

Chloride Sulfate Mass Ratio (CSMR) and Nitrate Acceleration of Galvanic Lead-Bearing Solder Corrosion

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ABSTRACT

Lead corrosion in premise plumbing systems from materials, such as lead pipes, soldered joints, and brass, can cause elevated lead in drinking water. This work examined mechanisms by which galvanic corrosion of lead solder:copper joints is accelerated by high chloride, low sulfate, and high nitrate in the water.

Galvanic corrosion studies conducted using simulated copper plumbing joints showed lowered pH and concentrated anions at the lead solder surface. A combination of low pH and high chloride can prevent passivation of the solder surface, indefinitely sustaining high corrosion rates and lead contamination of potable water supplies. The mass of lead leached to water correlated with predictions based on Faraday's law, although a portion of the oxidized lead remained attached to solder in a scale layer. When the level of sulfate in water increased relative to chloride, galvanic currents and associated lead contamination could be greatly reduced.

The impact of chloride-to-sulfate mass ratio (CSMR) on lead leaching from 50:50 lead:tin solder galvanically coupled to copper was examined at the bench scale. The CSMR can be affected by coagulant changeover, use of desalinated water, anion exchange, brine leaks, and other treatment changes. Consistent with prior experiences, increasing the CSMR in the range of 0.1 to 1.0 produced dramatic increases in lead leaching from this source. Above this range, while lead leaching was generally very high, there was little correlation between lead release and CSMR.

The impact of nitrate was tested at the bench scale using synthesized water. Results consistently showed that increasing nitrate in the range of 0 to 10 mg/L $\text{NO}_3\text{-N}$, could dramatically increase lead leaching from simulated soldered pipe joints. Although higher nitrate slightly increased the galvanic current, the main factor affecting lead release appears to be initiation of non-uniform corrosion, with small pieces of solder detaching into the water. Under some circumstances, the decay of chloramine after it leaves the treatment plant, and formation of nitrate via nitrification, can markedly increase corrosivity of distributed water to lead solder.

The bench scale experiments conducted in this work illuminated many issues related to accelerated lead corrosion of solder. However, future research is necessary to further elucidate the mechanisms behind nitrate-accelerated corrosion, as well as methods for inhibition of corrosion due to chloride and nitrate.

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AUTHOR'S PREFACE

The first three chapters have been submitted to journals for publication and are written in Journal article format with authorship clearly indicated. Chapter 1 has been submitted to *Environmental Science and Technology*, chapter 2 has been submitted to *Journal American Water Works Association*, and chapter 3 has been submitted to *The Journal of Corrosion Science and Engineering*. Chapter 1 examines self-perpetuating mechanisms of lead corrosion in potable water systems and elucidates the mechanisms contributing to lead contamination of potable water via corrosion of lead solder in copper pipe joints. The first author on this manuscript is Carolyn Nguyen. Kendall Stone and Carolyn Nguyen shared in experimental design, collection and analysis of data, and Kendall Stone assisted in the editing of the chapter and in making up graphs. Chapter 2 focuses on the impact of chloride-to-sulfate mass ratio on lead leaching from lead solder:copper couplings. This chapter highlights four common treatment and water quality changes that can negatively effect lead leaching in drinking water systems. As in the first chapter, Kendall Stone and Carolyn Nguyen shared in experimental design, collection and analysis of data, but Kendall Stone was the lead author and Marc Edwards and Carolyn Nguyen edited. Chapter 3 explores the negative impacts of nitrate on corrosion of lead solder connected to copper. Consistent high lead leaching was found associated with the presence of nitrate in the range of potable drinking water. The collaboration on Chapter 3 was the same as for Chapter 2.

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CHAPTER 1: Self-perpetuating lead contamination of drinking water due to galvanic corrosion of lead solder

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ABSTRACT. Galvanic corrosion of simulated copper plumbing joints lowered pH and concentrated anions at the lead solder surface. A combination of low pH and high chloride can prevent passivation of the solder surface, indefinitely sustaining high corrosion rates and lead contamination of potable water supplies. The mass of lead leached to water correlated with predictions based on Faraday's law, although a portion of the oxidized lead remained attached to solder in a scale layer. When the level of sulfate in water increased relative to chloride, galvanic currents and associated lead contamination could be greatly reduced.

KEYWORDS. Galvanic corrosion, current, solder, anode, pH, ion migration

BRIEF. Mechanisms contributing to lead contamination of potable water via corrosion of lead solder joints are elucidated.

INTRODUCTION

Seemingly innocuous changes in chemistry can sometimes dramatically increase a water's propensity to mobilize lead from pipes, soldered joints, and brass (Schock et al, 2001; Dudi, 2004; Lytle et al, 2005; Edwards et al, 2007; Giammar, 2009). In some cases the changes have resulted in exceedances of the United States Environmental Protection Agency (US EPA) Lead and Copper Rule (LCR), elevated blood lead, and even lead poisoning (Edwards et al, 2007; Miranda et al, 2007; Edwards et al, 2009; Renner, 2009).

One important subset of influential treatment changes, as highlighted by Edwards et al., involves dramatically increased lead release from lead solder:copper joints triggered by increases in the chloride-to-sulfate mass ratio ($CSMR = \text{mg/L chloride in the water divided by the mg/L sulfate}$) of the water supply (Edwards et al, 2007). These problems with elevated lead occurred and were not mitigated in some cases while utilities practiced optimized corrosion control using orthophosphate inhibitors (Edwards et al, 2007).

The nature and importance of the galvanic attack on contamination of water from lead solder was first demonstrated in England (Oliphant, 1983; Gregory, 1990). These authors discovered that waters with a CSMR above about 0.6 (CSMR) created very high and persistent galvanic currents between copper pipes and lead solder. The anodic lead solder, sacrificed by the connection to the cathodic copper, was believed to contribute to severe lead contamination of potable water (Oliphant, 1983; Gregory, 1990). If the CSMR of the water was lower, galvanic currents between lead solder and copper decreased markedly with time (Oliphant, 1983; Gregory, 1990), which is consistent with observations of Reiber et al in continuous flow testing

of waters to which sulfate was added AwwaRF, 1996). Later practical data demonstrated very strong links between the reported 90th percentile lead at certain utilities and the CSMR (Dodrill et al, 1995), as well as elevated CSMR due to changing coagulant chemical from aluminum sulfate to either ferric chloride or polyaluminum chloride (Edwards et al, 2007). Increased leaching and galvanic corrosion of lead solder at higher CSMR has also been unambiguously demonstrated at bench scale by Dudi (2004) and Edwards et al. (2007).

Although the practical link between higher CSMR and higher lead leaching from solder is well established in the literature, the precise mechanisms of the phenomenon have never been elucidated. The goal of this work was to unambiguously identify the key steps by which higher CSMR can cause persistent galvanic corrosion currents between copper and lead bearing materials.

Development of a working hypothesis based on literature review. When lead is connected to copper, the lead surface generally becomes anodic, and the rate of lead corrosion is accelerated. The free lead (Pb^{2+}) released to the water is a Lewis acid, which decreases pH upon removal of OH^- ions from the water via formation of complexes or precipitation of solids that contain OH^- . The lower pH at the anode surface was hypothesized to occur via chemical modeling by Dudi and was tentatively confirmed via microelectrode measurements of low pH at the lead anode surface (2004). Because low pH also prevents passivation of films on lead surfaces, it could contribute to self-perpetuation of the attack.

Another factor contributing to lead corrosion involves migration of anions such as chloride or sulfate to the lead anode surface, which is necessary to balance electroneutrality of the released Pb^{2+} . The increased concentration of anions at anode surfaces versus bulk water levels is well understood and, in fact, has been considered as a means of removing anionic contaminants from soils via electromigration (Horng, 1993; Kim et al, 2010). The net concentration of anions at anode surfaces can be predicted using a one dimensional model that accounts for anion migration and diffusion (Lim et al, 1984). Key results of this model illustrated two extremes in behavior that are relevant to the current application. Specifically, if the current density exceeds about $2 \mu\text{A}/\text{cm}^2$, net anion transport towards the anode becomes significant relative to net diffusion of the anions away of the anode, allowing significant accumulation of Cl^- or SO_4^{2-} at the anode surface relative to bulk water levels (Horng, 1993). In other words, when this threshold of current density was exceeded, the anion concentration factor (= anion concentration at the anode divided by the anion concentration of the bulk water) becomes quite significant. At another extreme, if the current density is very low, net transport of anions towards the anode is low relative to diffusion away from the anode, preventing significant concentration of anions near the anode surface. In the experimental data, sulfate was concentrated at the anode surface by a factor of 1.4 to 5 when the current density increased from $10 \mu\text{A}/\text{cm}^2$ to $25 \mu\text{A}/\text{cm}^2$ (Horng, 1993).

In general, the range of chloride and sulfate levels commonly encountered in potable water are not expected to significantly influence lead solubility due to formation of either complexes or precipitates (Schock, 1989). However, if these ions were to become concentrated significantly at the surface of the anode, significant impacts are predicted based on existing

solubility models. Specifically, at high levels, chloride is predicted to form soluble complexes with lead and increase its solubility, whereas sulfate can form relatively insoluble precipitate with lead and decrease its solubility (Nguyen et al, 2008; DeSantis et al, 2009). Work by Guo with polarized lead electrodes suggested that insoluble metal salts, such as PbSO_4 or other salts containing multivalent anions, could passivate the scale from the active state even in acidic conditions (Guo, 1992; Sato, 1996). However, in the presence of chloride, very rapid corrosion (metal polishing) could occur as metal chloride complexes form (Sato, 1996).

To demonstrate the effects of chloride and sulfate on lead solubility at the surface of lead anodes at relatively low pH, illustrative equilibrium modeling with MINEQL+ (Schecher et al, 1998) was conducted. The soluble lead in the micro-layer at the surface of the lead plumbing material can be predicted at different pH and anion levels. For example, if 50 mg/L Pb^{2+} was released to water at pH 6.5 near a lead solder surface, and if the sulfate level at equilibrium was 240 mg/L, only 2.3 mg/L of the Pb^{2+} would be soluble (Figure 1-1). The remaining 95% of the released lead would form a $\text{PbSO}_4:\text{PbO}$ solid precipitate on the anode surface that could reduce the rate of corrosive attack. The 240 mg/L SO_4^{2-} at the anode surface could be obtained by a 10X concentration of 24 mg/L SO_4^{2-} in the bulk water. In contrast, if chloride were present at the molar levels mentioned for sulfate in the preceding example, the solubility of lead at the anode would be increased by 160% to 3.4 mg/L soluble Pb due to the formation of soluble PbCl^+ complexes (Figure 1-1).

The effect of chloride relative to sulfate on soluble lead is much more dramatic at greater concentration factors resulting from higher galvanic current densities or at lower pHs at the

anode surface. For example, if 240 mg/L SO_4^{2-} were present at the anode surface and 50 mg/L Pb^{2+} were released to pH 4 water, 3.4 mg/L Pb would remain soluble while 93% of the lead would precipitate as PbSO_4 (Figure 1-1). Conversely, chloride, if present in the same molar amount as sulfate in the previous scenario, would form no precipitate and all of the released lead would remain soluble as free Pb^{2+} (91%) or as PbCl^+ (9%) at pH 4. Hence, another benefit of sulfate is that the PbSO_4 solid is relatively insoluble even in strong acid solutions.

EXPERIMENTAL SECTION

Pipe Setup. A simulated pipe joint macrocell, designed to track changes in water chemistry that resulted from galvanic corrosion between copper pipe and lead solder at joints during stagnation, was constructed (Appendix A, Figure A-1). The macrocell started with a $\frac{3}{4}$ " diameter copper pipe (31 cm long) and a $\frac{1}{2}$ " diameter copper pipe (6.4 cm long), connected by clear Tygon tubing with a 2-mm gap separation between the pipes. A 50:50 lead:tin, pure tin, or pure lead wire was inserted through the center of a silicon stopper, and then the stopper with wire was inserted into the $\frac{1}{2}$ " diameter copper pipe. The wetted surface area of lead solder (or pure lead or pure tin wire) was 6.2 cm² (Case Studies 1 and 3) or 5.2 cm² (Case Study 2). The smaller diameter ($\frac{1}{2}$ ") copper pipe was used to isolate water near the surface of the anodic solder. The larger diameter ($\frac{3}{4}$ ") pipe had the dual purpose of allowing collection of samples from various depths within the pipe using a pipette and also providing a large copper-to-solder surface area of approximately 34:1 in Case Studies 1 and 3 and 41:1 in Case Study 2. To simulate the galvanic connection between copper pipes and solder in joints while having the ability to measure galvanic corrosion with an ammeter, each lead or tin bearing wire was externally connected to the copper pipes via copper wires. The apparatus was oriented vertically so that the lead solder,

lead, and tin wires were at the bottom and the larger diameter copper pipes were in the upper part of the apparatus.

Water chemistry. The pipes were exposed to different water chemistries to simulate real-world problems encountered in practice (Table 1-1). Raw water from the utility in Case Study 1 was received and treated at bench scale with the specified coagulants and disinfectants to simulate full-scale treatment (Table 1-1). In Case Study 2, treated water, but prior to disinfection, was received at Virginia Tech from Utility 2. Water for Case Study 3 was prepared using reagent grade chemicals. The chloride and sulfate levels were selected to represent the range of chloride and sulfate levels quantified in potable water. The pH, inhibitor dose, and disinfectant concentrations were adjusted for all waters prior to exposure to the macrocells. Details of the bench scale treatment for each case study are provided in the Supporting Information and elsewhere (Nguyen et al, 2010).

Experimental protocol. The water in the pipes was changed three times per week using a “dump-and-fill” protocol. Each water condition was tested in triplicate. Water exposed to the pipes was collected and analyzed for metals at the end of each week.

Analytical methods. Total lead release was quantified by acidifying water samples with 2% nitric acid for at least 24 hours. Lead, chloride, and sulfate in the bulk water were measured using an inductively coupled plasma mass spectrophotometer (ICP-MS) in accordance with Standard Method 3125-B (Clesceri et al, 1998). The concentrations of chloride and sulfate were cross-checked using DIONEX, DX-120 ion chromatography according to Standard Method 4110

(Clesceri et al, 1998). Chloride microelectrode measurements were made with an ion-selective microelectrode by Lazar for Case Studies 1 and 3. Chloride and sulfate levels used in the calculation of the concentration factors were determined from ICP analysis of “anode” and “cathode” water samples. “Anode” samples consisted of the 9-mL solution closest to the solder wire, and “cathode” samples comprised the 10 mL solution withdrawn from the apparatus top, farthest from the solder wire (Appendix A, Figure A-1). The pH in the bulk water was measured with an Accumet electrode in accordance with Standard Method 4500-H⁺ B (Clesceri et al, 1998). The anode and cathode pH was measured using a flat membrane microelectrode and a reference electrode from Microelectrodes, Inc. Electrochemical measurements between the copper pipes and the solder, lead, or tin wires were conducted using RadioShack multimeters that had internal resistances between 100 and 102 Ω .

RESULTS AND DISCUSSION

Effect of galvanic corrosion on lead release. Galvanic current measured between the anode (lead solder, lead wire, or tin wire) and the cathode (copper pipe) is an indicator of galvanic corrosion. For this study, a convention was used in which negative current values indicated that the lead-tin solder, lead, or tin wires were anodic (sacrificed) while the copper pipes were cathodic (protected). As the magnitude of the measured galvanic current increased, lead release to the water increased for solder wires across all three case studies and for pure lead wire in the third case study (Figure 1-2). Lead release followed a roughly linear relationship with the galvanic current, consistent with expectations based on Faraday’s law. For example, when the current doubled, the lead released to the water also doubled. This is consistent with recent work by Sastri et al. which also linked galvanic corrosion to lead leaching from solder in drinking water (2006).

For 50:50 Pb/Sn solder, the measured currents reflected not only the lead corrosion rate but also tin release from solder. Solder corrosion may proceed with preferential leaching of one metal more than another, but if it is assumed that each metal corroded at the same rate, the lead released from 50:50 Pb/Sn solder to the water was approximately three times lower than predicted (Figure 1-2). However, consistent with Oliphant's findings (Oliphant, 1983), the remainder of the oxidized lead accumulated in lead oxide and other lead scales, which was confirmed by mass balances at the end of the experiment (Appendix A, Figures A-2 and A-3).

Chloride and sulfate migration. As expected, anions such as chloride and sulfate were drawn to the anodic lead solder (Figure 1-3), and cations such as sodium (Na^+) migrated toward the cathode (results not shown). Other work by Kim (Kim et al, 2010) and Horng (1993) also measured chloride and sulfate migration to the anode. Concentration factors were used to compare anion accumulation at the anode versus the cathode in this work and that observed in Horng's work. The concentration factors in this study were calculated by dividing the concentration in the 9 mL of solution closest to the anode by the concentration at the cathode. As the galvanic corrosion rate increased, the sulfate and chloride concentration factors increased as electromigration became dominant over ion diffusion (Figure 1-2). For instance, sulfate was concentrated at the anode surface by a factor of 1.4 when the current density was approximately $-1.2 \mu\text{A}/\text{cm}^2$. When the current density quadrupled to $-4.8 \mu\text{A}/\text{cm}^2$, 2.6 times more sulfate was measured in the anode compartment than in the cathodic area of the pipe. Similar trends were observed in Horng's work, although the amount of ion migration was lower than that measured in this work. Specifically, a current density of $-10 \mu\text{A}/\text{cm}^2$ resulted in a sulfate concentration

factor of 1.4 at the anode, and the concentration factor increased to 5 when the current density more than doubled to $-25 \mu\text{A}/\text{cm}^2$ (1993). Although significant concentration factors for sulfate and chloride in Case Study 3 were not detected with the macro-measurement technique used in the other two case studies, chloride concentration factors of 4 were measured using a microelectrode (Appendix A, Figures A-4 and A-5).

Both research studies found that in situations with very low galvanic currents, lead levels were not as strongly impacted by the levels of chloride and sulfate in the water (for example in Case Study 2), when compared to other tested conditions with higher galvanic currents. When the current was low enough, ion diffusion became dominant and concentration factors were very low. For example, Horng did not quantify significant anion concentration until the magnitude of the current density was above $10 \mu\text{A}/\text{cm}^2$ (1993). Although significant concentration factors for sulfate and chloride in Case Study 3 were not detected with the macro-measurement technique used in the other two case studies, chloride migration by a factor of 4 times to the lead solder anode was measured when using a microelectrode (results not shown).

As expected based on the transport numbers of sulfate versus chloride (Arrhenius, 1902; Tower, 1905), sulfate had a slightly higher concentration factor for a given current than did chloride (Figure 1-2). As a result, the effective CSMR at the lead anode surface may not be the same as in the bulk water.

Pure lead and pure tin wires were also evaluated in Case Study 2. However, there were no trends in the sulfate and chloride concentration factors with increasing galvanic corrosion

activity. For pure tin wire in Case Study 2, this was because of the low galvanic currents, which ranged from -0.5 to -3.2 $\mu\text{A}/\text{cm}^2$. In the case of pure lead wire, sulfate migrated to the anode by a factor of 1.2 to 7.6 for some water conditions; however, there appeared to be no trend between the migration and the galvanic current density, which ranged from -0.9 to -6.9 $\mu\text{A}/\text{cm}^2$. Chloride migration toward the lead wire was not detected via macro-measurements.

pH at anodic solder surface. As the galvanic corrosion rate increased, the pH decreased at the anodic solder surface due to the Lewis acidity of lead and tin (Figure 1-2). In fact, pH as low as 3.7 for Case Study 1 and as low as 2.5 for Case Study 3 were measured in the section of copper pipe near the solder surface after a two-day stagnation period. Even when the galvanic corrosion activity was relatively low as in Case Study 2, the pH still dropped from pH 7.3 in the bulk water to as low as pH 3.8 at the solder surface. Consistent with expectations and prior research (Kuhn et al, 1983), the pH increased with increasing distance from the anode due to the cathodic reaction with net OH^- production (Figure 1-3).

Effect of pH on lead leaching. When the pH decreased at the lead anode surface and the galvanic current was persistent, much more lead was present in the water (Figure 1-2). As a result, a self-perpetuating situation occurs where lead continues to dissolve and the anode surface cannot passivate. Without additional reactions at the surface of the anode, such as precipitation of lead sulfate solids to form a protective layer and to limit corrosion activity, the lead solder can continue to corrode and contaminate the water indefinitely.

Implications for drinking water systems. Galvanic reactions can drive corrosion of lead solder in copper joints and contribute to exceedance of the USEPA LCR. Furthermore, in waters supporting relatively high galvanic currents, higher chloride and lower sulfate can worsen corrosion of lead solder. The detriments of chloride are hypothesized to be attributed to its concentration near the anode surface and resulting formation of soluble PbCl^+ complexes, whereas the benefits of sulfate are attributed to formation of relatively insoluble PbSO_4 solids. This work is the first to demonstrate that large gradations in pH can be produced via galvanic corrosion of lead solder:copper joints, concomitant with concentration of anions near the lead surface, under stagnant water conditions similar to those encountered in home plumbing. Recently, similar conclusions about low local pH, high chloride, high sulfate, and high lead concentrations were drawn by Desantis et al. based on mineralogical examination of lead:copper pipe connections from extracted service line samples (2009). Additional work is needed to better understand situations in which persistent galvanic currents occur, and how they can be practically mitigated through control of water chemistry.

