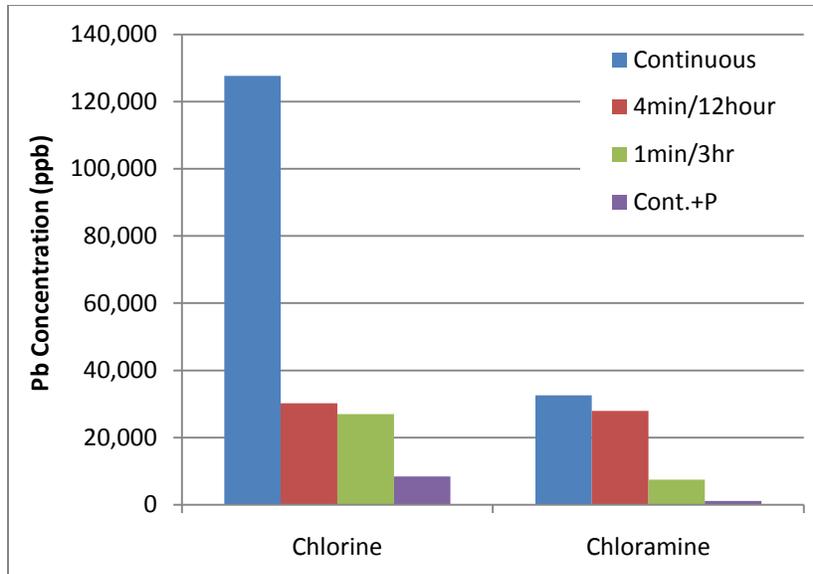


Figure B- 8. Average lead concentration during 1-week stagnation phase at end of experiment. Reductive dissolution of Pb(IV) solids after dissipation of chlorine residual resulted in extreme lead release under stagnant conditions.

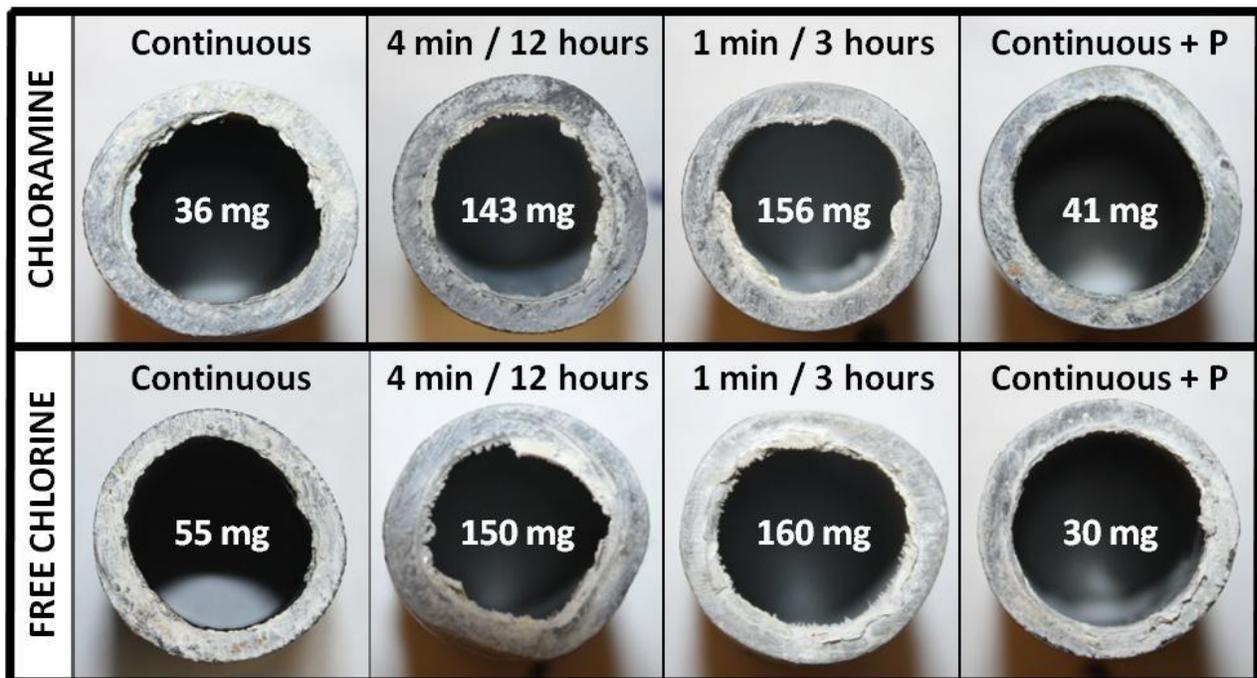


Figure B- 9. Photographs of lead coupons at the end of the experiment showing side of coupon adjoined to copper pipe. Mass of scale collected from each coupon displayed on photo. Besides the condition with free chlorine and continuous flow, a white scale formed on all lead coupons, with the greatest accumulation directly adjacent to the joint with copper pipe, indicative of galvanic corrosion. In the condition with free chlorine and continuous flow, a dense dark-brown scale formed uniformly over the length of the lead coupon, with minimal accumulation at the joint with copper, indicative of lead pipe acting as the cathode.

Table B- 1. Details of Pb Mass Balance

Pb in Scale (g)										
Flow	Disinfectant	Pb Before Removal	Pb After Removal	Difference	Cu Before Removal	Cu After Removal	Difference	Scale on tygon	Sum of Scale	Pb in Scale
Continuous	CA	123.4108	123.3746	0.0362	34.24075	34.23797	0.00278	0.00603	0.04501	0.03598
Continuous	Cl	122.4616	122.3945	0.0671	34.39274	34.39247	0.00027	0.00100	0.06837	0.05470
Continuous +P	Cl	123.2270	123.1854	0.0416	34.35318	34.35236	0.00082	0.04008	0.10250	0.08202
Continuous +P	CA	123.4063	123.3765	0.0298	34.13723	34.13618	0.00105	0.00065	0.03150	0.02592
4min/12hour	CA	123.3940	123.2514	0.1426	33.50057	33.48590	0.01467	0.02051	0.17778	0.14211
4min/12hour	Cl	122.9565	122.8070	0.1495	34.33852	34.32100	0.01752	0.03050	0.19752	0.15789
1min/3hour	Cl	123.0822	122.9218	0.1604	34.40130	34.38245	0.01885	0.03789	0.21714	0.17358
1min/3hour	CA	122.9751	122.8190	0.1561	34.62595	34.60905	0.01690	0.03472	0.20772	0.16605
Pb Released to Water (g)										
Flow	Disinfectant	Mass in Water	Mass in Basin	Total Mass Measured	Mass Predicted	% of Predicted Pb Measured	% of Measured Pb in Scale			
Continuous	CA	0.0316	0.2838	0.3514	0.3734	94.1%	10.2%			
Continuous	Cl	0.0050	0.4938	0.5535	0.1320	419.4%	9.9%			
Continuous	Cl+P	0.0097	0.1363	0.2274	0.3618	62.9%	36.1%			
Continuous	CA+P	0.0047	0.0769	0.1066	0.3349	31.8%	24.3%			
4min/12hour	CA	0.0353	0.2843	0.4616	0.4149	111.3%	30.8%			
4min/12hour	Cl	0.0329	0.3109	0.5017	0.4266	117.6%	31.5%			
1min/3hour	Cl	0.0445	0.6200	0.8381	0.4944	169.5%	20.7%			
1min/3hour	CA	0.0673	0.1892	0.4674	0.4726	98.9%	35.5%			