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SUPPORTING INFORMATION AVAILABLE. Additional descriptions, figures, and tables regarding the experimental setup, bench scale water treatment, mass balance of oxidized lead, and chloride concentrations in Case Study 3 are included in Appendix A.

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1 **Table 1-1.** Water quality of test waters.

(Case Study #) Water Type	Cl, mg/L Cl	SO₄²⁻, mg/L SO₄	CSMR*	Alkalinity, mg/L as CaCO₃	pH	Inhibitor (dose)	Disinfectant, mg/L as Cl₂
(1) Alum-treated	27	21	1.4	25	7.7		
(1) PACl-treated**	32	6	5.3	25	7.7	Ortho-phosphate	Various - free chlorine or chloramines (3.5 mg/L)
(1) PACl-treated**, simulated road salt runoff (+16 mg/L Cl)	48	6	8.5	25	7.7	(1 mg/L P)	
(2) Typical treated water subjected to corrosion control strategies	15	3	5.0	8	7.3	Ortho-phosphate (various: 0-1 mg/L P)	Free chlorine (2 mg/L)
(3) Low chloride and high sulfate	22	121	0.2	10	8.3		
(3) High chloride and low sulfate	129	8	16	10	8.3	None	Chloramines (4 mg/L)

* Chloride-to-sulfate mass ratio (CSMR) is given as mg/L Cl⁻ per mg/L SO₄²⁻.

** PACl – polyaluminum chloride.

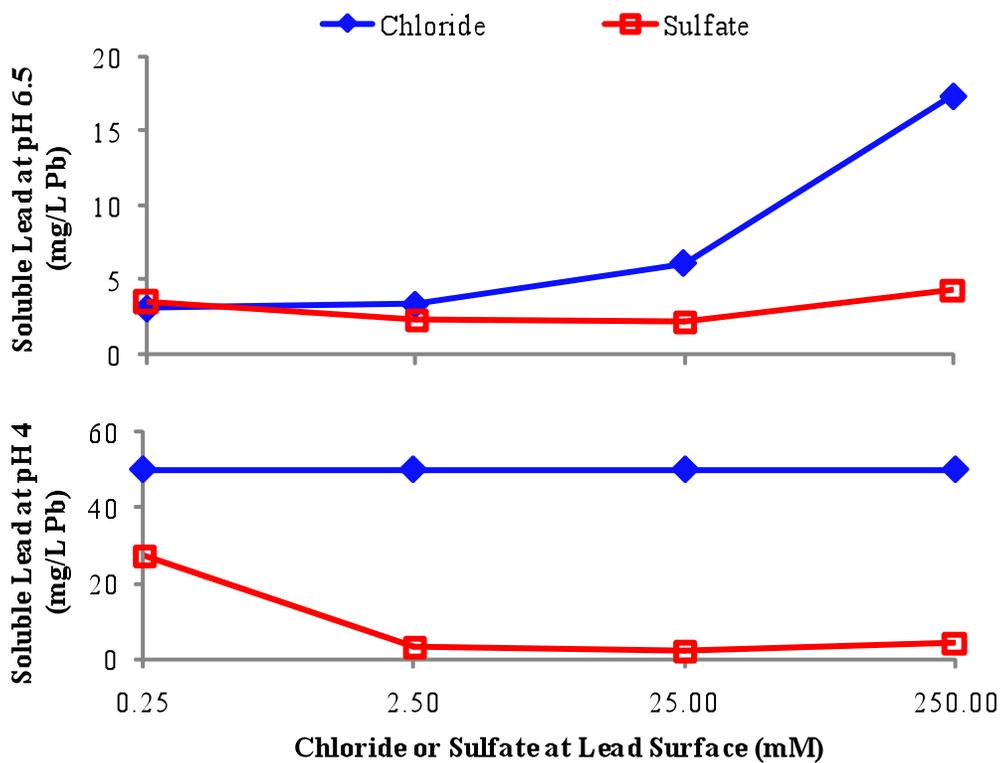


Figure 1-1. Equilibrium soluble lead concentrations at pH 6.5 (top) and pH 4.0 (bottom) at a lead surface if 50 mg/L Pb²⁺ is released to the water. Sulfate and chloride concentrations at the lead surface can be higher than in bulk water due to electromigration. In water with sulfate, PbSO₄:PbO or PbSO₄ solids are predicted to form at pH 6.5, and PbSO₄ solids are predicted at pH 4.0. If chloride were dominant in the water and at the lead anode, Pb(OH)₂ solids would form at pH 6.5, and no precipitates are predicted to form at pH 4.0.

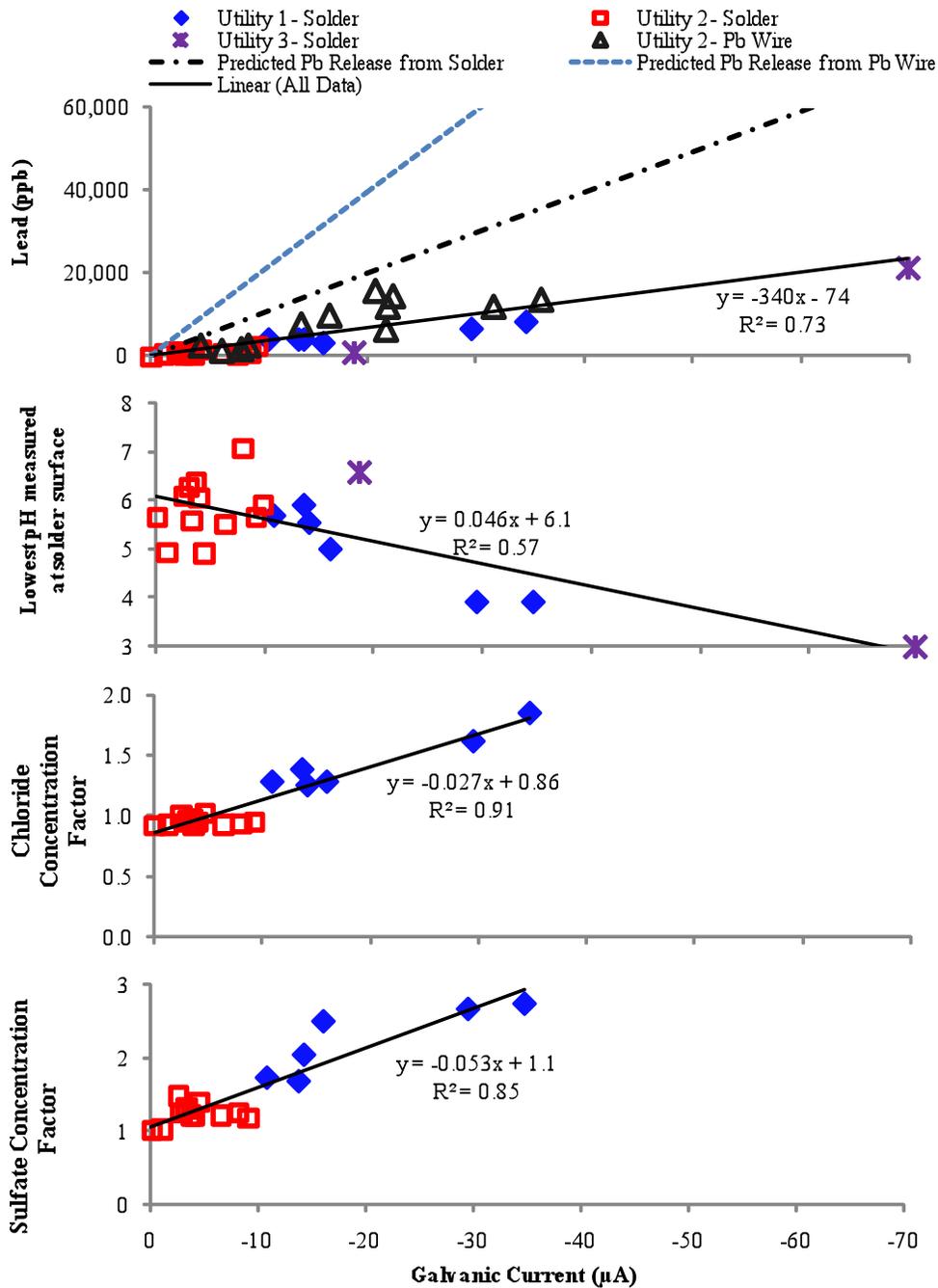


Figure 1-2. Lead release to bulk water, pH at solder surface, chloride concentration factor and sulfate concentration factor at solder anode as a function of galvanic current. Measurements were taken after two days of water stagnation inside the pipes. The concentration factor is equal to the concentration at anode divided by the concentration at cathode.

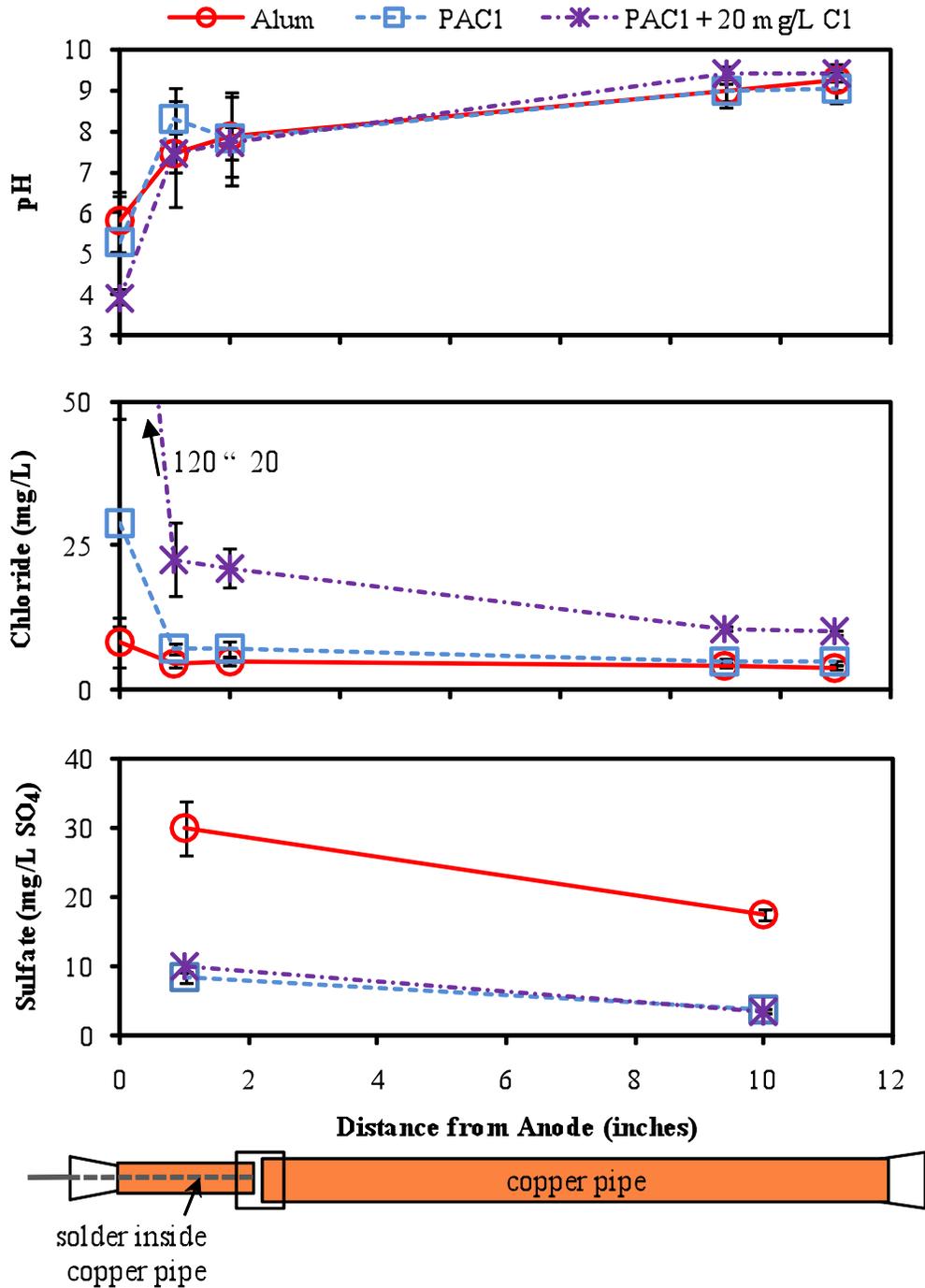


Figure 1-3. pH, chloride concentration, and sulfate concentration as a function of distance from the bottom-most part of the solder anode for Utility 1. Error bars represent 95% confidence intervals over triplicate measurements.

CHAPTER 2: Chloride:Sulfate Ratio: Practical Lead Solder Corrosion Case Studies

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ABSTRACT. The impact of chloride-to-sulfate mass ratio (CSMR) on lead leaching from 50:50 lead:tin solder galvanically coupled to copper was examined using bench scale testing and field data collected from water utilities. The CSMR can be affected by coagulant changeover, use of desalinated water, anion exchange, brine leaks, and other treatment changes. Consistent with prior experiences, increasing the CSMR in the range of 0.1 to 1.0 could produced dramatic increases in lead leaching to potable water.

INTRODUCTION

Lead corrosion is sometimes severely impacted by seemingly innocuous changes in drinking water treatment, and in a few cases has been linked to elevated blood lead levels in children (Renner, 2006; Edwards et al, 2009; Renner, 2009). The literature reveals numerous instances in which higher chloride-to-sulfate mass ratio (CSMR) was linked to increased galvanic corrosion and associated problems with lead solder pipe joints (Edwards et al, 2007; Dodrill et al, 1995; Oliphant, 1983; Gregory, 1985).

The CSMR is expressed as a ratio of mg/L Cl⁻ to mg/L SO₄²⁻. For example, in a water with 10 mg/L Cl⁻ and 20 mg/L SO₄²⁻, the CSMR is 0.5:

$$\text{Chloride to Sulfate Mass Ratio (CSMR)} = \frac{[\text{Cl}^-]}{[\text{SO}_4^{2-}]} = \frac{10 \text{ mg/L Cl}^-}{20 \text{ mg/L SO}_4^{2-}} = 0.5 \quad (\text{Equation 2-1})$$

Levels of CSMR exceeding about 0.6 have been associated with accelerated lead solder corrosion (Oliphant, 1983; Gregory, 1985; Dodrill et al, 1995; Edwards et al, 2007).

Galvanic corrosion. The problems attributed to higher CSMR result from accelerated galvanic corrosion of lead pipe:copper or lead solder:copper connections in water distribution systems. Oliphant first showed that galvanic currents between lead solder and copper pipes increased with higher CSMR, although lead in water was never measured (Oliphant, 1983). Supporting Oliphant's findings, Edwards et al observed higher lead in water when lead solder was connected to copper in the presence of high CSMR (2007), but the CSMR had little effect for lead solder alone. The galvanic corrosion dropped pH to as low as 3.4 at the solder surface during periods of stagnation, allowing the attack on the lead-bearing material to proceed without passivation (Edwards et al, 2007). Other research by Reiber suggested that galvanic corrosion was short-lived (Reiber, 1991; Reiber et al, 2006), based on surface potential and current measurements between lead solder and copper, but this was for waters that were amended by addition of sulfate or under continuous flow conditions (AwwaRF, 1996). Reiber (1991, 2006) also did not measure lead in water. Work by Porter et al studied galvanic corrosion of lead

solder and observed significant impacts on lead leaching and corrosion rates; however, effects of the CSMR on the magnitude of the problem was not quantified (1995).

Changes in the CSMR. Studies by Oliphant (1983) and Gregory (1985) determined that a CSMR of greater than 0.5 increased galvanic corrosion of lead solder connected to copper. An independent study by Dodrill et al (1995) found that the increase of chloride relative to sulfate correlated with higher 90th percentile lead levels for certain utilities. In their work examining certain high pH and low alkalinity waters, Dodrill et al (1995) identified a CSMR threshold of approximately 0.58, below which 100% of the utilities surveyed met the United States Environmental Protection Agency (USEPA) Lead and Copper Rule (LCR). Above that threshold, only 36% of the utilities surveyed were in compliance with the LCR.

The CSMR can be impacted by many changes such as coagulant changeover, implementation of anion exchange treatment, an accidental hypochlorite generator leak, and blending of desalinated water into a distribution system. Coagulant changes can increase the CSMR and trigger lead contamination of potable water. For example, one utility switched from aluminum sulfate (alum) to polyaluminum chloride (PACl), and later exceeded the United States USEPA LCR action level of 15 ppb Pb (Edwards et al, 2007). In another case, high lead in water was temporally linked to use of ferric chloride in an attempt to enhance particle removal. The utility switched to ferric sulfate in an attempt to reduce lead levels (Hewlitt, 2007). However, the CSMR was not unambiguously identified as the cause of the high lead in water at that time.

Anion exchange treatment has been used to remove arsenic and natural organic matter from drinking water (Edwards et al, 2008; Edwards et al, 2007). In fact, after one utility implemented anion exchange to remove arsenic, lead at the tap in one apartment building spiked above 1,000 ppb, and a child was identified with elevated blood lead (Edwards et al, 2007). It was suspected that these high lead levels were caused by the large increase in CSMR as a result of anion exchange treatment, coupled with a concurrent decrease in pH from 7.0 to 5.5 due to frequent regeneration of the anion exchange resin.

Since 2006, Utility 5 in Tennessee has exceeded the LCR with 90th percentile lead as high as 110 ppb Pb in 2006. Before 2006, the utility distributed water at pH 8.7 and reported no lead problems. In 2006, the utility began distributing water at pH 7.3 and dosing a polyphosphate/orthophosphate blend for corrosion control. Shortly after these changes, Utility 5 began to exceed the lead action level. They then discovered that a brine leak from their on-site hypochlorite generator was increasing chloride levels five times above normal levels. It was deemed possible that this could have triggered the higher lead in water.

A few studies have shown that desalinated water has a very high CSMR and can increase lead leaching. However, a study suggested that passivation could occur after about 6 weeks of exposure (Blute et al, 2008). A limitation of that work is that only brass meters were tested, and lead solder connected to copper was not tested. In other work, relatively low levels of lead leaching from brass were measured in waters with high CSMR compared to very high amounts of lead from simulated lead soldered joints (Edwards et al, 2007; Nguyen et al, 2010). Other studies illustrated that desalinated water increased the CSMR and sustained high levels of lead

release from coupons with lead solder (Taylor et al., 2005; Tang et al., 2006). However, results were never clearly tied to higher CSMR, given that the pH and alkalinity of the water were also changing among the different blends.

The goal of this work was to develop a simple test that could be easily deployed at water utilities to quickly examine impacts of changes to CSMR on lead leaching from simulated lead:solder joints. Moreover, the test was used to verify practical experiences of water utilities that may have experienced higher lead from higher CSMR, and to see if the test could be used proactively to screen for potential problems with treatments.

MATERIALS AND METHODS

Bench test protocol. A 1” length of 3-mm diameter 50:50 Pb:Sn solder was placed on the inner edge of a 1” length of ½” diameter copper couplings. The solder coupons were exposed to 100 mL of each water in triplicate. The water was changed using a static dump-and-fill protocol twice per week (Monday/Thursday or Tuesday/Friday), and weekly composite samples were collected for each water condition at the end of each week. Each study lasted for at least 5 weeks. Once trends were established using the composite samples, water from individual replicates were analyzed to determine statistical confidence.

Test Water Treatment. Water was shipped to Virginia Tech from each of the six participating water utilities (Table 2-1). Raw waters from Utilities 1, 2, and 3 were treated by coagulation and filtration at bench scale to simulate the full-scale treatment to the extent possible. In the Utility 4 study, distribution system water was obtained, and anion exchange

treatment was simulated at bench scale. Water from Utility 5 was obtained from the plant, and potential corrosion inhibitors were dosed to the water. Water from Utility 6 was obtained from the current distribution plant, and finished desalinated water was obtained from the utility's pilot desalination plant. Sodium bicarbonate was added to Utility 6's desalinated water to increase the alkalinity from 25 mg/L to 40 mg/L as CaCO₃.

For all water conditions, the pH, inhibitor dose, and disinfectant concentrations were adjusted prior to exposure to the plumbing materials (Table 2-2). To reach target pH values, 0.1 M NaOH was added to increase the pH, or acid was added in the form of 0.1 M HNO₃ for Utilities 1, 2, 5, and 6 or CO₂ for Utilities 3 and 4 to decrease the pH (Table 2-2). When nitric acid was added, nitrate levels in the water increased less than 0.1 mg/L NO₃-N. When chloramines were dosed, a 4:1 mg Cl₂:mg N ratio was used in all cases except for Utility 6, which had a ratio of 5:1 mg Cl₂:mg N.