*Note: Cl= free chlorine, CA= chloramine

*Sum of scale = Scale on Pb + Scale on Cu + Scale on tygon;

*Pb in Scale = Sum of scale x 0.8, based on approximate stoichiometry of solids;

*Total mass measured = Mass in Water + Mass in Bottom + Mass of Pb in scale

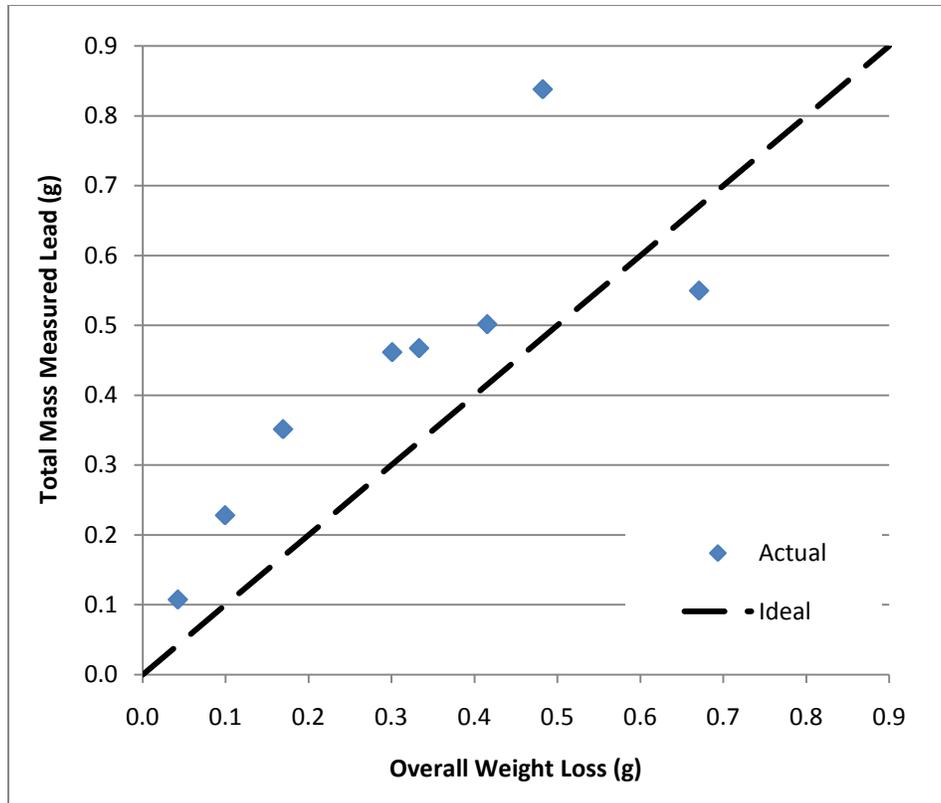


Figure B- 10. Comparison of Total Mass of Measured Lead to Overall Weight Loss; Overall weight loss= (mass of lead coupon prior to experiment)-(mass of lead coupon at end of experiment after scale removal)

Chapter 3: Controlling Copper Corrosion in New Construction

ABSTRACT

An elementary school in Florida experienced persistent elevated copper corrosion by-product release from a new copper plumbing system. Bench-scale laboratory experiments examined pH increase, orthophosphate dosing, and GAC treatment as potential corrosion control measures. By removing NOM, which interferes with natural copper aging to a desirable protective scale of low solubility on the pipe surface, GAC treatment ultimately decreased copper release by over 85%. More importantly, the benefit was maintained after GAC treatment was terminated. Increasing the pH and addition of a high dose of orthophosphate both reduced copper release but had significant long-term drawbacks. The results indicate that temporary GAC treatment in certain waters may be a holistically attractive option to reduce problems with copper release in new construction.

Introduction

Release of elevated copper to potable water in new construction can result in taste complaints, fixture staining, and mild health concerns related to gastrointestinal distress. The Lead and Copper Rule established a regulatory limit of 1.3 mg/L of copper in drinking water at the tap, but compliance is determined based on sampling of older buildings (built before 1986) across the distribution system which are relatively unlikely to have problems with copper release.

A two year old elementary school near Miami, Florida had continuous problems with elevated copper (greater than 6 mg/L) in the water, causing occurrence of blue ice cubes, staining (Figure 1), and a switch to use of bottled water. Older buildings located elsewhere in the distribution system receiving the same water consistently had copper levels that were below 1 mg/L in first draw samples, consistent with expectations for waters with high organic content, high alkalinity, and low pH. Specifically, in new pipes, copper solubility can initially be very high due to the presence of highly soluble cupric hydroxide or other metastable scales (Schock et al., 1995; Edwards, Schock, Meyer, 1996) but becomes low in older pipes due to the natural aging process to more insoluble surface scales such as malachite (Korshin et al., 1996; Edwards, Meyer,

Rehring, 1996). A high organic content and low pH of the supply water can prevent the desired transition to a protective scale indefinitely (Edwards and Sprague, 2001), and in such situations, copper solubility can be reduced by dosing of orthophosphate as a corrosion inhibitor which rapidly forms less soluble cupric phosphates on the pipe surface (Schock et al, 1995; Edwards et al., 2002).

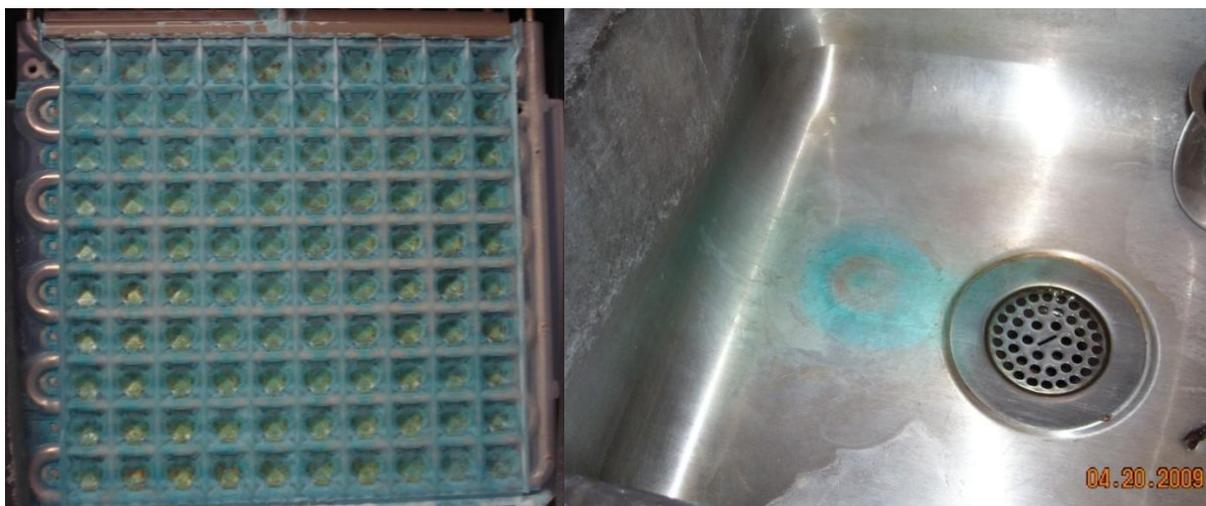


Figure 3-1. Photographs of blue ice cubes (left) and blue staining in sink (right) at Miami elementary school.