Coagulation (Utilities 1, 2, and 3). Waters coagulated at bench scale were treated with coagulation, sedimentation, and filtration. Optimal coagulant doses were provided by the plant for each batch of water received at Virginia Tech. Coagulation mixing speeds and times (rapid mix for one minute, 20 rpm for 20 minutes, and settling for 30 minutes) were selected to simulate full-scale treatment using jar tests. Deep bed filtration was simulated using glass wool filters. Qualitatively, a deep sand filter does a better job of removing particles than the glass wool filter used at bench scale in the lab tests, but the relative performance advantages in this work for glass wool in terms of turbidity removal between coagulants, were the same as those noted by

the utilities in treating the actual waters using deep bed sand filters. Aside from the coagulant type and dose, each test water was treated identically.

The CSMR increased for water treated with coagulants containing chloride (e.g., PACl and ferric chloride) because the coagulants added chloride and no sulfate. In contrast, sulfate-based coagulants resulted in lower CSMR because sulfate was increased but not chloride. For coagulant blends, such as ferric sulfate/aluminum chlorohydrate, both sulfate and chloride were added; however, the particular proprietary blend evaluated in this study added much more chloride than sulfate to the water, thereby increasing the CSMR.

Utility 1, NC. Within the last few years, Utility 1 has implemented four different coagulants with varying chloride and sulfate levels, and high lead measurements in 13% of samples collected from homes and schools coincided temporally with use of chloride-based coagulants. At least one sample contained 79 ppb Pb (Hewlitt, 2007). To potentially enhance coagulation while maintaining a relatively low CSMR, Utility 1 was interested in testing a new proprietary type of coagulant that contained a ferric sulfate polymer blend. Therefore, five coagulants were evaluated for Utility 1 water: (1) alum, (2) ferric chloride, (3), a ferric sulfate/aluminum chlorohydrate blend, (4) ferric sulfate, and (5) a ferric sulfate polymer blend (Table 2-3).

Utility 2, NC. Four types of coagulants were tested including: (1) ferric chloride, (2) ferric sulfate, (3) ferric chloride/ferric sulfate blend resulting in a CSMR of 0.4, and (4) ferric chloride/ ferric sulfate blend resulting in a CSMR of 1.1. Anion exchange in combination with a

third of the typical dose of ferric sulfate or ferric chloride was also evaluated. At bench scale, the anion exchange treatment was simulated in batch treatment using the same method used for Utility 4. The CSMR in Utility 2's water that was pre-treated with ferric sulfate increased from 0.2 to 1.4, and water pre-treated with ferric chloride increased from 4.5 to 13 as a result of the chloride-based anion exchange treatment (Table 2-3).

Utility 3, NC. Greenville Utilities Commission (Utility 3) in NC currently coagulates using alum but wanted to use some level of PACl to enhance the removal of natural organic matter. In the past, switching completely to PACl resulted in LCR exceedances (Edwards et al, 2007). Therefore, five types of coagulation treatment were evaluated for effects on lead leaching: (1) alum, (2) PACl, (3) alum/PACl blend with a resulting CSMR of 0.7 (4) alum/PACl blend with a resulting CSMR of 0.9, and (5) alum/PACl blend with a resulting CSMR of 1.3 (Table 2-3).

Anion exchange for arsenic removal (Utility 4). Fifteen gallons of water were collected at a point prior to arsenic removal from Utility 4. Five gallons of this water were subjected to no anion exchange treatment and pH adjustment to 7.0 to simulate the original distribution system water that did not have a lead problem. The remaining ten gallons of water were treated by anion exchange in a batch process to simulate impacts of arsenic treatment without a column. Chloride-based anion exchange resin was mixed with the water from Utility 4 at a ratio of 1.7 mL of resin per 1 L of treated water at 100 RPM for 30 minutes, followed by 30 minutes of settling. Bio-Rad AG 1-X8 resin (50-100 mesh size) in the chloride form was used for this study. Prior to its use, the resin was rinsed several times with deionized water to remove excess

chloride. Half of the water treated with anion exchange was reduced to pH 5.5 by bubbling CO₂ to simulate the low pH that occurred in practice after frequent anion exchange column regeneration. After pH adjustment for all three water conditions, no further treatment of the water was conducted, as occurs in practice. Thus, three water conditions were tested for Utility 4: (1) distribution water with no arsenic treatment at pH 7.0, (2) water treated with anion exchange and pH adjusted to 7.0, and (3) water treated with anion exchange and pH adjusted to 5.5 (Table 2-4). After the 6-week study, the anion exchange treated condition at pH 5.5 was adjusted to pH 7.0 for a 5-week period.

Arsenic in the water was reduced from 4.5 to 1.8 ppb As as a result of the treatment. The anion exchange treatment increased chloride from 4.4 mg/L to 13.2 mg/L Cl⁻ and decreased sulfate from 4.1 mg/L to 1.7 mg/L SO₄²⁻, effectively increasing the CSMR from 1.1 to 7.8 (Table 2-4). Using this method, less arsenic and sulfate was removed from the water compared with anion exchange through a column, which is the method that has been used in practice by Utility 4. As a result, the CSMR after treatment was not as high as it may be in practice when arsenic and sulfate are removed more efficiently (and replaced with chloride) from the resin. Thus, any changes observed in this experiment due to the higher CSMR would likely underestimate the actual impacts if the water had been treated using a column.

Brine leak (Utility 5). Test water was obtained from the UV channel of Utility 5's treatment plant and subjected to a number of corrosion control strategies including the addition of poly-orthophosphate blend corrosion inhibitor, orthophosphate, and alkalinity. Details of the corrosion control strategies that were tested are listed elsewhere (Nguyen et al, 2010). The

treated water from Utility 5 typically has a chloride concentration of 3 mg/L Cl^- and a very low sulfate concentration of about 2 mg/L SO_4^{2-} . However, the chloride in the treated water increased five times to 15 mg/L Cl^- when the brine solution from the hypochlorite generator leaked into the water. To investigate the possible impacts of this leak at the utility, solde coupons were initially exposed to waters with 3 mg/L Cl^- for 12 weeks, followed by exposure to waters with 15 mg/L Cl^- for 8 weeks to simulate the effect of the accidental brine leak. Simulation of the brine leak from the on-site hypochlorite generator was accomplished by adding chloride as sodium chloride.

Desalination (Utility 6). Utility 6 shipped groundwater and water desalinated by multiple stage nanofiltration to Virginia Tech. The alkalinity of the desalinated water was adjusted to 40 mg/L as CaCO_3 by adding NaHCO_3 prior to blending with groundwater. Distribution water (groundwater) and desalinated water were blended at four different ratios: (1) 100% distribution or current water, (2) 25% desalinated water and 75% distribution water, (3) 50% desalinated water and 50% distribution water, and (4) 75% desalinated water and 25% distribution water (Table 2-5).

To provide mechanistic insights to changes in corrosivity due to variable chloride and sulfate in the blends, two additional tests were conducted. For one batch of distributed water, chloride (30 mg/L Cl^- added as CaCl_2) was added to match the chloride level that was present in the highest desalinated water blend, or 25% distributed and 75% nanofiltered (NF) blend. Likewise, for one aliquot of 25% distributed and 75% NF water, sulfate (50 mg/L SO_4^{2-} added as CaSO_4) was added to match the sulfate level present in the 100% distribution water (Table 2-6).

Analytical methods. Samples were acidified with 2% nitric acid for at least 24 hours to dissolve metals. The samples were analyzed for metals with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) in accordance with Standard Method 3125-B. The pH in water samples was measured with an electrode according to Standard Method 4500-H⁺. Ammonia was measured using a Hach DR 2700 spectrophotometer salicylate method, according to Standard Method 4500-NH₃. Total and free chlorine were measured on a Hach DR 2700 spectrophotometer according to Standard Method 4500-Cl (Clesceri et al, 1998).

RESULTS AND DISCUSSION

Effect of coagulation. It has already been established that in a few cases, the type of coagulant used to treat water is a major factor controlling the CSMR and lead leaching from galvanic solder-copper couplings (Edwards et al, 2007). This work extended the testing to many other waters where similar problems were suspected (Table 2-3).

Utility 1, NC. To evaluate the effect of each coagulant on lead leaching and to test one new type of coagulant for the utility, five different types of coagulants in treated waters were compared head-to-head in terms of lead leaching from solder. Consistent with theory and practical experience at this utility, lead leaching increased with higher CSMR of the water. The ranking from least to most lead leaching was: (1) ferric sulfate, leaching 60 ppb Pb, (2) alum, leaching 140 ppb Pb, (3) the ferric sulfate polymer blend, leaching 200 ppb Pb, (4) ferric chloride, leaching 530 ppb Pb, and (5) the ferric sulfate/aluminum chlorohydrate blend, leaching 790 ppb Pb.

Statistically, the ferric sulfate-treated and the ferric sulfate polymer blend-treated waters resulted in lower lead release from lead solder than the other conditions (p-value < 0.05). On average, the sulfate-based coagulants (ferric sulfate, alum, and the ferric sulfate polymer blend) released 4.9 times less lead than the chloride-based coagulants (ferric chloride and ferric sulfate/aluminum chlorohydrate blend). Coagulation with the ferric sulfate/aluminum chlorohydrate blend did not decrease lead leaching compared to coagulation with a 100% chloride-based coagulant because the sulfate contributed by the ferric sulfate was not sufficient to decrease the CSMR to a non-corrosive level (Table 2-3). Consistent with theory, lead leaching to water was roughly positively correlated with the CSMR (Figure 2-1).

Utility 2, NC. Four coagulants (ferric chloride, ferric sulfate, ferric chloride/ferric sulfate blend at low CSMR, and ferric chloride/ferric sulfate blend at high CSMR) in treated waters, and two coagulants in conjunction with anion exchange treatment, were compared head-to-head in terms of lead leaching from solder connected to copper. With the exception of the solder coupons exposed to water treated with 100% ferric chloride, higher CSMR correlated with increased lead release (Figure 2-1). The water with the lowest CSMR, the 100% ferric sulfate condition with a CSMR of 0.2, resulted in the least amount of lead release of about 520 ppb Pb. By doubling the CSMR to 0.4, the lead release increased 1.7 times to a concentration of 880 ppb Pb. The coagulant blend with a CSMR of 1.2 caused 1,730 ppb Pb release, or an increase in 3.4 times compared to ferric sulfate (CSMR 0.2). The water treated with ferric chloride (CSMR 4.0) had lead release that was not statistically different from that at a CSMR of 1.2, but all other results were different at greater than 95% confidence.

Utility 3, NC. Historically, Utility 3 experienced lead exceedances when treating with PACl, and the problem was remediated by switching back to alum (Edwards et al, 2007). However, this utility would like to use some amount of PACl to reap benefits from improved coagulation and particle removal. Therefore, bench scale tests were conducted to determine if blending alum and PACl coagulants was possible to obtain benefits of PACl while also maintaining a lower CSMR.

Consistent with theory, CSMR had a positive correlation with lead release (Figure 2-1). For instance, the lowest CSMR condition (100% alum with a CSMR of 0.4) had the lowest lead release at 70 ppb Pb. Increasing the CSMR to approximately 0.9 increased lead release 26 times up to more than 1,900 ppb Pb compared to the alum-treated water. The highest CSMR level of 1.8 (100% PACl) caused lead concentrations 44 times higher than the lowest CSMR condition (100% alum), releasing about 3,200 ppb Pb. The trends were confirmed at greater than 95% confidence. For this utility, increasing the CSMR from 0.4 to 0.7 did not result in a significant increase in lead. Therefore, these results indicate that in this water, higher CSMR blends of PACl and alum generally increased lead release. However, the blended coagulant with a CSMR of 0.7 was not significantly different from the 100% alum condition (CSMR 0.4), and the utility could use a small amount of PACl without markedly increasing the lead in water.

Effect of anion exchange treatment: Utility 2, NC. The utility was considering anion exchange in combination with coagulation to remove natural organic matter from the water. The

use of anion exchange significantly increased the CSMR from 0.2 to 1.4 in the case of ferric sulfate, and from 4.5 to 13 in the case of ferric chloride (Table 2-3).

The anion exchange treatment, in conjunction with lower doses of both ferric sulfate and ferric chloride coagulant, increased lead release. Furthermore, the lead leaching to water correlated with increases in the CSMR (Figure 2-1). The lead release in the ferric sulfate-treated water increased from 700 ppb to 2,400 ppb Pb (a 3.4X increase) with anion exchange as the CSMR increased from 0.2 to 1.4. When a lower dose of ferric chloride was used with anion exchange, lead release increased from 1,500 ppb to 11,000 ppb Pb (a 7X increase) as CSMR increased from 4.5 to 13. It was concluded that anion exchange might be problematic in this water because it dramatically increased the CSMR and the potential for lead leaching.

Utility 4, ME. Consistent with suspicions at Utility 2, a dramatic increase in lead release for Utility 4 was observed in water treated with anion exchange. Anion exchange treatment increased lead release an average of 47 times during week 6 of the study from 40 ppb to 1,830 ppb Pb (Figure 2-2). This illustrates that levels of lead in water over 1,000 ppb observed in apartments at this utility are well within the realm of possibility (Edwards et al, 2007).

The combined effect of higher CSMR and lower pH resulted in even higher lead leaching than from high CSMR alone. Decreasing the pH from 7.0 to 5.5 increased lead in the water from 1,830 ppb to 4,800 ppb Pb (Figure 2-2). To further illustrate the exacerbating effect of lower pH, the pH 5.5 anion exchange-treated water was increased to pH 7.0 for a period of 5 weeks. After

about 3 weeks, the lead release decreased to the level that had been observed for the condition at pH 7.0 for the duration of testing (Figure 2-3).

Anion exchange treatment, and the resultant increase in the CSMR, by itself was enough to cause a dramatic increase in lead release; however, the decrease in pH also contributed to serious problems in this water.

Effect of brine leak (Utility 5). In each and every water condition evaluated for Utility 5, the simulated brine leak, increasing chloride from 3 mg/L Cl⁻ to 15 mg/L Cl⁻ caused an increase in lead release, regardless of the level of alkalinity or corrosion inhibitor that was dosed (Figure 2-4). This increase ranged from a 1.5 times increase when zinc orthophosphate was present, to a 15 times increase with orthophosphate. At the typical low chloride of 3 mg/L Cl⁻, dosing orthophosphate caused the least amount of lead release (40 ppb Pb) amongst all conditions tested. In contrast, the same condition with the simulated brine leak caused 85 times more lead and resulted in the highest lead release of 3,370 ppb Pb. Clearly, changes in the CSMR can produce profound changes in lead leaching even in system with orthophosphate corrosion inhibitor, consistent with practical data gathered by Edwards et al (2007).

Effect of desalination (Utility 6). Blending desalinated water with the current distribution water clearly increased lead release from the solder coupons. The current distribution water with no desalinated water had relatively low lead of 20 ppb, but the blend with 75% desalinated or nanofiltered water exhibited high lead levels of 1,300 ppb Pb, which is an increase of 65 times. Even a blend with 25% nanofiltered water increased the amount of lead in

the water by 16 times compared to the current distribution water (Figure 2-5). These results were consistent with trends observed by Tang et al (2009) and Taylor et al (2004).

The increased corrosivity of the nanofiltered water was consistent with expectations based on the high CSMR and the lower alkalinity of the water compared to the current distribution water (groundwater) (Table 2-1). To isolate the effects of chloride and sulfate, when the current distribution water was dosed with enough chloride to equal the chloride concentration in the 75% desalinated water (Table 2-5), the lead concentration was increased 3 times (Figure 2-6). When the 75% desalinated water was dosed with sulfate to match the current distribution water (Table 2-5), the lead released was decreased 2.3 times (Figure 2-6). Thus, while it is possible that the higher alkalinity of the current distribution water also played a key role in its reduced corrosivity relative to lead leaching, the change in chloride and sulfate of the water was the key concern.

CONCLUSIONS

- A simple bench scale test was developed that could rapidly screen for significant changes in lead leaching from various water treatment changes. In the cases where field data on relationships between coagulant changes and 90th percentile or other lead leaching data were available, the short-term tendencies from the bench scale tests were in qualitative agreement with practical utility experiences and longer-term test results.
- In every water tested, increasing the CSMR in the range of 0.1 to 1.0 increased lead leaching from galvanic lead solder:copper coupons. If the CSMR was over the range of

about 1.0, increasing the CSMR further had little adverse effect, although lead leaching to water was generally very high.

- The CSMR can increase from the following changes: (1) switching from a sulfate-based coagulant to a chloride-based coagulant, (2) implementing anion exchange treatment, (3) use of desalinated water, and (4) a brine leak from an on-site hypochlorite generator. Changes (1) and (2) increase the chloride in water while reducing the amount of sulfate added to the water, (3) decreases sulfate more so than chloride, while (4) adds chloride to the water.
- For Utility 1, the best coagulant to use in terms of lead leaching from solder was ferric sulfate. Use of ferric chloride coagulant and the ferric sulfate/aluminum chlorohydrate blend created significant problems with lead release.
- Coagulating with ferric sulfate resulted in the lowest lead leaching for Utility 2. The addition of ferric chloride in a coagulant blend resulted in significant increase in lead leaching.
- Utility 3 can potentially use some PACl, blended with alum, without causing a significant increase in lead corrosion of solder.
- Using anion exchange treatment, even in conjunction with a sulfate-based coagulant, increased the CSMR and lead release significantly for Utility 2.
- The lead issues reported in the community served by Utility 4 were consistent with expectations based on bench tests due to the increase in CSMR, and were exacerbated by a very low pH due to frequent regeneration of the resin.
- The higher lead experienced at Utility 5 was consistent with expectations based on results of bench tests examining impacts of chloride on CSMR.

- Blending desalinated water that has a high CSMR with the currently distributed groundwater of Utility 6 which has a lower CSMR markedly increased lead leaching from solder coupons.

ACKNOWLEDGEMENTS

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Table 2-1. Water quality of raw water or partially treated water from each utility.

Parameter	Water Utility						
	1, NC	2, NC	3, NC	4, ME	5, TN	6 Current, CA	6 Desalinated, CA
Typical pH	7.3	8.0	7.7	7.0	7.3	8.2	8.2
Alkalinity (mg/L as CaCO ₃)	40	35	25	12	8	125	25
Chloride (mg/L Cl)	14	9	12	4.4	10	50	87
Sulfate (mg/L SO ₄)	9	13	16	4.1	2	68	0.85
Nitrate (mg/L N)	<i>BD</i>	<i>BD</i>	0.44	0.08	<i>BD</i>	0.12	<i>BD</i>
Phosphate (mg/L P)	0.35	0.1	0.041	<i>BD</i>	<i>BD</i>	0.001	<i>BD</i>
Sodium (mg/L)	12	28	12	2.4	7.1	67	68
Calcium (mg/L)	5.4	6.2	9.3	8.6	2	29	0.015
Magnesium (mg/L)	2.1	2.5	3.7	0.4	0.63	6.9	0.018
Silica (mg/L)	5.5	0.8	3.8	5.2	2.2	6.6	0.077

BD = Below Detection

Table 2-2. Target corrosion inhibitor doses, pH, and disinfectant concentrations.

Utility	Target pH	Corrosion inhibitor (Dose)	Disinfectant (Dose)	Other Treatment
1, NC	7.3	Orthophosphate (1 mg/L P)	Free Chlorine (2.5 mg/L Cl ₂)	--
2, NC	8.0	None	Chloramines (3.5 mg/L Cl ₂)	Fluoride (0.9 mg/L F)
3, NC	7.7	Orthophosphate (1 mg/L P)	Chloramines (3.5 mg/L Cl ₂)	--
4, ME	7.0 or 5.5	None	None	--
5, TN	7.3	None	Free Chlorine (2 mg/L Cl ₂)	--
6, CA	8.2	None	Chloramines (3.5 mg/L Cl ₂)	Desalinated water dosed with 40 mg/L as CaCO ₃

Table 2-3. Finished water chloride and sulfate after coagulation.

Utility	Coagulant	Chloride (mg/L Cl)	Sulfate (mg/L SO ₄ ²⁻)	CSMR*
1, NC	Alum	14	32	0.4
	Ferric chloride	28	9	3.0
	Ferric sulfate / aluminum chlorohydrate blend	18	10	1.8
	Ferric sulfate	13	30	0.4
	Ferric sulfate polymer blend	14	32	0.4
2, NC	Ferric chloride	55	12	4.5
	Ferric sulfate	15	72	0.2
	Ferric chloride + AE**	52	4	13
	Ferric sulfate + AE**	31	22	1.4
	Ferric chloride/ Ferric sulfate blend	22	64	0.4
		40	37	1.1
3, NC	100% Alum	16	40	0.4
	100% PACl***	22	12	1.8
	Alum and PACl*** Blend	21	30	0.7
		22	24	0.9
		23	18	1.3

*Chloride-to-sulfate mass ratio (CSMR)

** Anion Exchange (AE)

*** Polyaluminum chloride (PACl)

Table 2-4. Summary of water quality for Utility 4.

Condition	Arsenic ($\mu\text{L As}$)	Chloride (mg/L Cl)	Sulfate (mg/L SO_4^{2-})	CSMR*
No anion exchange	4.5	4.4	4.1	1.1
Anion exchange treatment, pH 7.0	1.8	13.2	1.7	7.8
Anion exchange treatment, pH 5.5	1.8	13.2	1.7	7.8

* Chloride-to-sulfate mass ratio (CSMR)

Table 2-5. Summary of finished water quality for Utility 6.

Blend	Chloride (mg/L Cl ⁻)	Sulfate (mg/L SO ₄ ²⁻)	CSMR*	Alkalinity (mg/L CaCO ₃)
100% Distribution	54	66	0.8	125
25% Desalinated: 75% Distribution	62	50	1.2	104
50% Desalinated: 50% Distribution	71	35	2.0	83
75% Desalinated: 25% Distribution	81	18	4.5	61
100% Distribution + Cl	76	69	1.1	125
75% Desalinated: 25% Distribution + SO ₄	75	70	1.1	61

* Chloride-to-sulfate mass ratio (CSMR)



Experimental Setup: 50:50 Lead: Tin solder inside a copper coupling exposed to 100 mL of water in a glass container.

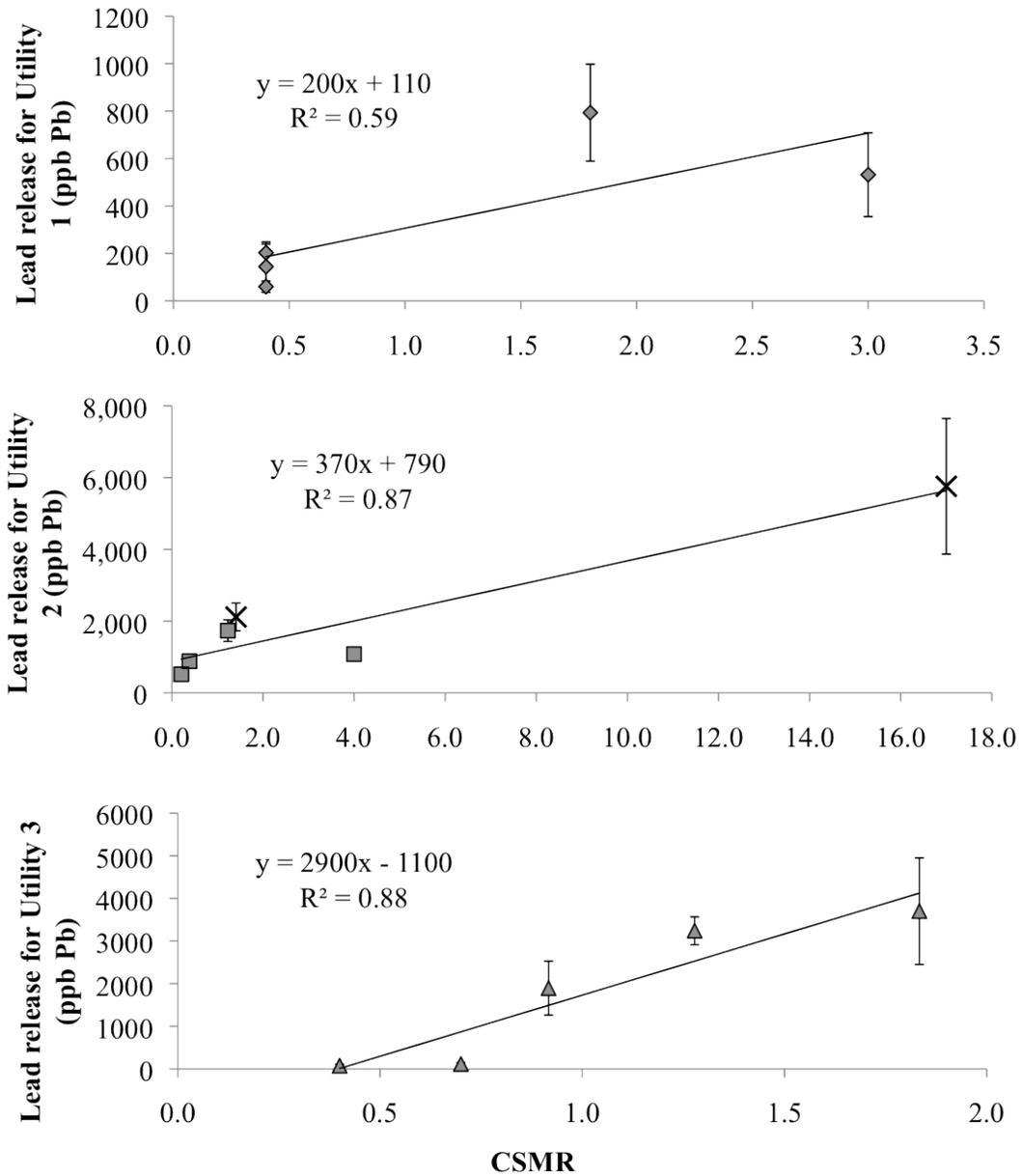


Figure 2-1. Lead release as a function of the chloride-to-sulfate mass ratio (CSMR) for waters treated with coagulation. Diamonds represent Utility 1; boxes represent Utility 2 with coagulation, X's represent Utility 2 with anion exchange and coagulation; triangles represent Utility 3. Error bars represent 95% confidence intervals. Results are the averages of triplicates for each water condition during Week 5 for Utility 1, Week 7 for Utility 2, and Week 9 for Utility 3.

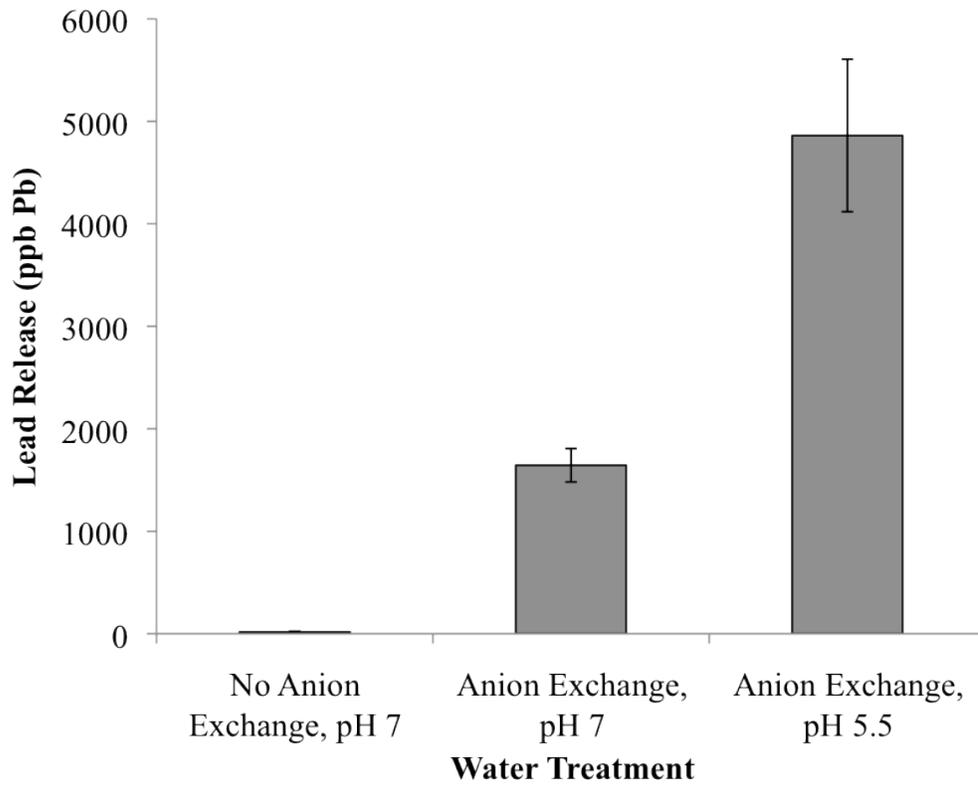


Figure 2-2. Effects of anion exchange and pH reduction on lead release for Utility 4. Results are shown from Week 6 of the study. Error bars represent 95% confidence intervals.

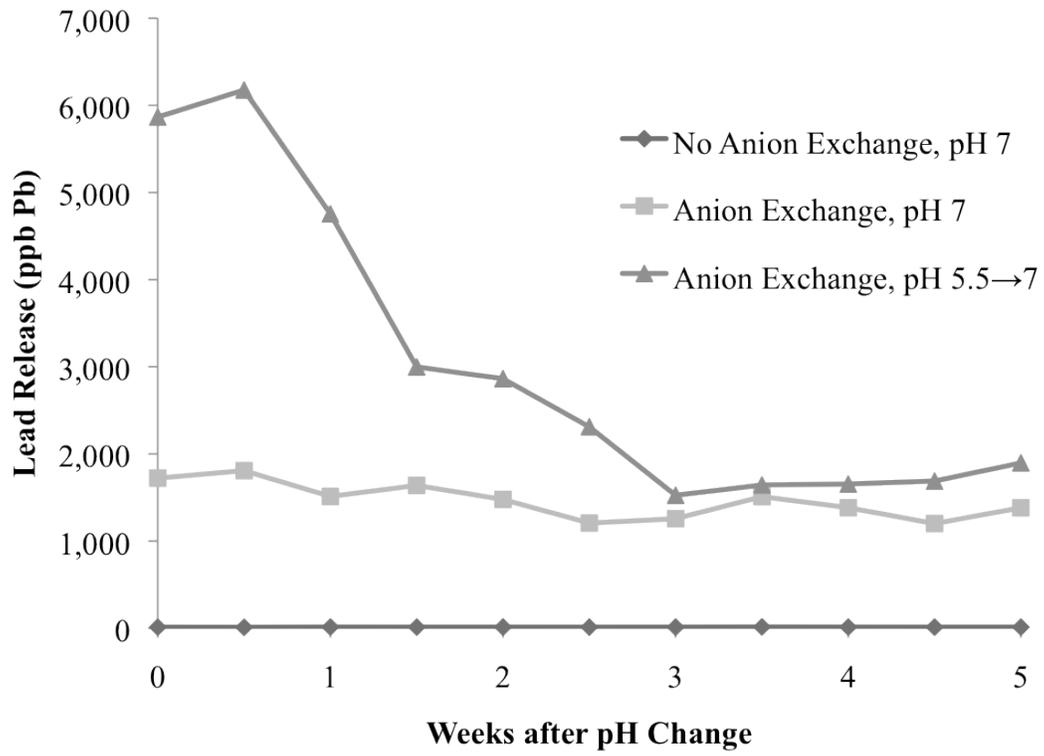


Figure 2-3. Effect of increasing pH from 5.5 to 7.0 with anion exchange treatment for Utility 4.

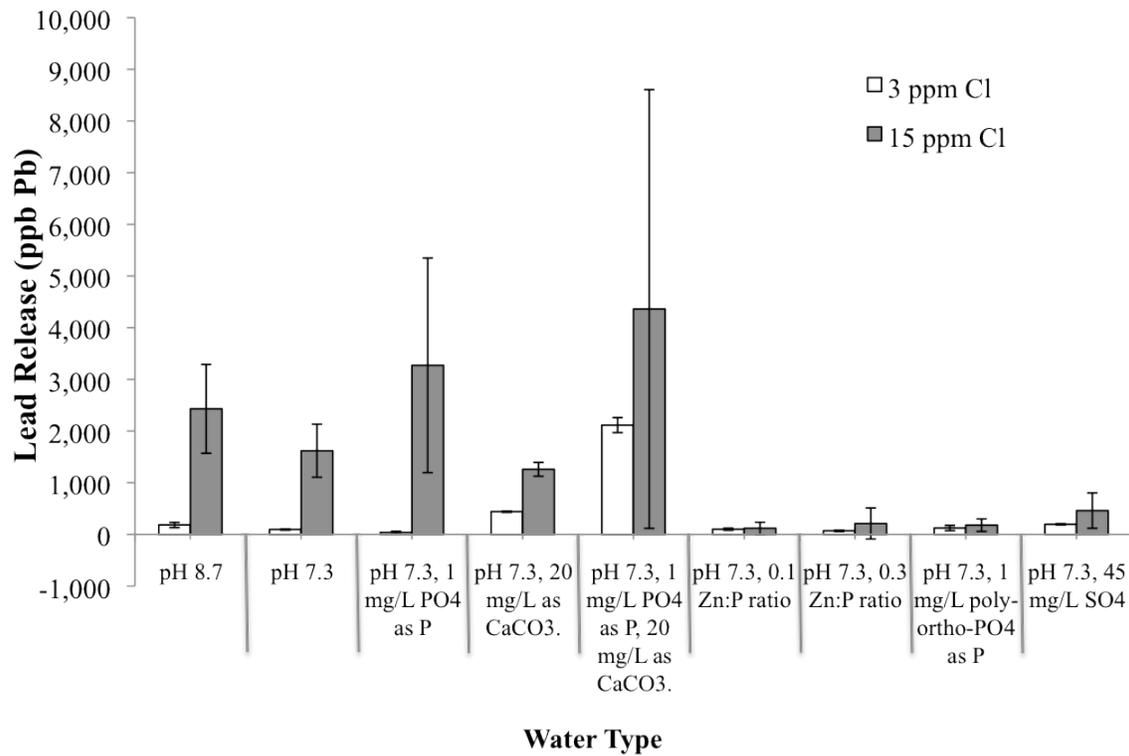


Figure 2-4. Effect of simulated brine leak on lead release from galvanic lead solder for Utility 5. Results are shown as an average of three weeks prior to (weeks 9-11) chloride increase and the average of the final three weeks of the study (weeks 18-20). Chloride was increased at Week 12. Error bars represent 95% confidence intervals.

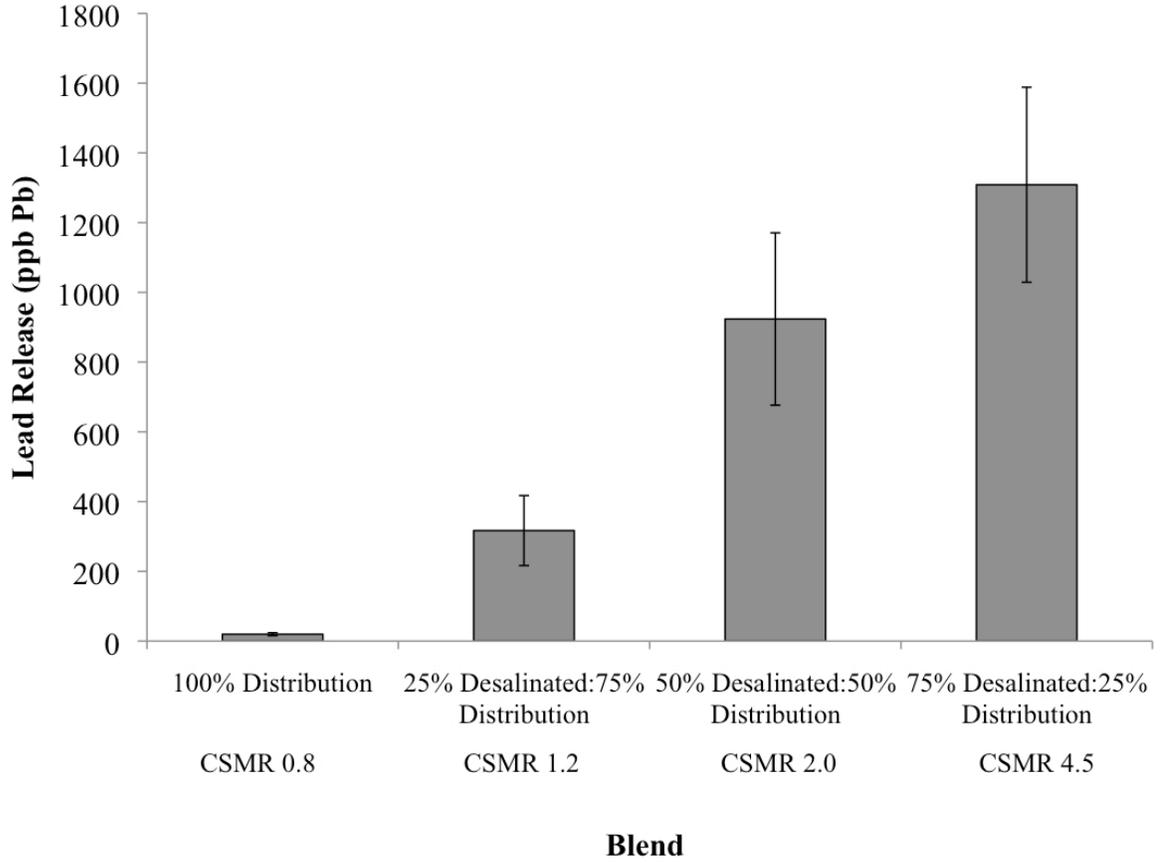


Figure 2-5. Effect of desalinated water on lead release for Utility 6. Results are shown from week 8 of the study. Error bars represent 95% confidence intervals.

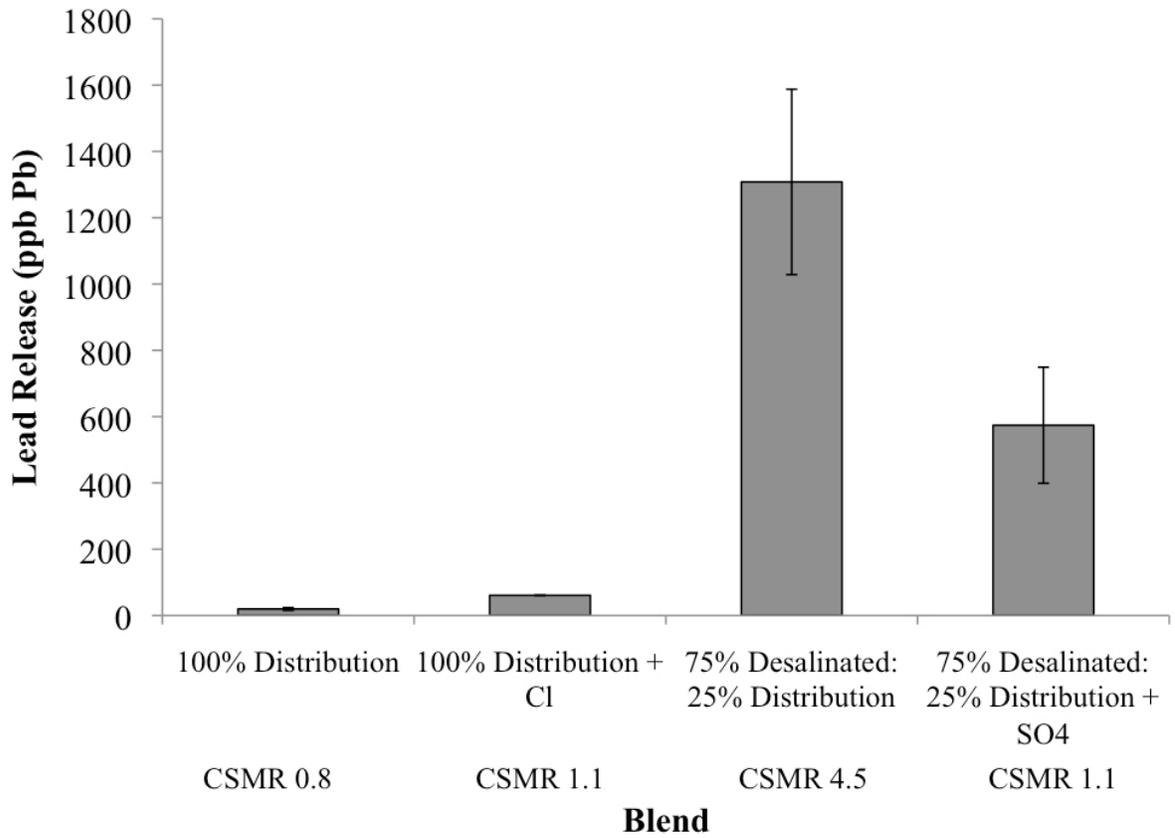


Figure 2-6. Comparison of lead release in 100% existing distribution water with and without the addition of chloride, and 25% existing distribution, 75% desalinated water with and without the addition of sulfate. Results are shown from week 8 of the study. Error bars represent 95% confidence intervals.

CHAPTER 3: Nitrate-induced corrosion of lead-bearing solder

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ABSTRACT. Increasing nitrate in the range of 0 to 10 mg/L NO₃-N, could dramatically increase lead leaching from simulated soldered pipe joints. Although higher nitrate slightly increased the galvanic current, the main factor affecting lead release appears to be initiation of non-uniform corrosion, with small pieces of solder detaching into the water. Under some circumstances, the decay of chloramine after it leaves the treatment plant, and formation of nitrate via nitrification, can markedly increase corrosivity of distributed water to lead solder.

INTRODUCTION

Nitrate levels in drinking water are increasing in some areas of the country due to fertilizer run-off, release of other nitrogen containing compounds from industry, and nitrification in chloraminated systems (Schlesinger et al, 2006; USGS, 1996; Zhang et al, 2009b). The U.S. Environmental Protection Agency (US EPA) has established a maximum contaminant level (MCL) of 10 mg/L NO₃-N in drinking water due to concern over adverse health effects (USEPA, 2004; Manassaram et al, 2006). While most waters from public sources contain less than 0.1 mg/L NO₃-N, exceedances of the nitrate MCL are not uncommon and may be increasing (USGS 1999, 2007).