Dosing of orthophosphate can have undesirable outcomes in many situations in general and at this elementary school in particular (Table 1). First, orthophosphate prevents aging to insoluble malachite, producing a short-term reduction in high levels of copper, but possibly causing higher long-term copper release relative to levels achieved after malachite and other low solubility species have formed (Edwards et al., 2002). Second, dosing of orthophosphate to an entire water supply to reduce copper levels in only a few new buildings is wasteful of scarce phosphorus resources which are increasingly expensive (Volk et al., 2000) and will also increase phosphorus removal costs at certain sewage treatment plants. Additionally, high levels of organic matter can decrease the efficiency of corrosion inhibition by orthophosphate (Li et al., 2003). Third, it is believed that dosing of orthophosphate must be continuous throughout the life of the building in order to maintain its low copper levels. Finally, phosphate itself can be a microbial nutrient in some cases, which was of concern for this particular school which had large water storage tanks on-site due to its design as a potential hurricane shelter.

Likewise, raising pH from ambient values of around 6.9 to 7.0 can reduce solubility of copper in water and accelerate the transition to malachite, and dosing of lime or caustic are therefore often successful in mitigating copper release (Hidmi et al, 1999; Edwards, Schock, Meyer, 1996). However, raising the pH of a hard water is practically complicated by precipitation of calcite and other scales. Calcite deposition can block pipes, reduce flow, and decrease the efficiency of boilers and water heaters. Moreover, as in the case of phosphate, it is inefficient and impractical to adjust pH of an entire water distribution system to control corrosion in a few buildings.

On the basis of previous research, it was hypothesized that removal of organic matter from the water supply by implementing point-of-use GAC treatment, could accelerate the rate of pipe aging and form permanently protective low solubility scale on pipes. Mechanistically, NOM increases copper corrosion by-product release through complexation and colloid mobilization (Korshin et al., 1996), but most importantly by preventing the formation of insoluble malachite (Edwards, Sprague, 2001). It was believed possible that if NOM was removed below a certain unspecified critical level, the aging of pipe surface scale to malachite would occur rapidly. Moreover, once malachite was formed, it was deemed possible that copper levels would remain low when GAC treatment was terminated and NOM levels were returned to ambient values. If this approach was successful, it could provide an effective and holistically pleasing method of reducing isolated problems with elevated copper release in potable water systems (Table 1). Especially when problems are limited to newer construction, site-specific corrosion control measures at the building point-of-entry may be more efficient for controlling isolated instances of corrosion problems.

In this work, bench-scale laboratory experiments were used to explore the viability of the GAC treatment approach to permanently mitigate elevated problems with copper in comparison to conventional approaches such as increasing the pH and dosing orthophosphate.

Table 3-1. Relative advantages/disadvantages of possible corrosion control methods to mitigate isolated cases of elevated copper in new buildings.

Method	Applied to Whole System	At Building Point-of-Entry
Orthophosphate (P)	Expensive, wasteful of limited P resource, possible increase in microbial growth, and increased sewage treatment costs.	Maintenance of chemical feed equipment, and once started, dosing must be continued indefinitely to maintain benefits.
Increased pH	Precipitation of calcite, chemical costs and on-site storage requirements, treatment of entire system for localized problems.	Maintenance of chemical feed equipment, potential clogging of building plumbing and chemical feed due to calcite formation in hard water.
<i>Proposed:</i> One-time use of GAC and accelerated formation of protective scale.	Not practical for one-time treatment, inefficient to treat entire system for localized problems, but benefit of reduction in DBP formation potential.	Applicable for temporary treatment to accelerate copper pipe "aging" after construction, minimal maintenance requirements, no need to repeatedly replace media.

Methods and Materials

Test Waters

Synthetic Water. For the preliminary experiments, synthetic water was prepared with de-ionized water. Two levels of alkalinity were tested, and sodium bicarbonate stock solution was used to adjust the alkalinity to 12 mg/L and 250 mg/L as CaCO₃. NOM stock collected from a reservoir was centrifuged and filtered prior to addition to the synthetic water in doses of 0, 1, and 4 mg/L as C. The two parameters yielded 6 discrete conditions, and each was tested in triplicate. The synthetic water had a free chlorine residual of 0.5 mg/L and a target pH of 7.3. Orthophosphate was later added via a sodium orthophosphate stock solution at subsequent doses of 1 mg/L as P and 2 mg/L as P.

Water from School. Water samples were collected at the school from a domestic backflow prevention valve and before contacting the building plumbing system (Table 2). Samples were shipped to Virginia Tech in 5 gallon containers and stored at 5 degrees Celsius until used in experiments. All experiments were conducted by treating water samples from the school, and a chlorine residual was not present during the experiments.

Table 3-2. Summary of Water Quality at Miami School

Parameter	Value
Alkalinity (mg/L as CaCO ₃)	200
Average TOC (mg/L as C)	2.5
Free Chlorine (mg/L)	0.18
Sulfate (mg/L)	19
Sodium (mg/L)	25
Silica (mg/L)	2.6
Chloride (mg/L)	45
Nitrate (mg/L)	2.0
Magnesium (mg/L)	5.9
Calcium (mg/L)	87
Iron (ppb)	6.2
pH Range	7.15-7.40
UV Absorbance	0.046

GAC Treated Water. A granular activated column was prepared by filling an 8-inch long section of 3/4-inch inner-diameter flexible tygon tube with GAC, resulting in a total empty bed volume of 3.5-in³. The GAC was supported by a thin layer of glass wool and a rubber stopper with a small hole drilled in the middle. To achieve moderate NOM removal, Miami water was passed through the GAC column twice, reflecting a cumulative empty bed contact time (EBCT) of approximately 16 seconds and an average TOC reduction of 60%. To achieve a higher degree of NOM removal, Miami water was passed through the GAC ten times, resulting in an EBCT time of approximately 80 seconds and a TOC reduction of over 90%. The GAC was replaced with fresh media prior to treating each batch.

Orthophosphate Treated Water. Sodium orthophosphate was dosed into Miami water meet the target inhibitor concentrations of 1 mg/L and 2 mg/L as P, and concentrations were verified by Inductively Coupled Plasma Mass Spectrometry.

Bench Scale Testing Protocol.

In the preliminary experiments, 1-foot sections of new 3/4" diameter copper pipe were filled with synthetic water and sealed at each end with silicone stoppers. The pipes were emptied and filled with freshly prepared synthetic water every Monday, Wednesday, and Friday. At each water change, the pH was adjusted to 7.3 by bubbling 99.9% pure CO₂ into solution, and sodium

hypochlorite was added to provide the appropriate free chlorine residual, which was verified by Hach colorimetry.

For experiments testing the effect of pH on copper release, 30-inch sections of new ½-inch diameter copper pipe were cut and sealed at each end with silicone stoppers. The pH was reduced to target values by dosing of carbon dioxide gas and increased to target values by briefly aerating the water to strip CO₂.

For all other experiments described herein, 1-foot sections of new ½-inch diameter copper pipe were used, each with an approximate volume of 50 mL, and sealed at each end with silicone stoppers. Prior to exposure to Miami water, all pipe sections were filled with a pH 10 NaOH solution for 24 hours and rinsed three times with DI water. All conditions were tested in triplicate with 3 pipe sections, except for the control condition with 4 pipe sections.