It is commonly believed that nitrate generally has little or no effect on corrosion of pure lead pipe or lead solder (AwwaRF, 1996). However, studies of galvanic corrosion due to lead solder:copper pipe noted that voltage was very unstable in waters with higher levels of nitrate (Gregory, 1985). Although Gregory did not measure effects of nitrate on metals release, follow-up research by Dudi noted a significant increase in lead release from leaded brass when 10 mg/L $\text{NO}_3\text{-N}$ was dosed (2004). There have also been reports of increased lead leaching after nitrifying bacteria reduced pH and converted ammonia to nitrate (Garrett, 1891; Douglas et al, 2004; Murphy et al, 1997; Zhang et al, 2009b). However, Zhang et al determined that for pure lead pipe the adverse effects were mostly attributable to the reduced pH and not due to creation of nitrate from ammonia (2009a).

Research on lead corrosion in waters with relatively high pH and nitrate concentrations determined that nitrate contributed to breakdown of passivating scale and created non-uniform corrosion. Rehim et al (1998) and Amin et al (2004) noted that increasing nitrate concentrations (0.00 to 3,360 mg/L $\text{NO}_3\text{-N}$) increased current density in electrochemical cells with lead anodes. Authors also observed that pitting corrosion on lead surfaces increased with higher nitrate levels (Rehim et al, 1998; Amin et al, 2004), and that alkalinity and phosphate can mitigate pitting to some extent (Amin et al, 2004; El-Naggarr et al, 2004).

In light of the observations regarding potentially adverse impacts of nitrate on aspects of lead corrosion, this work was aimed at: 1) determining if changes in nitrate in the range commonly encountered in potable water (0-10 mg/L N) could adversely affect lead corrosion, as manifested by increased lead contamination; and 2) isolating possible abiotic impacts of nitrification on lead leaching from soldered joints in systems practicing chloramination. Because Zhang et al (2009a) confirmed the conventional wisdom that slight changes in nitrate (0-2 mg/L N) had little or no effect on lead leaching from lead pipe alone, potential impacts on galvanic corrosion of lead solder:copper joints was a focus of this research.

MATERIALS AND METHODS

Experimental apparatus. Two types of bench scale apparatus were used to quantify impacts of nitrate. The first was a simulated copper pipe joint macrocell, capable of quantifying the impact of nitrate on galvanic corrosion between copper and 50:50 lead:tin solder. The macrocell was constructed with 50:50 lead:tin solder wire and copper pipes (Figure 3-1). The copper cathode and the lead solder anode were connected electrically via an external wire that allowed quantification of galvanic corrosion voltages and currents as per ASTM Standard G71. Each piece of 50:50 lead-tin solder wire had a wetted surface area of 6.44 cm², and the total copper pipe surface area was approximately 219 cm² (cathode:anode ratio of approximately 34:1). The macrocell apparatus was oriented vertically during testing with the lead solder anode at the bottom portion of the apparatus.

The second apparatus was a galvanic lead solder:copper coupon, created by melting a 1” length of 3-mm diameter 50:50 Pb:Sn solder to a 1” length of ½” diameter copper pipe coupling (Figure 3-2). The approximate copper cathode to lead solder anode wetted surface area was 7.3:1. The solder coupons were placed in glass containers and exposed to 100 mL of each test water and each condition was tested in triplicate. The water was changed using a static “dump-and-fill” protocol twice per week (Monday and Thursday) to simulate “worst case” 3-day stagnation conditions encountered in school plumbing systems over weekends. Once trends were established using weekly composite samples collected by combining water from each of the triplicate samples, the water from individual replicates was analyzed separately to determine statistical confidence intervals.

Water chemistry and testing sequence. Work was conducted in four phases. Phases 1 and 2 were carried out using macrocells (Figure 3-1), and Phases 3 and 4 were conducted using solder coupons (Figure 3-2). Test water in Phases 1 through 3 had 24 mg/L alkalinity as CaCO₃, 21 ± 1 mg/L Cl⁻, 45 ± 3 mg/L SO₄²⁻, and a chloride-to-sulfate mass ratio (CSMR) of about 0.47 (Table 3-1). Similar water was used in Phase 4, but the levels of chloride varied in the different water conditions as would occur during chloramines decay in a distribution system (Table 3-2). The pH of all conditions was adjusted to 7.7 ± 0.1 by bubbling CO₂, before adding the water to the test cells. If chloramine disinfectant was added, a 4:1 mg Cl₂:mg N ratio was used.

Analytical methods. Samples were acidified with 2% nitric acid for at least 24 hours to dissolve metals, before quantification on an Inductively Coupled Plasma Mass

Spectrometer (ICP-MS) according to Standard Method 3125-B. The pH in the bulk water was measured with an electrode according to Standard Method 4500-H+. Ammonia was measured using a Hach DR 2700 spectrophotometer salicylate method, according to Standard Method 4500-NH₃. Total and free chlorine were measured on a Hach DR 2700 spectrophotometer according to Standard Method 4500-Cl. Nitrate and nitrite were measured using DIONEX, DX-120 ion chromatography, according to Standard Method 4110 (Clesceri et al, 1998).

RESULTS AND DISCUSSION

Effect of nitrate on galvanic corrosion between lead-bearing solder and copper pipes. Waters with 0, 1, 2.5, 5, and 10 mg/L NO₃-N were used in Phase 1 (added as reagent grade NaNO₃), and waters with 0, 1, 2.5 and 10 mg/L NO₃-N were used in Phase 2 (Table 3-1). No disinfectant was added. Conductivity ranged from 172 μS to 311 μS as nitrate increased (Table 3-1). It has been shown that galvanic current can increase with an increasing conductivity (AwwaRF, 1996).

In Phase 1, three macrocell replicates were filled with each of the five test waters in succession, with 15 minutes in between each water change. Current (μA) measurements were taken immediately prior to each water change by disconnecting the solder wire from the copper pipes and inserting an ammeter. The successive water changes and galvanic current measurements were conducted twice, with the second run immediately following the first. The macrocells were exposed to approximately 110 mL of each test water, and water was changed using a static “dump-and-fill” protocol.

In the convention of this work, negative currents between the copper pipes and the lead solder wires in the macrocells indicated that the lead solder was the anode and was being sacrificed while the copper pipe was the cathode and was being protected. The magnitude of the current increased from approximately 20 μA to 35 μA when the nitrate concentration increased from 0 to 10 mg/L $\text{NO}_3\text{-N}$ (Figure 3-3). This doubling in the amount of current between the lead solder and copper could be due to the higher nitrate or it could be due to the concurrent doubling in the conductivity. A two-tailed t-test confirmed the relationship between higher nitrate (higher conductivity) and the higher galvanic current with greater than 95% confidence.

In Phase 2, four macrocells were exposed to each of the four waters (0, 1, 2.5, and 10 mg/L $\text{NO}_3\text{-N}$) in triplicate for a period of 10 days. The water was changed three times (every 3 or 4 days) using the “dump-and-fill” method. Triplicate samples were collected, and each sample was analyzed for lead. The lead released from lead solder increased nearly 2 times from 1,100 ppb Pb to 2,100 ppb Pb when nitrate increased from 0 to 10 mg/L as N (Figure 3-4).

After examining the mechanistic impacts of higher nitrate on aspects of galvanic corrosion using separated lead anode and copper cathodes in the macrocells, potential adverse effects of nitrate on lead contamination of potable water were quantified using more realistic simulations of lead solder:copper joints using solder coupons (Figure 3-2).

Effect of nitrate on lead release from galvanic lead solder:copper coupons.

Phase 3 tested whether increasing nitrate from 0 mg/L to 10 mg/L NO₃-N increased lead release from solder coupons (Figure 3-2). Waters with 0, 1, 2.5, 5, and 10 mg/L NO₃-N were used to represent the range typically found in drinking water (Table 3-1). Water was disinfected with chloramines (3.5 mg/L as Cl₂). Although essential trace nutrients for nitrification were not added to the waters (Zhang et al, 2009a), to confirm that nitrification or other redox reactions were not occurring, a nitrogen mass balance (i.e., nitrate, nitrite, and ammonia) were measured before and after a 4-day stagnation period. There were no significant changes in nitrite, total ammonia or nitrate during the tests after accounting for trace residual nitrate from glassware due to nitric acid washing.

Increasing nitrate from 0 to 10 mg/L NO₃-N dramatically increased lead leaching from solder coupons. The condition with 0 mg/L NO₃-N had the lowest lead release with 18 ppb Pb (Figure 3-5). When the nitrate level was increased from 0 to 1 mg/L NO₃-N, lead release to the water increased by 2 times to 29 ppb Pb, and further increases in nitrate to 2.5 mg/L NO₃-N increased lead to 3,500 ppb Pb. Impacts of nitrate asymptoted somewhat above this level, but higher nitrate still increased lead leaching. T-tests confirmed that the highest three nitrate conditions (2.5, 5, and 10 mg/L NO₃-N) released significantly more lead (with greater than 95% confidence) than the lower two nitrate conditions (0 and 1 mg/L NO₃-N).

Visually, the coupons exposed to 10 mg/L NO₃-N in Phase 3 were corroded to a much greater extent than coupons without nitrate (Figure 3-6). In fact, the water with

more nitrate caused pieces of the lead solder to peel away from the surface of the copper coupon, and the surface of the solder became non-uniformly corroded. In some cases, pieces of metallic solder detached from the solder coupon into the water. The measurements of lead in water confirmed the visual observations of aggressive attack on the lead solder.

Clearly, the impacts of nitrate in the longer-term testing with solder coupons were dramatically worse than observed in testing with the macrocells. Specifically, addition of 2.5 mg/L nitrate with the solder coupons increased lead leaching by 8.6 times after two weeks versus the control without nitrate (nearly 200 times after six weeks) (Figure 3-5), whereas the same change in the macrocell test had a less significant effect on galvanic currents and lead leaching, with only a 1.7 times increase (Figure 3-4). Impacts of nitrate appear to be attributable to a highly localized attack on the lead solder, causing pieces of solder to fall into the water. This is illustrated by the lead in water measurements that increased significantly, although relatively slight increases in galvanic current due to the nitrate (or concomitant increase in conductivity) were observed in the macrocell arrangement. Other possible explanations for the discrepancy include 1) melting of the solder in the solder coupon versus using Pb/Sn solder wire in the macrocell, and 2) larger physical distance between the lead solder wire and the copper pipe cathode in the macrocell ($\frac{1}{2}$ cm path length through water) compared to the solder coupon (direct connection of 0 cm). In any case, results suggest that in a potable water system, the nitrate effect could be severe.

Effect of disinfectants and simulated nitrification on lead release from galvanic lead solder:copper coupons. The impacts observed in Figure 3-5 raised serious questions about whether changes in nitrogen speciation occurring in systems using chloramines could impact lead leaching from solder coupons. A series of tests was designed to simulate extreme abiotic changes in nitrogen chemistry that can occur in a distribution system as water leaves a treatment plant and passes through a distribution system. That is, chloramine first decays to chloride and ammonia, followed by conversion of ammonia to nitrite and nitrate (Table 3-3).

Lead release from conditions with less than 2.5 mg/L nitrate. To examine a “worst-case” scenario based on results of Phase 3, where the threshold of corrosiveness occurred with 2.5 mg/L nitrate as N, all waters in Phase 4 were dosed with 1.25 mg/L NO₃-N. If a 4 mg/L dose of chloramine with 1 mg/L NH₃-N and a 4:1 ratio of Cl₂:NH₃-N, if nitrification formed 1 mg/L NO₃-N it was expected the water could become highly corrosive to solder. The six water conditions evaluated in Phase 4 were designed to simulate the extremes that could be encountered in a ground water system with chlorine, chloramines, and various stages of chloramines decay/nitrification, but at constant pH to isolate changes in ammonia speciation (Table 3-2).

The control condition (with 1.25 mg/L NO₃-N) released 110 ppb Pb from the solder coupons (Figure 3-7). Disinfectant dosing of either free chlorine or chloramines significantly decreased lead leaching relative to the control. Specifically, dosing with 1 mg/L free chlorine disinfectant (as Cl₂) decreased lead leaching by about 50%, whereas 4

mg/L chloramines (as Cl₂) decreased lead leaching by about 75% (Figure 3-7). It should be noted that during stagnation, the free chlorine decayed 100% to chloride, whereas the chloramine decayed about 90%.

In the test simulating complete decay of chloramines to Cl⁻ and NH₃, lead leaching increased to about 190 ppb Pb, or 1.7 times higher than the control condition and 7.2 times higher than the chloramine condition. In the condition representing complete conversion of chloramines to nitrate and Cl⁻, lead leaching increased to 520 ppb Pb, which was 4.7 times more lead than the control condition, and 20 times more lead than the chloramine condition (Figure 3-7). Interestingly, the condition simulating complete conversion of chloramine to Cl⁻ and nitrite was similar to the control condition, but was about 3.7 times higher than the chloramine condition (Figure 3-7).

T-tests confirmed all the trends with greater than 95% confidence with Bonferroni correction. The results illustrate that even without accounting for the potentially important impacts of reduced pH due to nitrification (Zhang et al, 2009a), corrosivity of water to solder in chloraminated systems can change markedly as it passes through the distribution system, especially if nitrification occurs with formation of nitrate.

Lead release from conditions with greater than 5 mg/L nitrate. To examine impacts of chloramine decay and nitrification in a system starting with a higher level of nitrate (Table 3-2), nitrate was dosed to a base level of 5 mg/L NO₃-N six weeks into the experiment. Within 1 week, lead leaching increased by 2 to 12 times for all conditions

due to the higher nitrate concentration (Figure 3-5). The previous trends observed at lower levels of nitrate were qualitatively different; for example, the system dosed with chloramines had the highest lead, whereas the condition simulating complete conversion to nitrate had the lowest lead (Figure 3-8). This work reinforces the findings of Dudi (2004), who discovered that nitrate caused very erratic leaching of lead from brass.

CONCLUSIONS

- There was a short-term increase in galvanic current with increased nitrate in the macrocell, which corresponded with a doubling of conductivity and lead leaching.
- Increasing nitrate in water from a low level (between 0 and 1 mg/L NO₃-N) to a high level (2.5 to 10 mg/L NO₃-N) could cause dramatic increases in lead leaching from solder coupons. The impact appeared to be due to non-uniform corrosion, resulting in small pieces of solder detaching onto the water.
- In a water with a low level of nitrate and disinfected with chloramines, changes in nitrogen speciation, representative of chloramine decay and nitrification, could increase corrosivity of the water to lead solder. Addition of chlorine and chloramines decreased lead leaching.
- Qualitatively different impacts were observed if the water initially had a higher level of nitrate.

ACKNOWLEDGMENTS

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Table 3-1. Summary of synthetic water quality used in Phases 1, 2, and 3.

Parameter	Target nitrate (mg/L NO ₃ -N)				
	0	1	2.5	5	10
Actual nitrate (mg/L NO ₃ -N)	0	0.93	2.4	5	11
Chloride (mg/L Cl ⁻)	22	21	21	21	21
Sulfate (mg/L SO ₄ ²⁻)	46	48	43	44	45
CSMR*	0.47	0.44	0.49	0.49	0.47
Alkalinity (mg/L as CaCO ₃)	24	24	24	24	24
Conductivity (μS)	172	177	251	273	314

*Chloride-to-sulfate mass ratio (CSMR).

Table 3-2. Summary of water conditions for Phase 4.

Parameter	Water Condition					
	Control ⁽¹⁾	Free Cl ₂ ⁽²⁾	NH ₂ Cl ⁽³⁾	Cl+NH ₃ ⁽⁴⁾	Cl+NO ₂ ⁻ ⁽⁵⁾	Cl+NO ₃ ⁻ ⁽⁶⁾
Target nitrate (mg/L NO ₃ -N)	1.25	1.25	1.25	1.25	1.25	2.25
Target nitrite (mg/L NO ₂ -N)	0	0	0	0	1	0
Target total chlorine (mg/L Cl ₂)	0	1	4	0	0	0
Target ammonia (mg/L NH ₃ -N)	0	0	1	1	0	0
Chloride prior to disinfectant decay (mg/L Cl)	21	21	21	28	28	28
Sulfate (mg/L SO ₄ ²⁻)	42	41	41	41	40	41
CSMR ⁽⁸⁾	0.50	0.51	0.51	0.68	0.70	0.68
Conductivity (μS)	192	204	223	235	243	241
Conductivity after increase ⁽⁷⁾ (μS)	283	292	311	323	332	332

⁽¹⁾Control water was the 1.25 mg/L NO₃-N from Table 3-1.

⁽²⁾Control water dosed with 1 mg/L chlorine disinfectant.

⁽³⁾Control water dosed with chloramine disinfectant (4 mg/L as Cl₂), 4:1 ratio Cl₂:NH₃-N.

⁽⁴⁾Chloraminated control water after Reaction 1.

⁽⁵⁾Chloraminated control water after Reaction 2, or converted to nitrite after Reactions 1 and 2.

⁽⁶⁾Chloraminated control water after Reaction 3.

⁽⁷⁾After 6 weeks, base-level nitrate was increased from 1.25 mg/L to 5 mg/L NO₃-N.

⁽⁸⁾Chloride-to-sulfate mass ratio (CSMR).

Table 3-3. Nitrate and ammonia values measured before and after a stagnation period during Phase 3. Nitrite values were always below detection (<0.1 mg/L NO₂-N).

Target Nitrate (mg/L NO₃-N)	Nitrate (mg/L NO₃-N)		Ammonia (mg/L NH₃-N)	
	Before	After	Before	After
0	0.00	0.24	0.89	0.82
1	0.93	1.66	0.89	0.80
2.5	2.37	2.58	0.91	0.78
5	4.98	5.59	0.88	0.82
10	10.68	11.03	0.92	0.80

Table 3-4. Summary of reactions and effects of chloramine decay on chloride, nitrate, and nitrite concentrations (Zhang et al, 2009b).

Reaction	Balanced equation	Key Impact
Reaction 1 (Vikesland et al, 1998)	$3\text{NH}_2\text{Cl} \rightarrow \text{N}_2 + \text{NH}_3 + 3\text{Cl}^- + 3\text{H}^+$	Increase in chloride (2 mg/L Cl^- per 1 mg/L Cl_2) and formation of $\text{NH}_3\text{-N}$
Reaction 2 (Grady et al, 1999)	$\text{NH}_4^+ + 1.9\text{O}_2 + 0.069\text{CO}_2 + 0.0172\text{HCO}_3^- \rightarrow 0.0172\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.983\text{NO}_2 + 0.966\text{H}_2\text{O} + 1.97\text{H}^+$	Increase in nitrite (1 mg/L $\text{NO}_2\text{-N}$ per 1 mg/L $\text{NH}_3\text{-N}$)
Reaction 3 (Grady et al, 1999)	$\text{NO}_2 + 0.00875\text{NH}_4^+ + 0.035\text{CO}_2 + 0.00875\text{HCO}_3^- + 0.456\text{O}_2 + 0.00875\text{H}_2\text{O} \rightarrow 0.00875\text{C}_5\text{H}_7\text{O}_2 + \text{NO}_3^-$	Increase in nitrate (1 mg/L $\text{NO}_3\text{-N}$ per 1 mg/L $\text{NO}_2\text{-N}$)

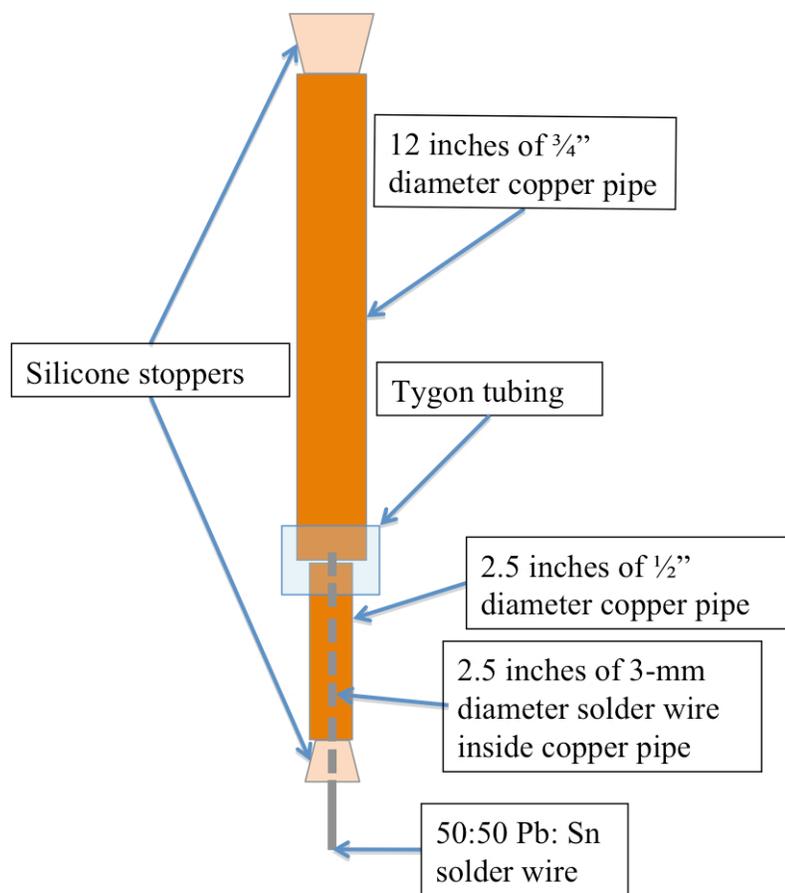


Figure 3-1. Schematic of the macrocell apparatus used in Phases 1 and 2. Solder was externally connected to the copper pipes with copper wire. The apparatus was oriented vertically so that the solder wires were at the bottom and the larger diameter copper pipes were in the upper part of the apparatus.