Pipe sections were emptied and refilled every Monday, Wednesday, and Friday, and the water remained stagnant between each change. To adjust pH, 99.9% CO₂ was bubbled into solution to meet a target pH of 6.9 +/- 0.02 immediately prior to filling the pipes. Samples were collected for analysis after 48 hour stagnation periods, and copper concentrations were measured by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

Dissolved oxygen was measured before and after 48 hour stagnation periods using a Hamilton VISIFERM DO 325 Dissolved Oxygen Sensor. Water from each copper pipe was poured gently along the side of a flask to minimize DO fluctuation, and measurements were taken immediately after pouring.

Results

Preliminary Results

Prior to bench-scale testing with water collected from the Miami school, preliminary experiments were conducted with a synthetic water to examine the effects of NOM, alkalinity, and orthophosphate on copper release. At both levels of alkalinity, NOM served to increase copper release. Its detrimental effect was more profound with high alkalinity, and copper release was approximately 5 times higher with 4 mg/L NOM compared to 0 mg/L (Figure 2).

Furthermore, copper release with 4 mg/L NOM exhibited an upward trend over time, but with high alkalinity and no NOM, copper release fell rapidly over the first 3 weeks and continued to decline steadily for the remainder of the experiment, suggesting that the absence of NOM accelerated aging to an insoluble surface scale in high alkalinity water. As the alkalinity of the Miami water was near that of the high alkalinity synthetic water, NOM removal was deemed a potential copper release mitigation strategy.

When orthophosphate was subsequently added to the water in the preliminary experiments, it yielded reductions in copper release at doses of 1 and 2 mg/L as P for all conditions except with high alkalinity and no NOM (Figure 2). Therefore, it was deemed possible that accelerated aging facilitated by NOM removal had the potential to result in lower copper release than orthophosphate addition. Also, the percent reduction in copper release as a result of a dose of 2 mg/L as P was considerably lower at high levels of NOM (Figure 2). Therefore, the preliminary experiments suggested that the presence of NOM increases the required dose of orthophosphate, and a very high dose of orthophosphate would be required to control copper corrosion in the highly organic test water. In light of the preliminary results, testing commenced to evaluate efficacy of NOM removal by GAC treatment against the traditional corrosion control measures of pH increase and orthophosphate dosing.

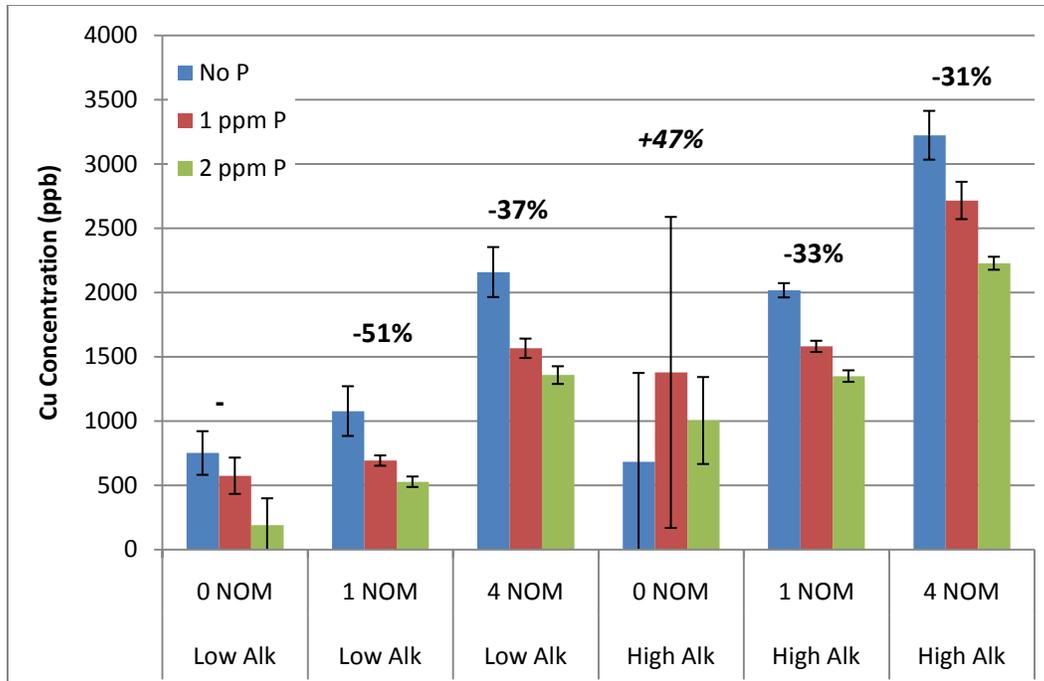


Figure 3-2. The effects of NOM and orthophosphate on copper release at low alkalinity (12 mg/L as CaCO₃) and high alkalinity (250 mg/L as CaCO₃) in preliminary experiments. (Percentage above each category represents the percentage change in copper release with a dose of 2 mg/L as P; Error bars represent 95% confidence intervals)

Effect of pH on Copper Leaching

The effect of increasing pH to 6.9 (control), 7.15, 7.5, and 7.8 was tested (Figure 3). The copper concentration decreased as the pH increased, and, based on a linear regression, approximately 4.6 mg/L less copper was released per unit increase in pH. Clearly, the problems with the elevated levels of copper could be solved by increasing the pH to 7.8, and at stagnation times less than 8 hours copper levels remained below 1.3 mg/L (data not shown). When caustic dosing was attempted full-scale at the point of entry to the building, calcite precipitation in the water rapidly clogged the chemical injection equipment, and raised concerns about the long-term implications for clogging the entire plumbing system (Figure 4). Hence, this potential control strategy was deemed impractical.

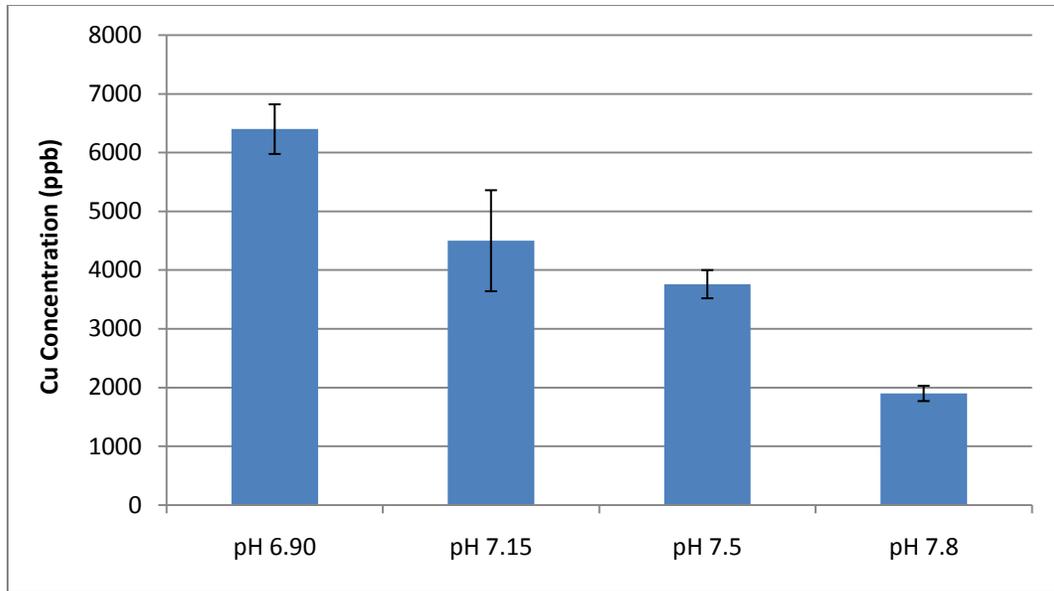


Figure 3-3. The effect of pH on copper release (error bars represent 95% confidence intervals)



Figure 3-4. Calcite scale clogging chemical feed equipment (left) and pipes (right) at the school

Effect of Orthophosphate

When orthophosphate was dosed into the Miami water at a concentration of 1 mg/L as P and subsequently at 2 mg/L as P as a corrosion inhibitor, benefits were observed at 1 mg/L as P, but a dose of 2 mg/L as P was necessary to reduce copper levels by over 80% (Figure 5). The benefits from orthophosphate were immediate in the presence of a 2 mg/L as P dose, and copper leaching remained relatively constant throughout the duration of the experiment. While there are some detriments associated with orthophosphate dosing (Table 1) especially considering the cost of a

high dose of 2 mg/L as P, it is a viable copper corrosion control strategy that could be employed at the point of entry the building.

Effect of GAC Treatment

Granular activated carbon treatment was used to remove natural organic matter from the Miami water samples. Two levels of TOC reduction were achieved by varying the empty bed contact time with GAC. At the beginning of the experiment, GAC treatment provided little benefit, but as copper leaching from pipes exposed to untreated water rose, copper concentrations in GAC treated water declined (Figure 5). After 50 days, the water treated to remove the higher level of high removal of NOM by GAC treatment was as effective at reducing copper release as dosing 2 mg/L as P of orthophosphate. Indeed, copper release from the water treated by GAC was eventually lower than in the same pipes treated by a very high dose (2 mg/L as P) of orthophosphate. While a 60% reduction in TOC provided a slight reduction in copper leaching, a TOC reduction of 90% was required to control copper release. Consistent with the results of previous work (Edwards, Meyer, Rehring, 1996; Edwards et al, 1999; Edwards and Sprague, 2001), the response of copper release to TOC concentration was not linear. The results suggest the existence of a threshold TOC concentration, above which problematic cupric hydroxide scale will persist, and below which a protective scale may form and minimize copper release.

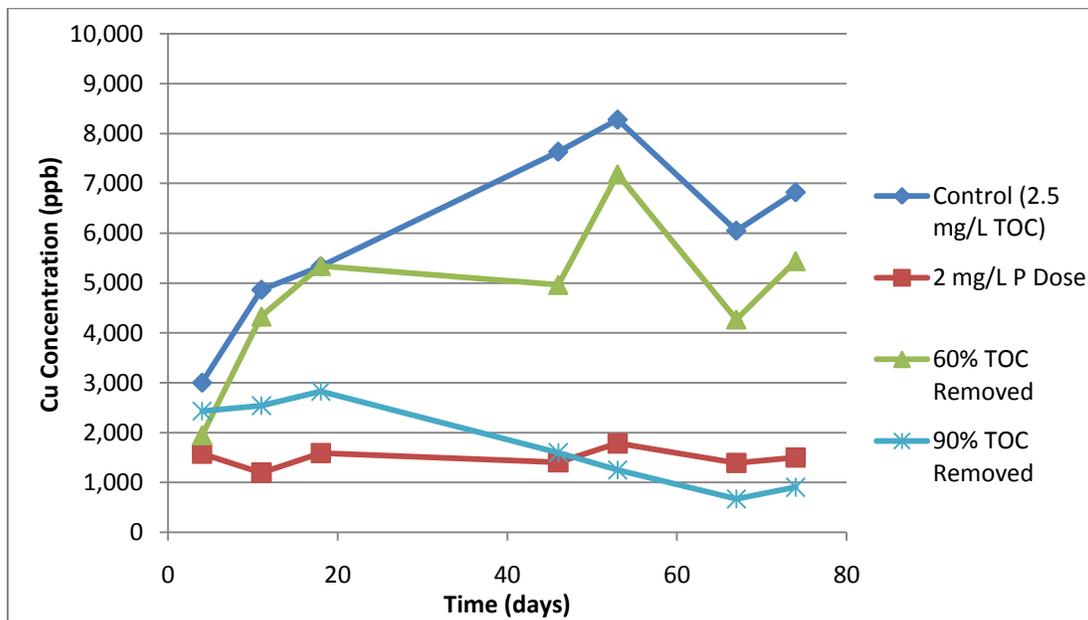
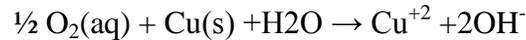


Figure 3-5. Effect of TOC and Orthophosphate on Copper Release from New Pipes

Dissolved Oxygen Consumption

Dissolved oxygen measurements were taken to compare the relative rates of corrosion in each condition (Figure 6). In the absence of a free chlorine residual, the overall corrosion reaction proceeds according to the following equation:



The theoretical total mass of oxidized copper was calculated by substituting the measured dissolved oxygen consumption into the stoichiometry of the equation. By comparing the result to the copper release data, a mass balance was performed to identify the fractions of oxidized copper that form a scale or remain soluble.

In the control condition, virtually all oxidized copper remained soluble in the pipe effluent, and little scale was formed (Figure 6). Orthophosphate reduced dissolved oxygen consumption compared to the control, signifying that less corrosion was taking place. Orthophosphate did increase scale formation, presumably of a cupric phosphate solid. Conversely, NOM removal increased dissolved oxygen consumption, and it also greatly increased the fraction of oxidized copper that forms a scale. Combining the two mechanisms, the results indicate that there was 200 times more scale formation with 90% TOC removal compared to the control. Therefore, dissolved oxygen consumption measurements demonstrate that GAC treatment was optimal from two perspectives; it minimized copper release to the water and maximized protective scale formation.

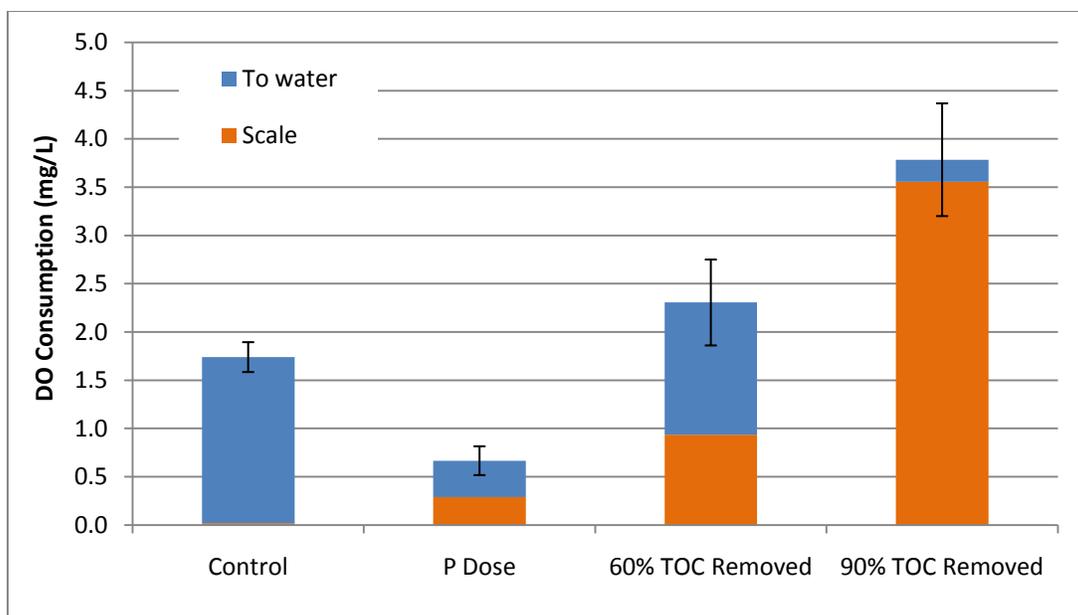


Figure 3-6. Dissolved Oxygen Consumption during 48 Hour Stagnation Period. The orange column represents the fraction of oxidized copper that formed a scale; the blue column above represents the fraction of oxidized copper that remained in the water (error bars represent 95% confidence intervals)