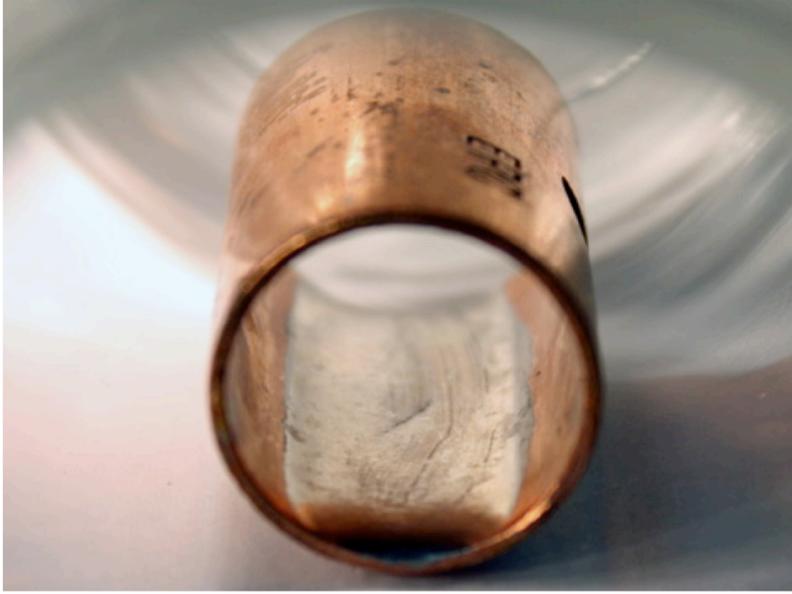


Figure 3-2. An example of the solder coupon apparatus used in Phases 3 and 4.

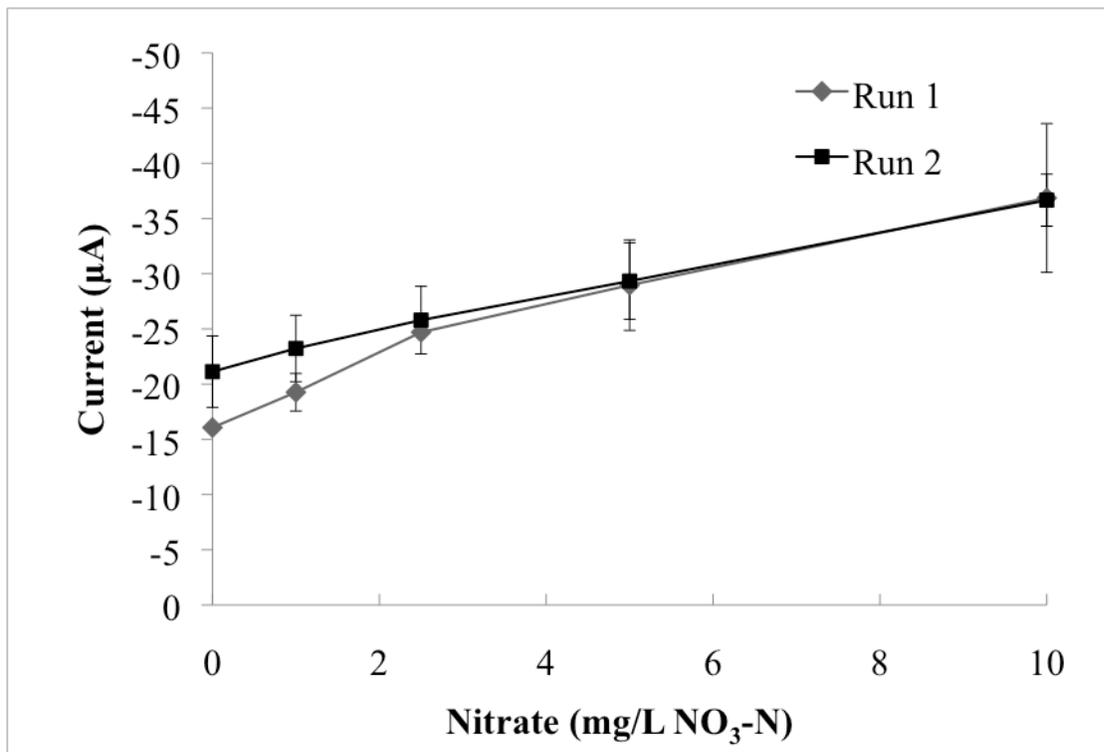


Figure 3-3. Impact of increasing nitrate in macrocells on current (μA) in Phase 1. Error bars represent 95% confidence. Negative currents indicate that lead solder was sacrificed and that copper was protected.

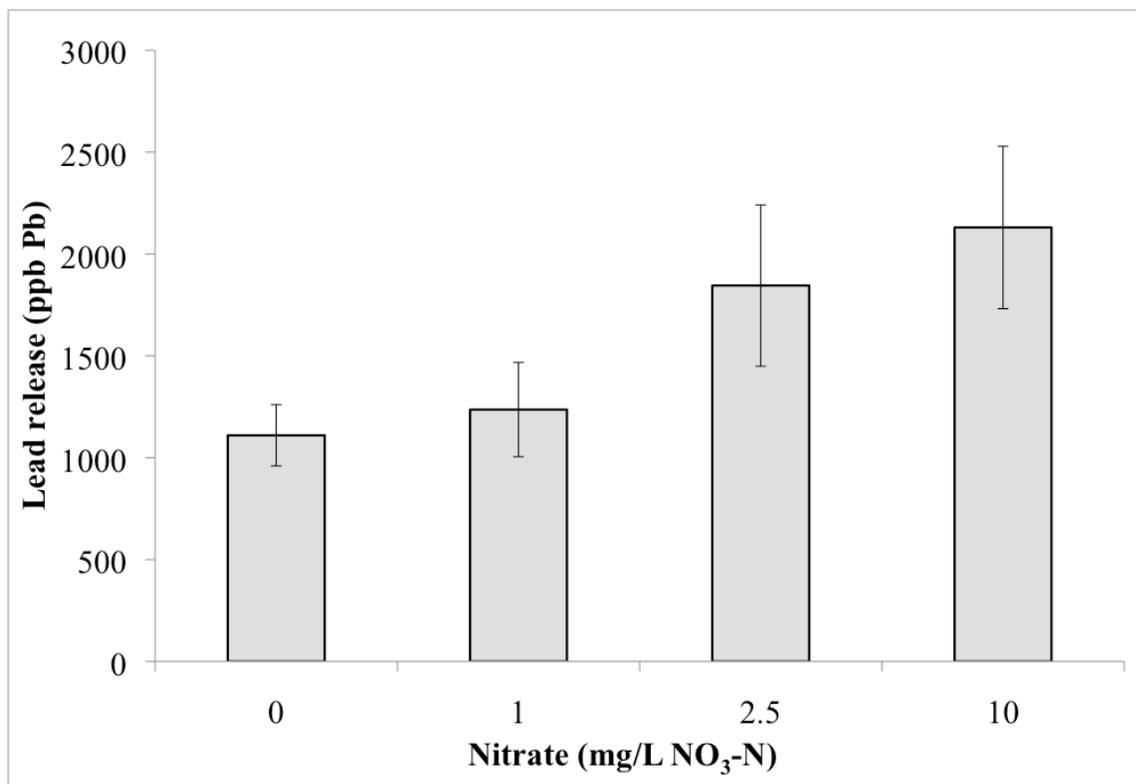


Figure 3-4. Results after 10 days of increasing nitrate concentration on lead release from macrocells in Phase 2. Error bars represent 95% confidence.

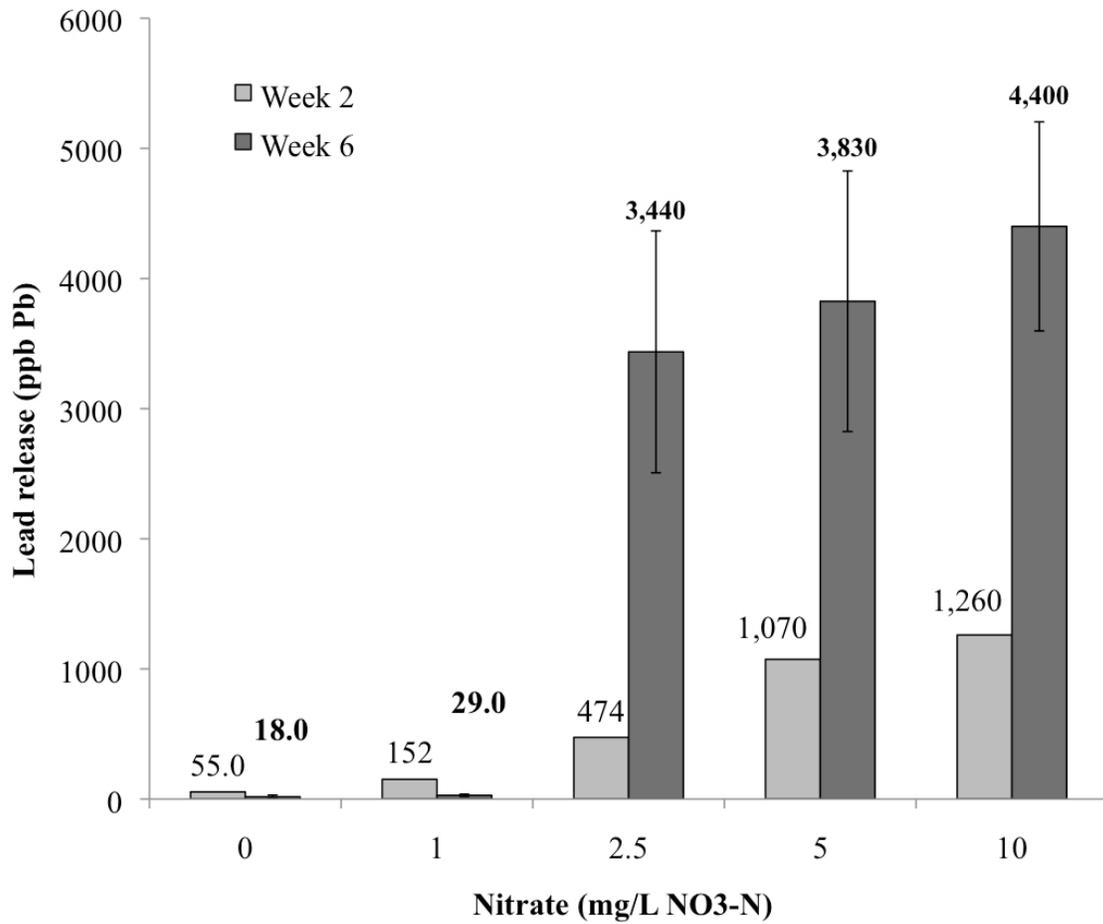


Figure 3-5. Effect of increasing nitrate on lead release from solder coupons in Phase 3. Results are shown from week 2 and week 6 of the study. Error bars for week 6 represent 95% confidence.



Figure 3-6. Galvanic lead solder coupons after 6 weeks of exposure to 0 mg/L NO₃-N (left) and 10 mg/L NO₃-N (right) in Phase 3.

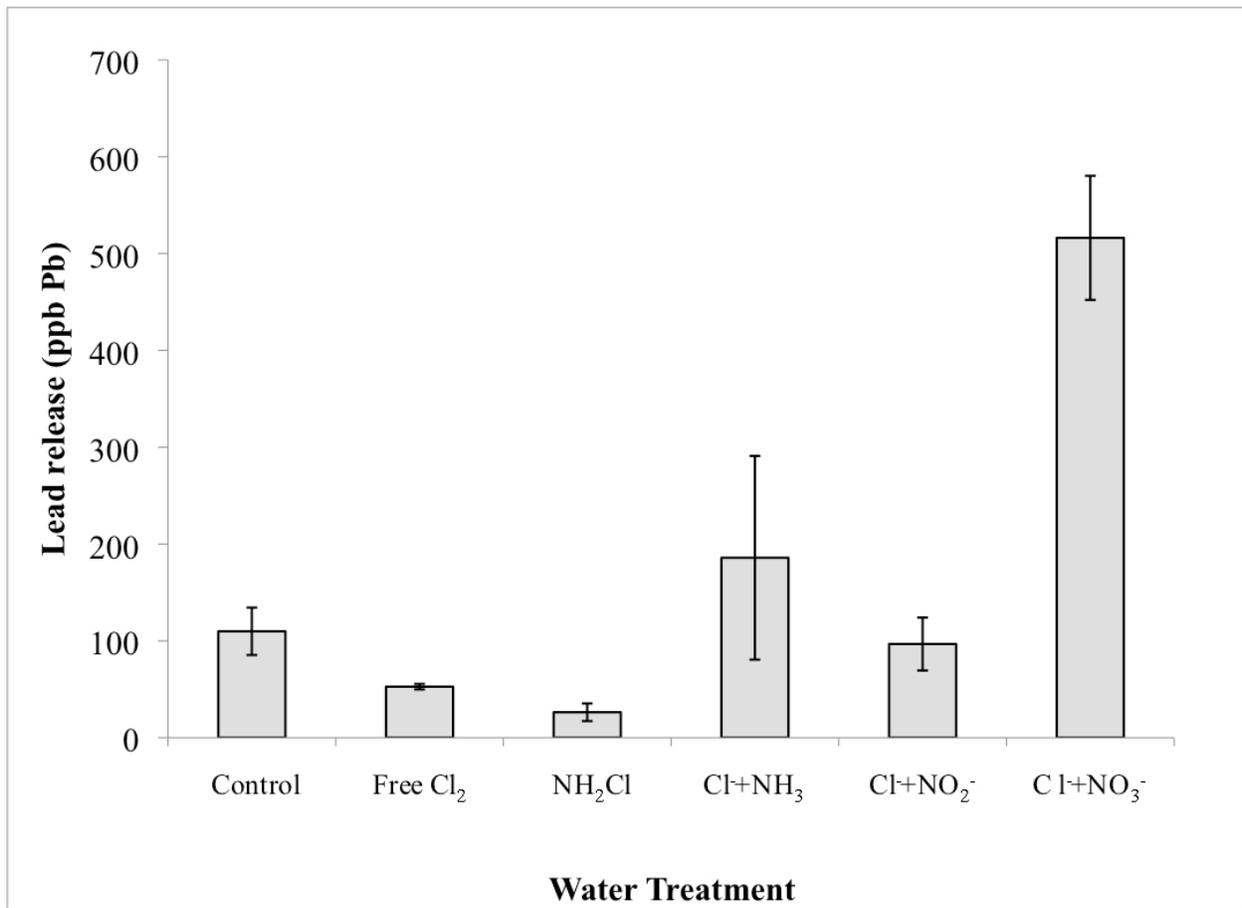


Figure 3-7. The effect of disinfectant decay on lead release from solder coupons in Phase 4. The galvanic lead solder coupons were exposed to test waters in Table 3-2. Error bars represent 95% confidence. Results are shown from week 6 of the study.

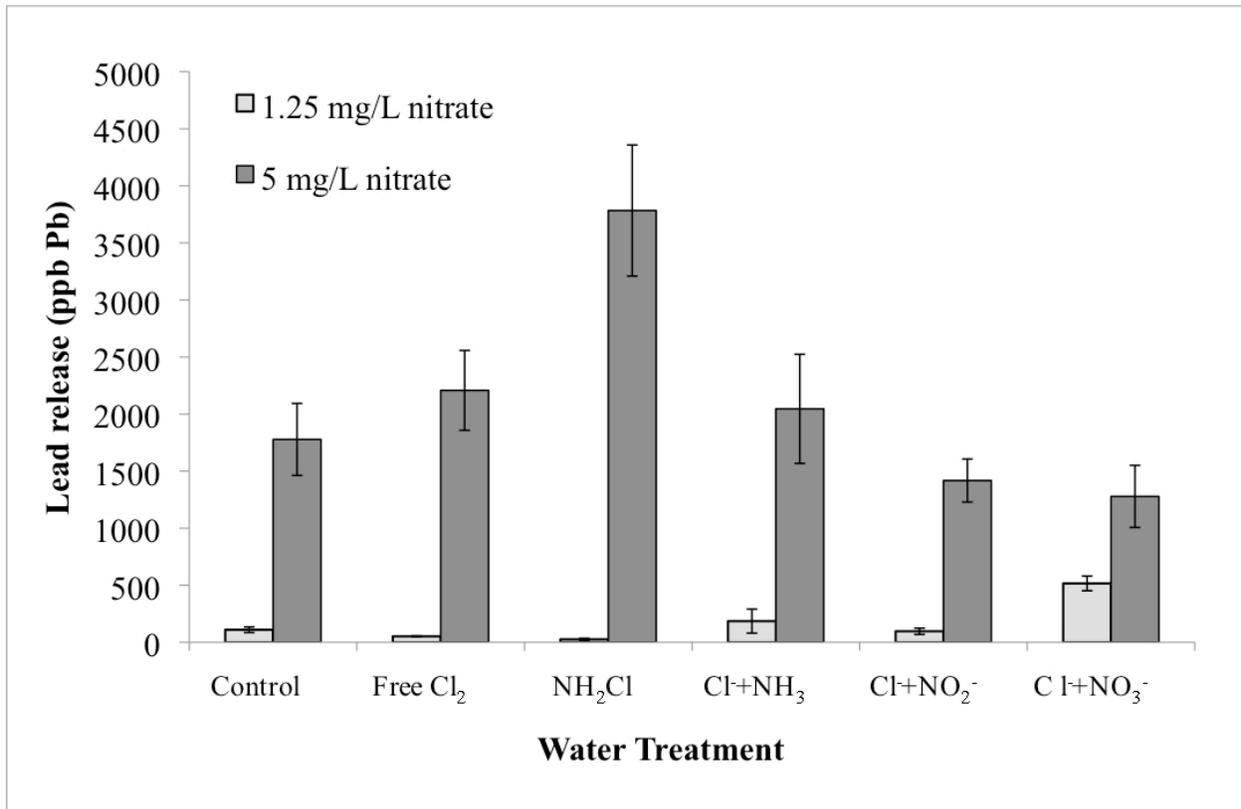


Figure 3-8. The effect of increasing base-level nitrate from 1.25 mg/L to 5 mg/L NO₃-N in Phase 4 on lead release from solder coupons. Error bars represent 95% confidence. Light gray bars show lead release prior to nitrate increase at week 6 of the study, and dark gray show lead release 2 weeks after nitrate increase, at week 8 of the study.

CHAPTER 4: Flushing lead from plumbing after very long stagnation times

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ABSTRACT. When water in pipes in schools is stagnant for long periods such as over summer vacation, it is possible for a large concentration of lead to build up in the system. The impact of chloride-to-sulfate mass ratio (CSMR), stagnation time, and flushing methods on the build-up and removal of lead was tested at the bench scale using 50:50 lead:tin solder coupled with copper pipe. The effect of dissolved oxygen on galvanic corrosion was also examined at low and high CSMR. Higher CSMR significantly increased the build-up of lead in test cells. The best methods to remove the reservoir of lead include high flushing volumes and turbulent flow.

INTRODUCTION

Galvanic Corrosion and Dissolved Oxygen. When 50:50 Pb:Sn solder and copper pipe are connected in water, a galvanic cell develops in which typically the lead solder becomes the anode and is corroded, while copper becomes the cathode and is protected. The galvanic corrosion of lead solder has been linked to lead contamination of potable water (Oliphant, 1983; Gregory, 1985). In the case of lead solder connected to copper, oxygen is reduced in the cathodic reaction, usually at the copper surface (Eq. 1), while lead is typically oxidized in the anodic reaction (Equation B-2). Oxygen drives this oxidation of the lead anode (Dudi, 2004).



Oxygen could react in the cathodic reaction to corrode lead, tin, copper, or a combination, and galvanic corrosion disappears when oxygen is depleted (Jones, 1996). Therefore, the worst-case scenario is a case in which 100% of the dissolved oxygen in a system reacts to corrode lead. When 100% of the oxygen is reacted in the corrosion of lead in a closed system with a saturated dissolved oxygen concentration of 10 mg/L O₂, a reservoir of 130,000 ppb Pb could build up in the water. However, in an open system where water is repeatedly exposed to oxygen, 130,000 ppb Pb could be released to the water for every 10 mg/L of oxygen reacted with lead (Figure 4-1). Consequently, the corrosion could proceed without passivation, indefinitely increasing the lead concentration in the water. One study found that metals corroded at an exponentially increasing rate when exposed to oxygen, only decreasing when oxygen levels fell to less than 1 mg/L O₂ (Lytle et al, 2000).