While both treatments reduce copper release into the water, the difference in dissolved oxygen consumption behavior provides valuable mechanistic insight. NOM removal increases the rate of corrosion, accelerating aging and facilitating the formation of less soluble crystalline corrosion products on the internal surface of copper pipe. These results are consistent with previous findings that NOM inhibits the deposition of crystalline corrosion products on the copper surface (Korshin et al., 1996; Edwards and Sprague, 2001).

Visual Observations

The visual appearance of the protective scale formed in pipes exposed to water with a high degree of GAC treatment (90% TOC reduction) is markedly different compared to other conditions (Figure 7). The appearance of the protective scale agrees with observations that protective malachite is a blue-green crystalline solid, and that this solid forms more rapidly at lower levels of TOC. No obvious blue-green scale was observed on control pipes, reaffirming the presumed presence of cupric hydroxide as an amorphous surface layer (Schock et al., 1995; Korshin et al., 1996). Pipes aged with orthophosphate also showed no signs of protective scale formation during the experiment. These visual observations serve to underscore the crucial distinction between a soluble amorphous scale and a relatively insoluble crystalline scale.

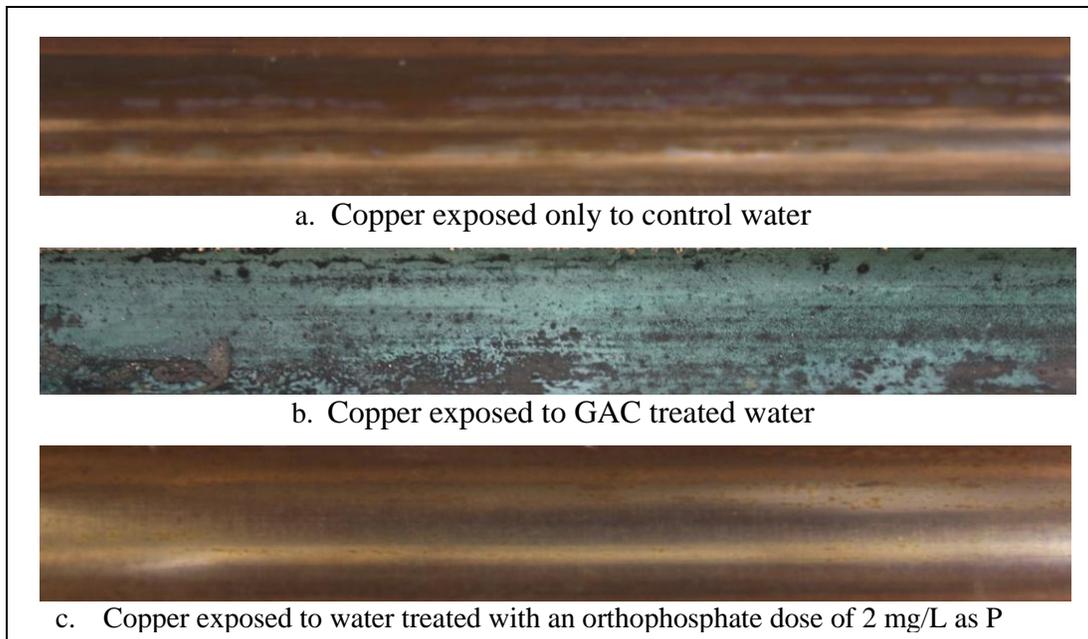


Figure 3-7. Photographs of internal pipe surfaces after approximately 6 months of exposure

Long-term Implications: Persistence of Benefits after Terminating Treatment

In order to assess the permanency of orthophosphate dosing and GAC treatment removing 90% of TOC, three changes were made to the initial experimental protocol for the remainder of the experiment:

1. Pipes aged with GAC treated water were exposed to the untreated water with high NOM, illustrating what would occur if temporary treatment using a GAC column was terminated.
2. Pipes initially aged with untreated control water, with very high copper release, were exposed to GAC treated water to illustrate the effects GAC treatment on an existing plumbing system previously exposed to high levels of NOM.
3. Pipes aged with orthophosphate inhibitor were exposed to untreated water, to examine what would occur if orthophosphate dosing were interrupted.

The pipes aged with GAC treated water exhibited a long-lasting effect when exposed to untreated water, as copper release remained low compared to the control (Figure 8). Following the temporary GAC treatment and formation of the protective scale on new pipes, copper concentrations remained at or below the 1.3 mg/L standard after long stagnation times of 48

hours even the presence of a high TOC concentration. Additionally, by decreasing scale solubility, the protective scale minimized the impacts of complexation and colloidal mobilization.

In contrast, copper release from pipes aged with orthophosphate increased immediately when the inhibitor was no longer dosed (Figure 8). As hypothesized, perpetual orthophosphate dosing would be required to maintain its benefits. Despite the short-term benefits, addition of orthophosphate hindered the formation of a low solubility protective scale and provided no long-term solution to copper release.

In the pipes aged with untreated water, switching to GAC treated water resulted in a gradual decrease in copper release, but copper concentrations did not drop as low as pipes always exposed to treated water. The results suggest that NOM accumulated in the scale is slowly removed by water treated with GAC and that a longer exposure period would be required before accelerated pipe aging occurs.