This is of particular concern in schools because of the extended stagnation times that schools experience. A typical school in the United States is vacant for approximately three months during the summer, about two weeks during the winter, and about a week during both the fall and the spring. These long periods of stagnation allow sufficient time for lead to accumulate in water remaining stagnant in the pipes. An independent sampling study conducted in Washington D.C. schools found that between 2 and 41% of taps sampled contained lead exceeding the United States Environmental Protection Agency (U.S. EPA) lead action level of 15 ppb Pb, with 77% of schools sampled having at least one contaminated tap (Triantafyllidou et al, 2009). Further, authors found that the sampling methods used by the utility, which included a minimum of 50 minutes of flushing the night before sampling, could be making lead in samples lower than the lead in the actual system by flushing out built-up lead out before taking a sample.

Galvanic Corrosion and CSMR. Elevated CSMR has been linked to increased galvanic corrosion of lead and higher lead in water (Gregory, 1985; Oliphant, 1983; Dodrill et al, 1995; Edwards et al, 2007). The CSMR is expressed as a ratio of mg/L Cl⁻ to mg/L SO₄²⁻. For example, in a water with 10 mg/L Cl⁻ and 20 mg/L SO₄²⁻, the CSMR is 0.5.

When the CSMR is low, galvanic corrosion of lead decreases (Oliphant, 1983; Gregory, 1985) and sulfate in the water can react with lead to form precipitates that passivate the anode even at low pH (Guo, 1992; Sato, 1996). Thus, after a long stagnation time, it is feasible that the lead reservoir would not increase indefinitely but could eventually level off due to the passivation of the lead surface. At the other extreme, when the CSMR is high, chloride continues to drive galvanic corrosion and forms soluble complexes with lead that can allow lead to continue to corrode (Sato, 1996). If oxygen continues to be present, lead could continue to dissolve indefinitely in the system.

The purpose of this research was to illustrate how lead accumulates during long stagnation periods in both high and low CSMR waters and to examine the effect of different types of flushing on the removal of the accumulated lead.

MATERIALS AND METHODS

Test Water. Water was synthesized for both high CSMR (13) and low CSMR (0.25) to examine the difference between the two waters (Table 4-1). Water was dosed with chloramines to a target level of 2.3 mg/L Cl₂, and pH was adjusted to 7.7±0.1 with CO₂ or NaOH.

Experimental protocol. This experiment was conducted in two phases. Phase 1 was designed to test the effect of long-term stagnation on the corrosion of lead solder connected to copper at high and low CSMR in an open system, and Phase 2 was designed to compare the effect of dissolved oxygen on galvanic current generated between copper pipes and lead or tin wires.

Phase 1. A 1” length of 3-mm diameter 50:50 Pb:Sn solder was placed on the inner edge of a 1” length of ½” diameter copper couplings (Figure 4-2). The galvanic lead solder:copper coupons were exposed to 100 mL of each water. For 14 weeks, 9 the solder coupons were exposed to each of the two water conditions. Two mL aliquots were collected from each test cell every 2 weeks to analyze for lead. After 14 weeks the 9 cells at each CSMR level were divided into groups of 3 to test flushing methods (Table 4-2). Water was changed once per day for one week using a “dump-and-fill” method according to the flushing method (Table 4-2).

This protocol was designed to represent a worst-case scenario in which oxygen was never depleted, and corrosion was allowed to proceed during the entire long stagnation time.

The low volume, no agitation flushing method involved no inversion of the test cell, and then refilling with fresh water (Table 4-1) once using the “dump-and-fill” protocol. This flushing method represented a typical water fountain, which has a flow of 1.3 L/min and low turbulence. The low volume, high agitation method involved vigorous inversion of the test cell, followed by dumping and filling with fresh water one time. This method represented a typical aerated faucet with a relatively low water flow rate of 6.5 L/min. The high water volume method

with no agitation involved no inversion of the test cell, followed by dumping and filling with fresh water ten times to represent higher flow as would occur after the removal of the aerator, increasing flow rate to 8.5 L/min, and high flushing volume at a faucet.

Phase 2. Lead or tin galvanic cells were constructed by placing 2.0-inch lengths of 2-mm diameter pure lead wire, or 1.25-inch lengths of 3.3-mm diameter pure tin wire, and 4.5-inch lengths of 3/4-inch diameter copper pipes in 1-L beakers with high and low CSMR waters. Each lead or tin wire was connected externally with copper wire to a copper pipe, such that an ammeter could be inserted between the lead or tin wires and the copper pipe to measure currents (Figure 4-3). The copper-to-lead wire or copper-to-tin wire surface area ratio was 41:1. The beakers were covered with Parafilm paper, and oxygen was slowly removed from saturation of about 8 mg/L O₂ by bubbling with 99.9% pure nitrogen gas, to the target dissolved oxygen concentrations of 4 mg/L, 2 mg/L, 1 mg/L, 0.5 mg/L, 0.25 mg/L, and close to 0.00 mg/L O₂. Ten minutes after each oxygen level was reached, the lead or tin wires and the copper pipes were disconnected, and an ammeter was inserted to measure the galvanic current between the two metals. This was conducted once at each condition with mild stirring (approximately 60 rpm with a 2-inch stir bar). pH ranged from 7.5 to 8.5, and was adjusted to 7.7 ± 0.2 prior to each dissolved oxygen adjustment.

Analytical Methods. Samples collected in Phase 1 were acidified with 2% nitric acid for at least 24 hours to dissolve metals. The samples were analyzed for metals with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) in accordance with Standard Method 3125-B. The pH in the bulk water was measured with an electrode according to Standard Method 4500-H⁺. Ammonia was measured using a Hach DR 2700 spectrophotometer salicylate method,

according to Standard Method 4500-NH₃. Total and free chlorine were measured on a Hach DR 2700 spectrophotometer according to Standard Method 4500-Cl. Dissolved oxygen was measured using a Hamilton ARC dissolved oxygen sensor with a range of 0.05% to 300% oxygen and a detection limit of 0.01 vol-%.

RESULTS AND DISCUSSION

Effect of Long Stagnation Time. After about 5 weeks of stagnation with exposure to the air, lead leaching from solder to the low CSMR water condition leveled off at about 8,000 ppb lead. Lead release in the high CSMR water never reached an asymptote, even after more than 3 months of stagnation, and reached levels of about 200,000 ppb lead after 15 weeks (Figure 4-2). High CSMR water caused the lead solder-copper galvanic cell to continue to release lead at the same linear rate over time, while the lead solder connected to copper in the low CSMR condition eventually passivated

Effect of Flushing Methods. In the low CSMR conditions, there was relatively little lead stuck to the container and the coupons compared to the high CSMR condition. As a result, flushing water through the test coupons removed most of was released into the water over the 15-week stagnation. Thus, the most effective method of removing the accumulated lead was by high volume flushing. After 2 water changes (1,000 mL of water flushed at each water change), the lead reservoir remaining in the test cells was approximately 95 µg Pb, compared to 150 µg and 210 µg at the low volume flushed conditions (100 mL of water flushed at each water change) (Figure 4-5).

The cumulative lead released from each of the three flushing conditions confirmed that the high flushing volume condition removed the greatest amount of lead from the reservoir. Flushing with a high volume of water removed 3,000 μg of lead after one water change (1,000 mL flushed), compared to 1,100 μg and 1,900 μg at the low flushing volume conditions (100 mL flushed) (Figure 4-6). The most effective method of removing lead that accumulated in the system with low CSMR water was by flushing a large volume of water from the test coupons.

In the high CSMR water conditions, much more lead was visible on the glass container, as well as on the coupons themselves. Removal of the oxidized lead required either high flushing or agitation of the coupons. The more effective methods of removing the built-up lead were the high agitation condition (100 mL flushed at each water change, and inversion of the test cells) and the high flow condition (1,000 mL flushed at each water change, and no inversion of the test cells). After two water changes, the high agitation and high flow conditions contained 2,100 μg and 1,600 μg of lead respectively, an order of magnitude below the low flow, low agitation condition, which still contained 10,100 μg of lead (Figure 4-7).

A plateau of cumulative lead release was reached after only one water change for both the high agitation and high flow conditions, while the low flow, low agitation condition required 4 water changes to level off (Figure 4-8). This indicates that the low water volume, low agitation condition did not remove lead as effectively or quickly as either high volume or high agitation. The best method of lead removal is a combination of high volume flushing (long flushing time) and turbulent flow.

Effect of Dissolved Oxygen. Consistent with theory, the galvanic current between copper and the lead or tin wires decreased as the dissolved oxygen concentration was decreased by bubbling nitrogen gas (Figure 4-9). Furthermore, consistent with findings by Oliphant (1983) and Gregory (1985), high CSMR water accelerated galvanic corrosion and resulted in higher galvanic currents than low CSMR water. Because lead is more anodic to copper on the galvanic series than tin is to copper, lead wire tended to have higher galvanic currents than tin wire. As expected, the highest current was measured for high CSMR water with high oxygen (8.4 mg/L) and lead wire. The removal of 99.99% of the dissolved oxygen in the water resulted in a 77% reduction in current between lead and copper in high CSMR water, and an 83% reduction in current between tin and copper in high CSMR water. The removal of 99.99% of the dissolved oxygen in the water resulted in a 75% reduction in current between lead and copper in low CSMR water, and 74% reduction in current between tin and copper in low CSMR water. These results show that not all current between the two dissimilar metals disappeared when oxygen was removed, and the remaining current is likely due to the mild stirring in the waters. However, the decrease in current that did occur can be attributed to the decrease in oxygen, indicating that if a system is not exposed to oxygen, corrosion could eventually slow down and possibly passivate.

CONCLUSIONS

- A much larger quantity of lead built up in the test cells at the high CSMR condition compared to the low CSMR condition.
- The best method of removing accumulated lead in the low CSMR condition in this study was by flushing a large volume of water.

- The best method to remove built-up lead from the high CSMR condition was by agitating the solder coupons to remove lead that was stuck to the coupons and glass container.
- The most effective lead reservoir removal strategy would be a combination of a high volume of flushing with a turbulent flow.
- As dissolved oxygen decreased, the galvanic current between the copper pipe and lead or tin wire decreased, slowing galvanic corrosion. However, the depletion of oxygen by lead corrosion potentially causes a release of 130,000 ppb Pb into the system.

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Table 4-1. Water quality of the high and low chloride-to-sulfate mass ratio (CSMR) waters.

Water	Chloride (mg/L Cl⁻)	Sulfate (mg/L SO₄²⁻)	CSMR	Alkalinity (mg/L as CaCO₃)	Conductivity (μS)
Low CSMR	20	80	0.25	10	392
High CSMR	91	7	13	10	304

Table 4-2. Summary of the three flushing methods.

Experimental Flushing Type	Practical Example
Low water volume flushed with no agitation	Water fountain
Low water volume flushed with high agitation	Faucet with aerator; low flushing time
High water volume flushed with low agitation	Faucet without aerator; long flushing time

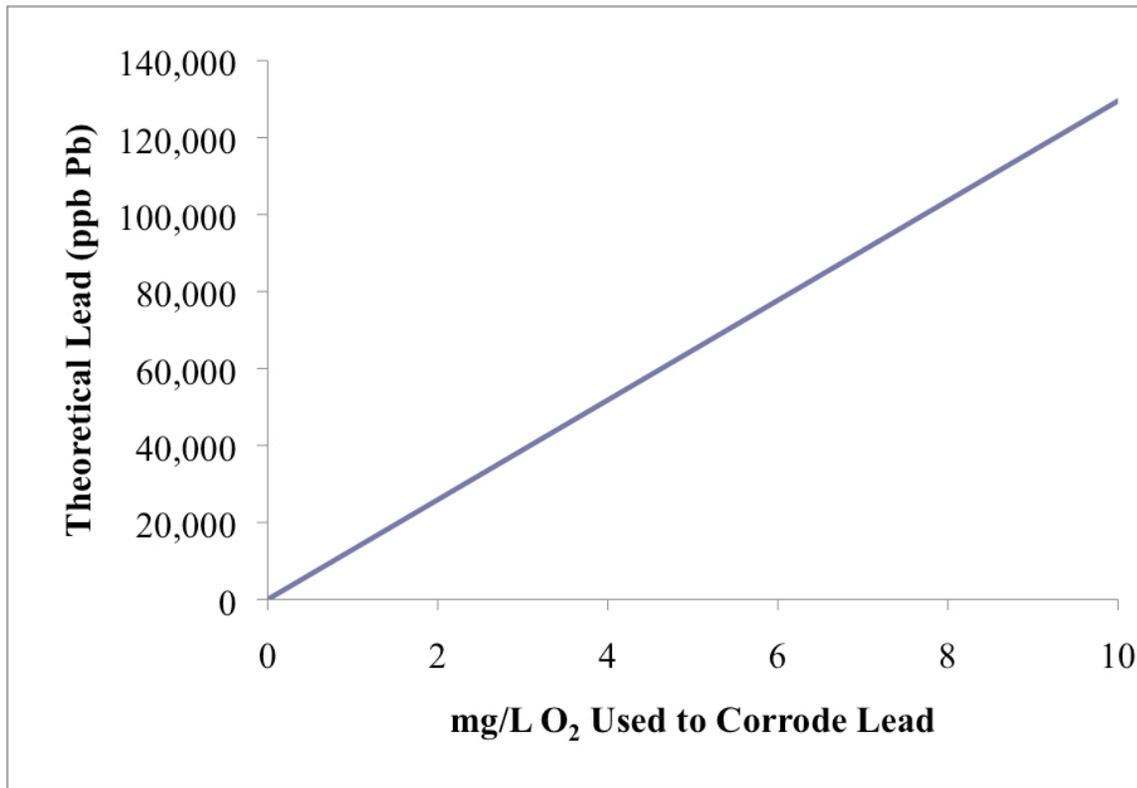


Figure 4-1. Theoretical lead released to the water as a function of percentage of the initial dissolved oxygen concentration (10 mg/L O₂) utilized for galvanic corrosion of lead.



Figure 4-2. Example of a solder coupon prior to exposure to test water in Phase 1.

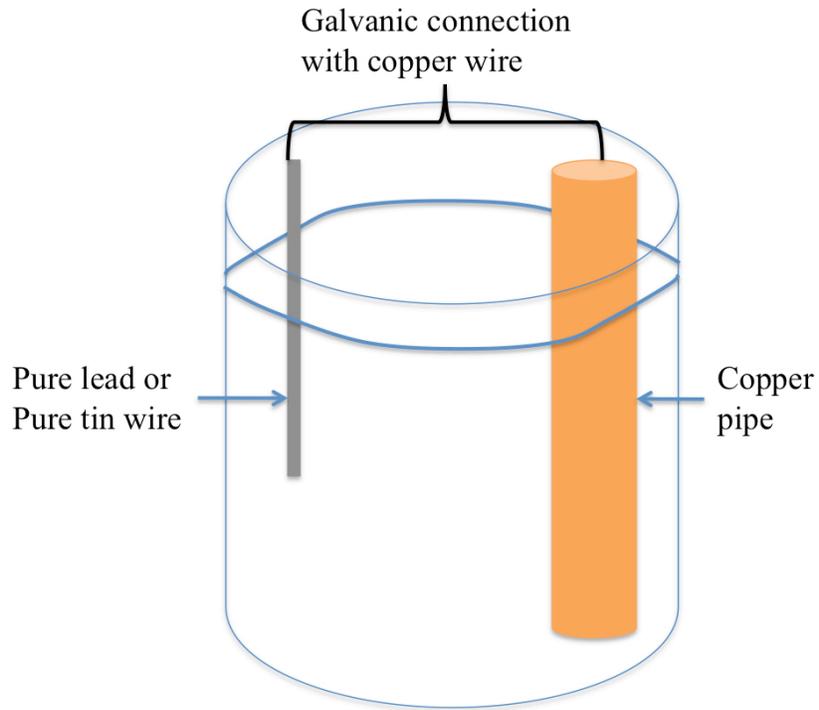


Figure 4-3. Galvanic cell schematic for phase 2. 2.0 inches of 3-mm pure tin wire or 2.25 inches of 3.3-mm pure lead wire was exposed to test water. 4.5 inches of $\frac{3}{4}$ -inch copper pipe was submerged. Container was stirred at 60 rpm.

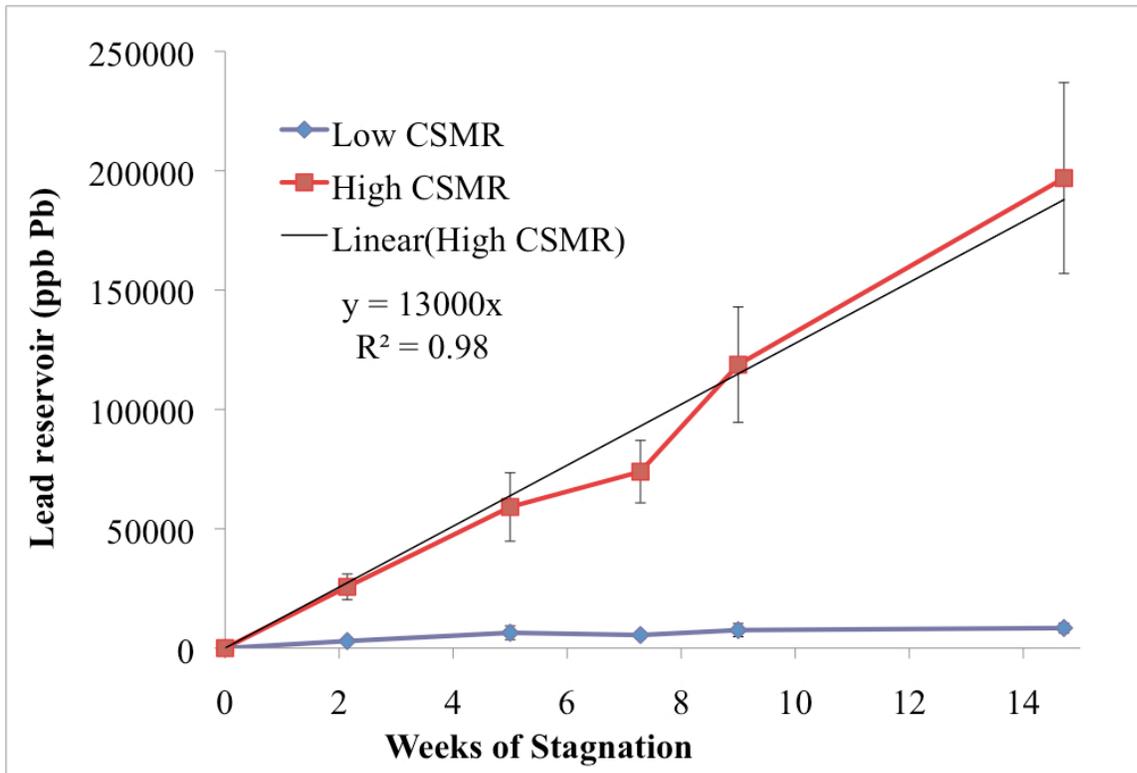


Figure 4-4. Buildup of lead concentration (ppb) reservoir in high (13) and low (0.25) CSMR waters over the 15-week stagnation period. The error bars represent 95% confidence intervals.

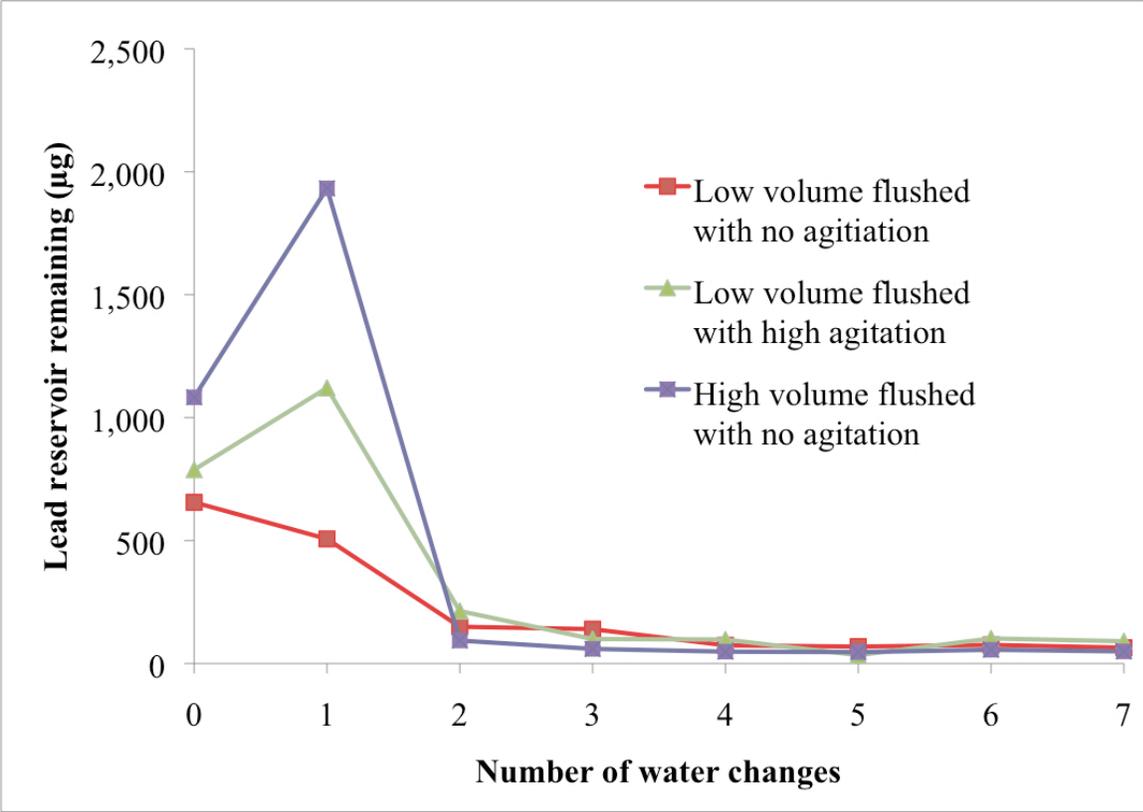


Figure 4-5. Effect of each of the three flushing methods on removal of the accumulated lead (µg) in low CSMR water. Water was changed once per day.