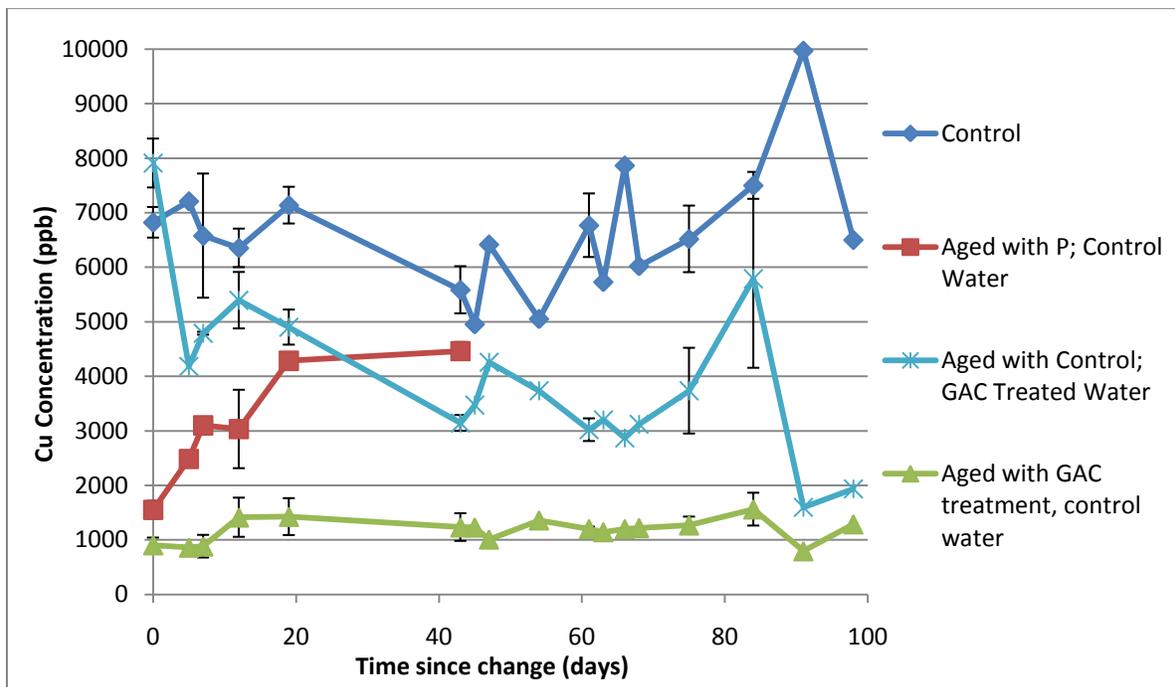


Figure 3-8. Copper Release Following Changes to Experimental Protocol (Cu concentration at time=0 represents copper release prior to change in experimental protocol; error bars represent 1 standard deviation above and below the mean)

Discussion

The results suggest that GAC treatment may provide a holistically pleasing and permanent solution to problems encountered with elevated copper release in new plumbing systems exposed to certain low pH, high alkalinity, and high organic matter waters. New plumbing systems could use GAC treatment immediately after installation to accelerate the formation of a protective scale, and while the approach could be effective for existing installations, the process of aging to a protective scale would likely require longer exposure times.

Conclusions

- Orthophosphate has immediate benefits for copper corrosion control but must be dosed perpetually to maintain reduced copper release. Orthophosphate does not facilitate the formation of a permanent protective scale.
- NOM interferes with the natural copper aging process and reduces the dissolved oxygen consumption during stagnation in copper pipes.
- The protective scale formed rapidly when NOM is removed to low levels can yield long-term reductions in copper release following temporary GAC treatment.

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APPENDIX C: Jar Testing of Malachite Inhibition

In junction with diagnostic testing of Miami water, additional jar tests were carried out in order to explore theoretical malachite inhibition potential. Two batches of Miami water was treated with GAC (for at least 90% TOC reduction), and sodium bicarbonate was added to one of the GAC treated batches to increase the alkalinity to 2000 mg/L as CaCO₃. Sodium bicarbonate was also added to a batch of Miami water without GAC treatment, and the control condition was untreated Miami water. Each jar was continuously stirred while cupric chloride stock solution was slowly added to the jar in equal increments, and the pH was maintained at 6.9 +/- 0.05. Total and soluble (filtered with 0.45 um pore size) samples were taken 2 minutes after each incremental addition of copper and after allowing the jars to sit undisturbed for one hour.

If all copper remained soluble, then the data points would fall on the dashed “ideal” line, and deviation below the ideal line indicates formation of copper solids. In the control water, there was some formation of solids after the addition of approximately 8 mg/L total Cu, but the transition to a solid of low solubility did not occur, with soluble copper remaining at about 9 mg/L. Conversely, aging occurred rapidly during the experiment in GAC treated water, and the transition to a copper solid of low solubility was associated with a drastic drop in soluble copper in the jar after the addition of approximately 7 mg/L total copper. Visually, aging was accompanied by the appearance of a blue hue in the jar of GAC treated water, while the jar containing control water remained nearly clear with only a slight tint of blue at high levels of total copper (> 14 mg/L). Despite additional increases in total copper, soluble copper decreased below 1 ppb during the experiment (Figure C-1). One hour after the experiment, soluble copper in the control condition dropped slightly to about 5.5 mg/L, but soluble copper in GAC treated water remained below 5 ppb (Figure C-4). The results of the jar tests agree with the conclusion of the bench-scale testing that NOM present in the Miami water inhibited copper aging, and according to mechanistic theory in the literature, adsorption of NOM to copper solid surfaces was likely the cause.

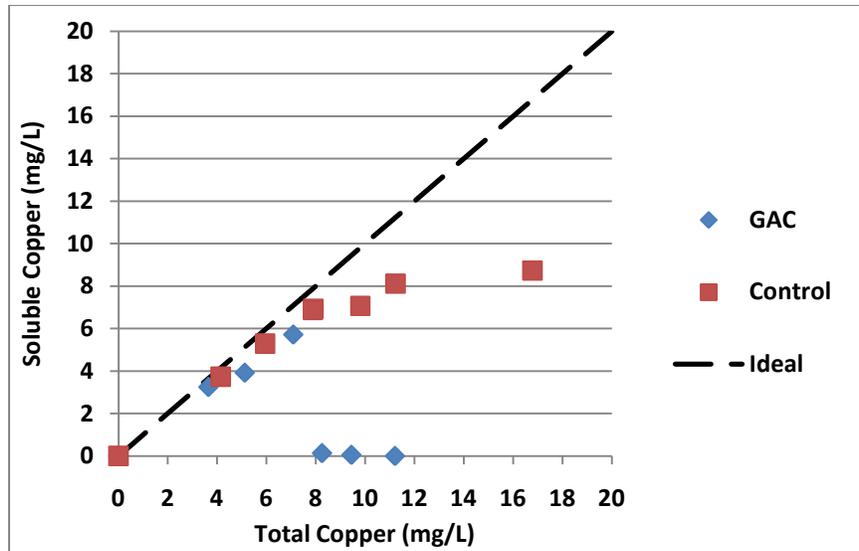


Figure C- 1. Impact of GAC treatment on malachite inhibition in Miami water

Considering the stoichiometry of malachite, a copper carbonate compound $\text{Cu}_2\text{CO}_3(\text{OH})_2$, adding bicarbonate to solution would increase the driving force for malachite formation. Therefore, bicarbonate addition could be a potential strategy to reduce malachite inhibition in Miami water. However, bicarbonate also acts as a ligand and may increase the soluble copper in the water due to formation of soluble copper complexes. When bicarbonate was added to the control water, the fraction of soluble copper remained close to 100% at all levels of total copper, and data points remained close to the ideal line (Figure C-2). However, one hour after the end the stirred jar test, soluble copper in control water with added bicarbonate fell below the concentration of soluble copper in the control water to 2 mg/L. This indicates that bicarbonate addition did increase the driving force for malachite formation but was not as effective as GAC treatment for facilitating the aging process. However, due to the high cost of GAC treatment, bicarbonate addition deserves further study as a potential remedial strategy, as it still yielded a significant reduction in soluble copper compared to the control.

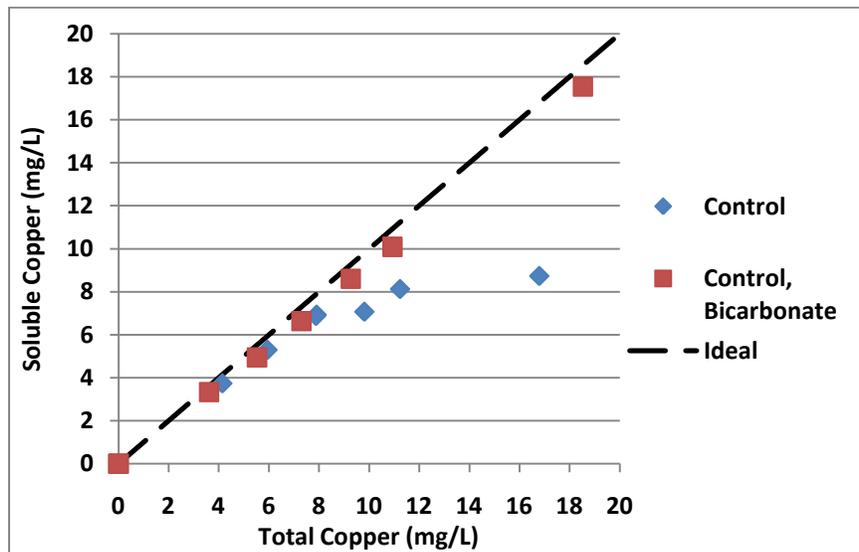


Figure C- 2. Impact of bicarbonate addition on malachite inhibition in Miami water without GAC treatment

Bicarbonate was also added to a batch of GAC treated Miami water, and bicarbonate addition again resulted in nearly 100% solubility at all concentrations of total copper (Figure C-3). While bicarbonate addition prevented aging during the jar test, a transition to a low solubility copper solid occurred during the next hour, and the soluble copper concentration fell to 40 ppb (Figure C-4). Soluble copper levels in both batches of GAC treated water were far below the Lead and Copper Rule Action Limit of 1.3 mg/L, but adding bicarbonate to GAC treated water increased the final soluble copper concentration by a factor of 8 compared to GAC treated without added bicarbonate. However, the delayed kinetics of aging in GAC treated water with added bicarbonate may be exploited for practical remedial purposes in order to prevent premature precipitation of copper solids and ensure that malachite formation occurs on the surface of copper pipes.

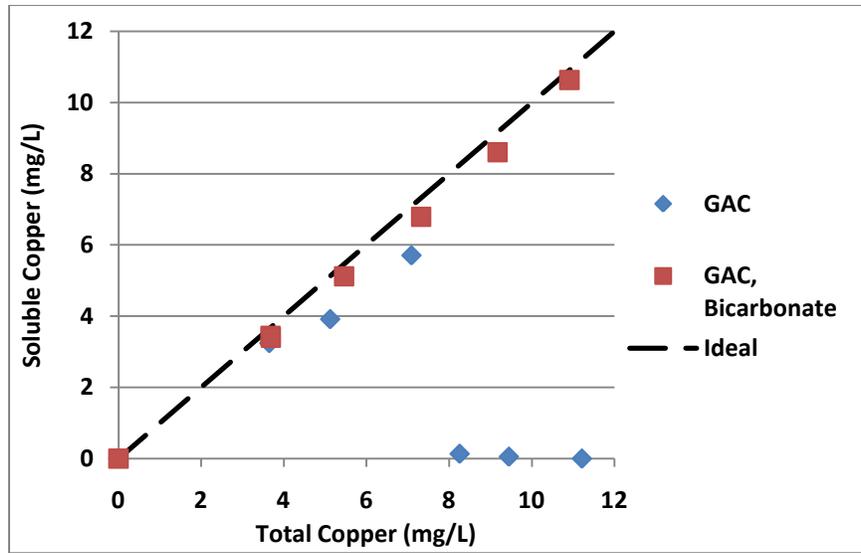


Figure C- 3. Impact of bicarbonate addition on malachite inhibition in GAC treated Miami water

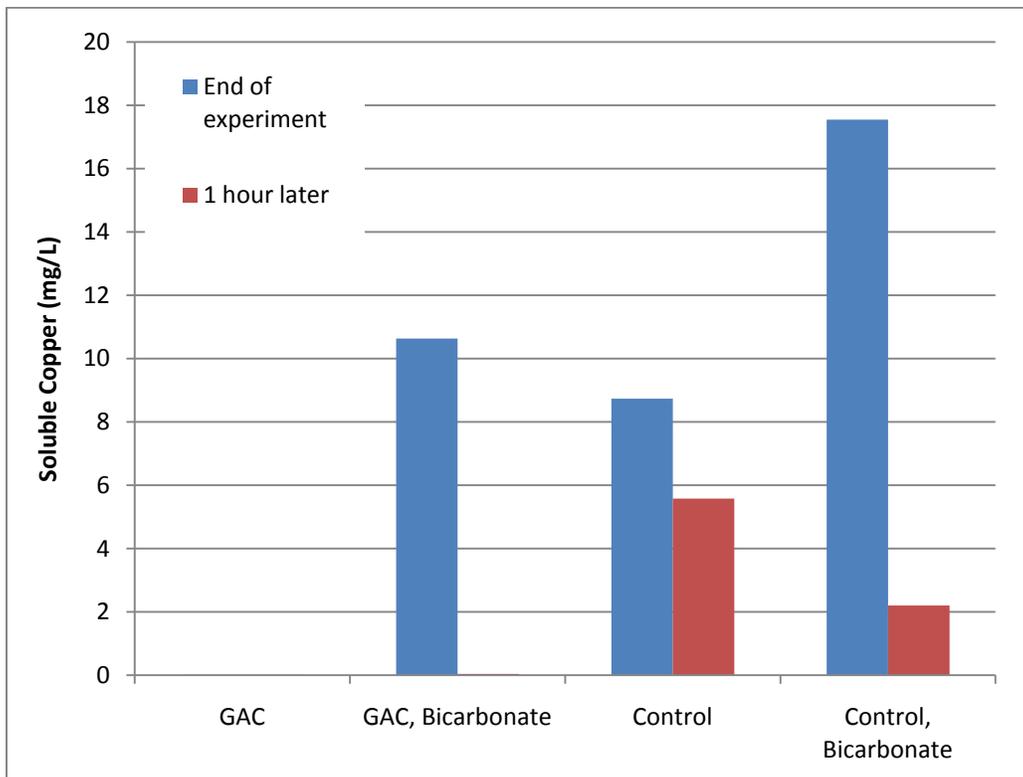


Figure C- 4. Soluble copper concentrations after jar test (soluble copper samples passed 0.45 um filter)

The results of the jar test reinforce the conclusion that NOM present in Miami water interferes with the aging process and prevents the transition to a copper solid of low solubility such as malachite, and the jar tests provide some additional mechanistic insight into the solids formation and aging processes that occurred inside the pipes during bench-scale testing. Bicarbonate addition effectively increased the driving force for malachite formation but delayed the aging kinetics. Further study of bicarbonate-facilitated formation of low solubility copper solids is warranted, and the potential practical usefulness of altering process kinetics should be explored.

Furthermore, the jars tests served as a simple and rapid method to assess malachite inhibition potential and the efficacy of possible remedial strategies. While months of bench-scale testing were required to definitively prove the benefit of GAC treatment for mitigating elevated copper release, the jar tests provided adequate results in less than two hours that accurately predicted the results of the bench-scale testing. As newly constructed facilities consider potential copper plumbing corrosion problems, the malachite inhibition potential jar tests described herein may be useful for quickly determining if the potable water supply will inhibit the aging process and result in extended periods of elevated copper release and could be used to assess the potential benefits of a remedial strategy such as GAC treatment for accelerating the transition to a low solubility protective scale.