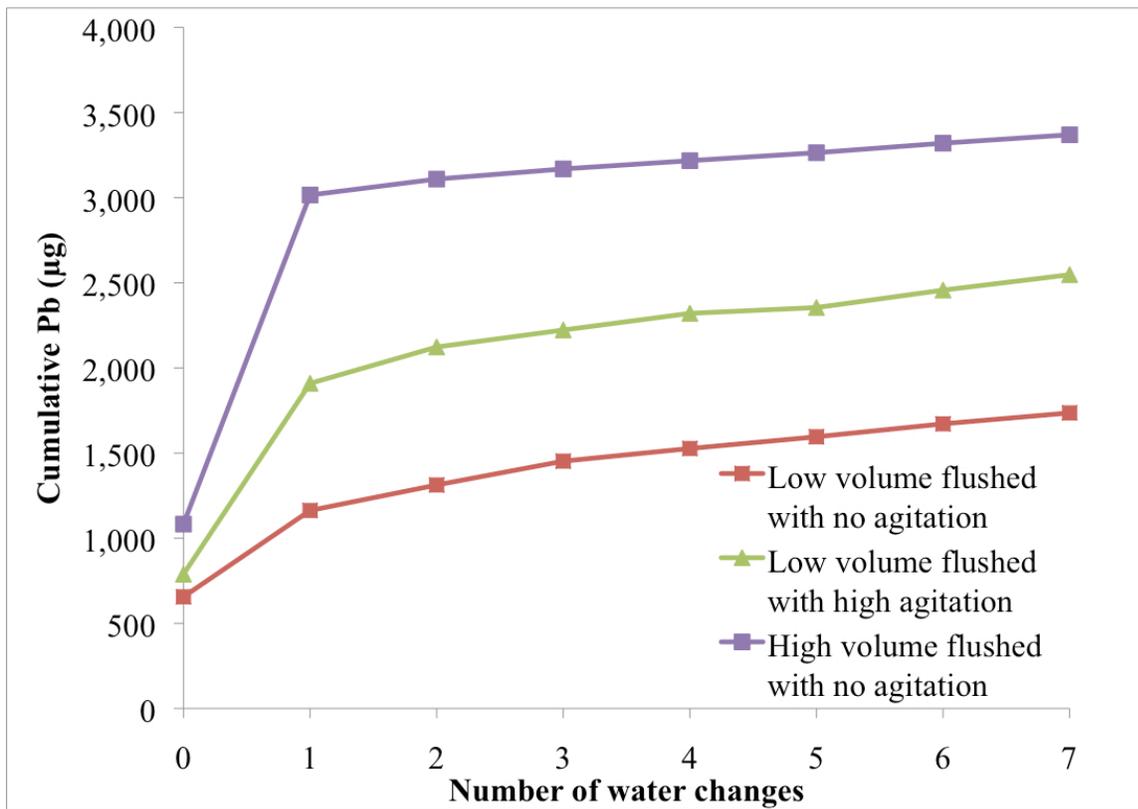


Figure 4-6. Effect of each of the three flushing methods on cumulative lead release (µg) from test cells in low CSMR water. Water was changed once per day.

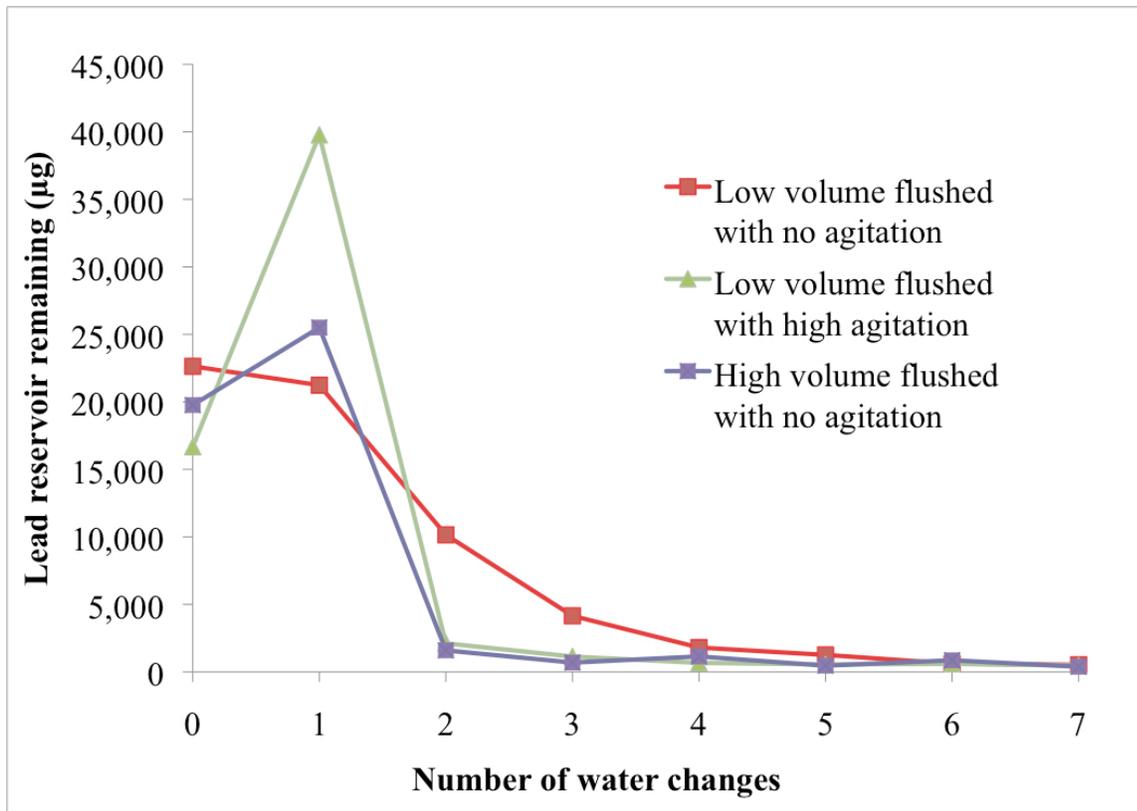


Figure 4-7. Effect of each of the three flushing methods on depletion of lead reservoir (µg) in High CSMR water. Water was changed once per day.

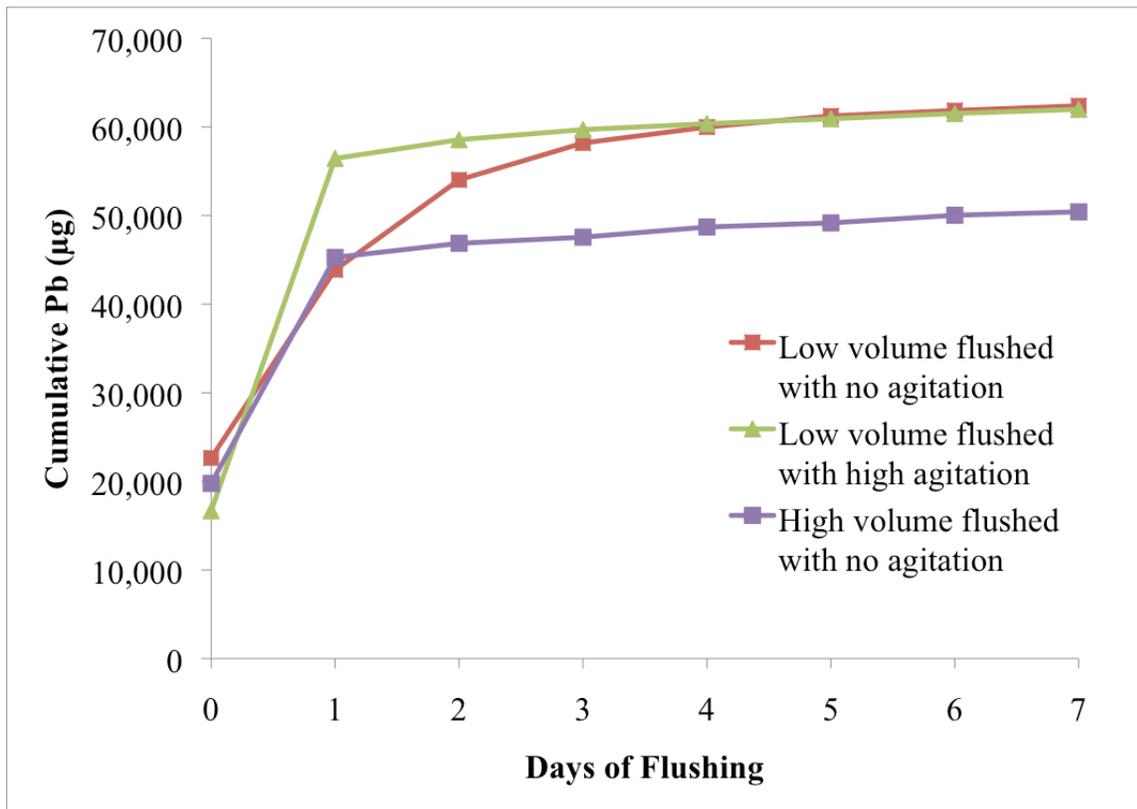


Figure 4-8. Effect of each of the three flushing methods on cumulative lead release (µg) from test cells in high CSMR water. Water was changed once per day.

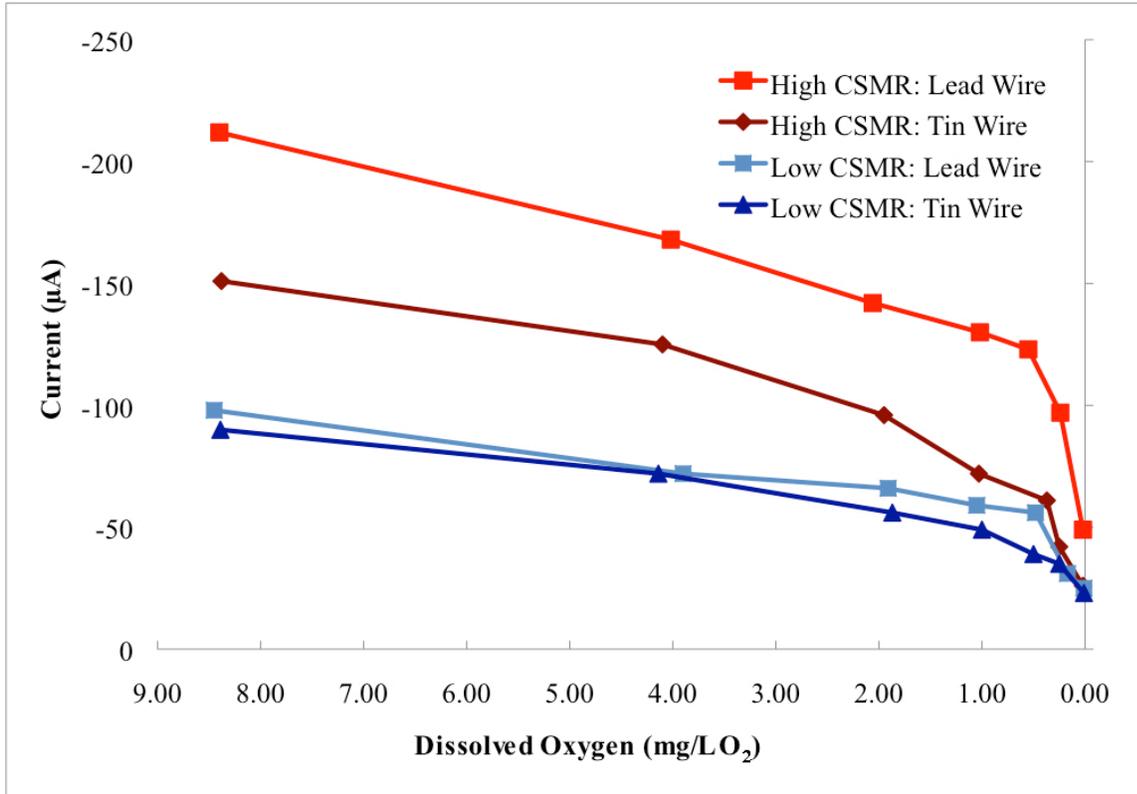


Figure 4-9. Effect of dissolved oxygen on galvanic current between lead or tin wire and copper in high and low CSMR waters. Negative currents indicate that lead and tin were sacrificed and copper was protected.

APPENDIX A: Supporting Information for Chapter 1:

Sustained lead contamination of drinking water due to galvanic corrosion of lead solder

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Experimental procedures, one table, and five figures are included.

Supporting Information 1

Experimental Procedure for Case Study 1

Test water from Utility 1 in Maryland was obtained at Virginia Tech by shipments of raw water from the Patuxent River reservoir. Collected water was separated and subjected to two simulated treatments, which were otherwise identical except for the type of coagulant used. Treatment involved coagulation with polyaluminum chloride (PACl) or aluminum sulfate (alum), filtration, phosphate corrosion inhibitor addition, disinfection with free chlorine or chloramines, and final pH adjustment. The pH for both treatments was adjusted to the same initial value, ranging from 7.6 to 7.8. Since PACl adds chloride to the water, it increases the ratio of chloride to sulfate whereas alum adds sulfate thereby decreasing the ratio. The PACl coagulant was provided by Utility 1. Doses, timing of addition and duration of treatments were selected to simulate the full-scale treatment practice to the extent possible.

To simulate future reservoir water quality conditions when road salts enter the source water at higher concentrations, 16 mg/L Cl was added to PACl-treated water in the form of NaCl. An overall upward trend has been observed for raw water chloride concentrations at Utility 1 over the last 15 to 20 years, with an increase in Cl⁻ from approximately 10 mg/L in 1990 to 20 mg/L in 2007. Therefore, a total of three CSMR levels were evaluated in this study: (1) alum-treated water (CSMR 1.4), (2) PACl-treated water (CSMR 5.3), and (3) PACl-treated water with simulated road salt (CSMR 8.5).

Supporting Information 2

Experimental Procedure for Case Study 2

Test water was obtained at Virginia Tech by shipments of Utility 2 treated water from the UV channel of the treatment plant. Collected water was separated into aliquots and subjected to various treatments (Table S-1). Chemicals added to the water included orthophosphate corrosion inhibitor with or without zinc, polyphosphate/orthophosphate blend, bicarbonate, sulfate, disinfection with free chlorine, and acid or base for final pH adjustment. All waters were dosed with 12 mg/L Cl to simulate a portion of the chloride that entered the water due to the hypochlorite generator brine leak.

The pH was adjusted with either 0.1 M NaOH or 0.1 M HNO₃ to the target value of pH 7.3 or 9.2. All water was also dosed with free chlorine at a concentration of 2 mg/L Cl₂. Orthophosphate was dosed from sodium phosphate (Na₂HPO₄). Alkalinity was adjusted with sodium bicarbonate (NaHCO₃). Chloride and sulfate were added from sodium chloride (NaCl) and sodium sulfate (Na₂SO₄).

Table A-1. Water quality conditions tested for Utility 2

Water Type		pH	Conductivity (μS)	Alkalinity (mg/L as CaCO ₃)	Chloride (mg/L Cl)	Sulfate (mg/L SO ₄)	Silica (mg/L Si)	Phosphate (mg/L P)
Current Water	No Phosphate	7.3	68	8	15	1.5	2.8	0.0
	Phosphate	7.3	72	8	15	1.5	2.8	1.0
Current Water + 10 ppm Sulfate	No Phosphate	7.3	91	8	15	1.5	2.8	0.0
	Phosphate	7.3	96	8	15	1.5	2.8	1.0
Current Water + 10 mg/L alkalinity as CaCO ₃	No Phosphate	7.3	83	18	15	1.5	2.8	0.0
	Phosphate	7.3	88	18	15	1.5	2.8	1.0
Current Water + 20 mg/L alkalinity as CaCO ₃	No Phosphate	7.3	102	28	15	1.5	2.8	0.0
	Phosphate	7.3	107	28	15	1.5	2.8	1.0
Current Water + 50 mg/L alkalinity as CaCO ₃	No Phosphate	7.3	167	58	15	1.5	2.8	0.0
	Phosphate	7.3	172	58	15	1.5	2.8	1.0
Current Water at pH 9.2	No Phosphate	9.2	71	8	15	1.5	2.8	0.0
	Phosphate	9.2	78	8	15	1.5	2.8	1.0

Supporting Information 3

Experimental Procedure for Case Study 3

The case study lasted a total of 11 weeks. The simulated copper joint macrocells (Figure S-1) were tested in triplicate and were exposed to synthetic water with low and high CSMR, which were 0.2 and 16, respectively. A CSMR of 16 was chosen to represent the worst-case scenario in terms of water corrosivity. CSMRs in excess of 16 have been measured for various communities, and the project team wanted to select an extremely aggressive condition. All waters were dosed with chloramines at a concentration of 4 mg/L as Cl₂ with a ratio of 4:1 mg Cl₂/mg N, and the pH of the water was adjusted to pH 8.3 ±0.1 at each water change. The water was changed three times per week using a “dump and fill” protocol.

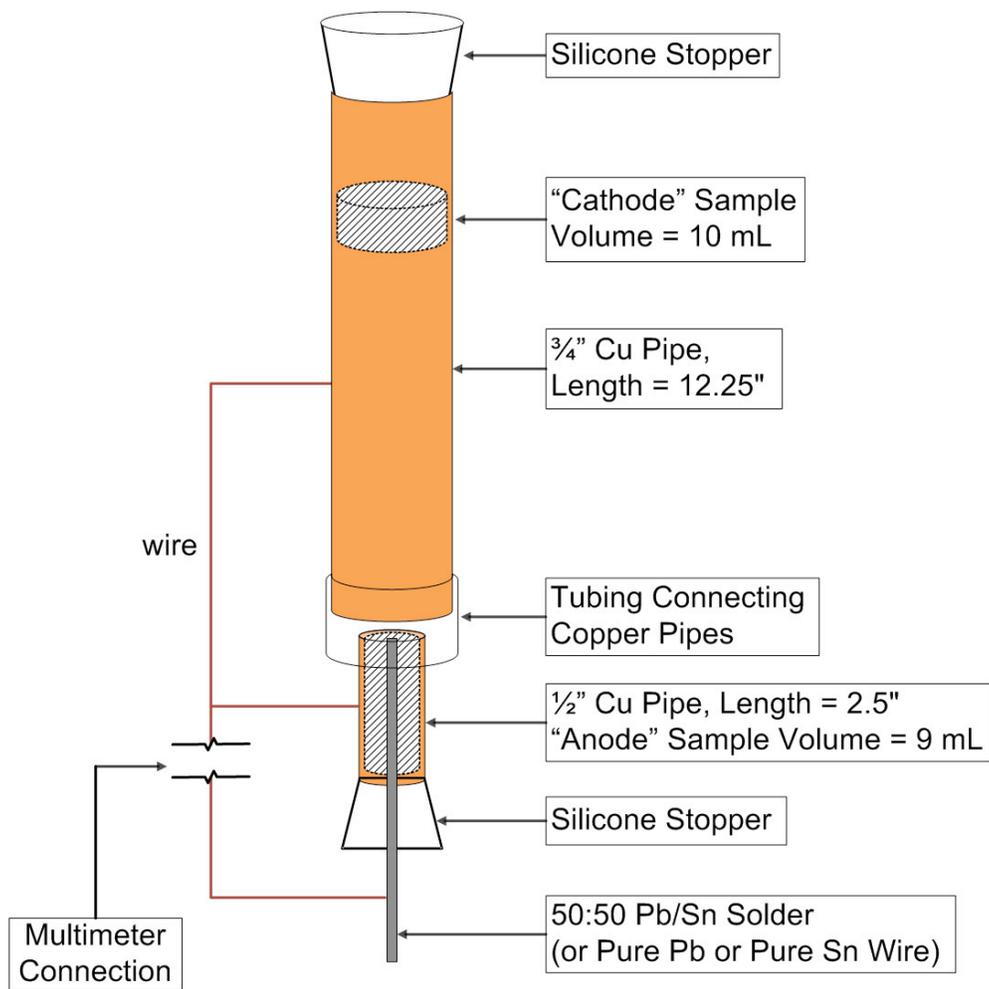


Figure A-1: Schematic of copper joint macrocell used in case studies.

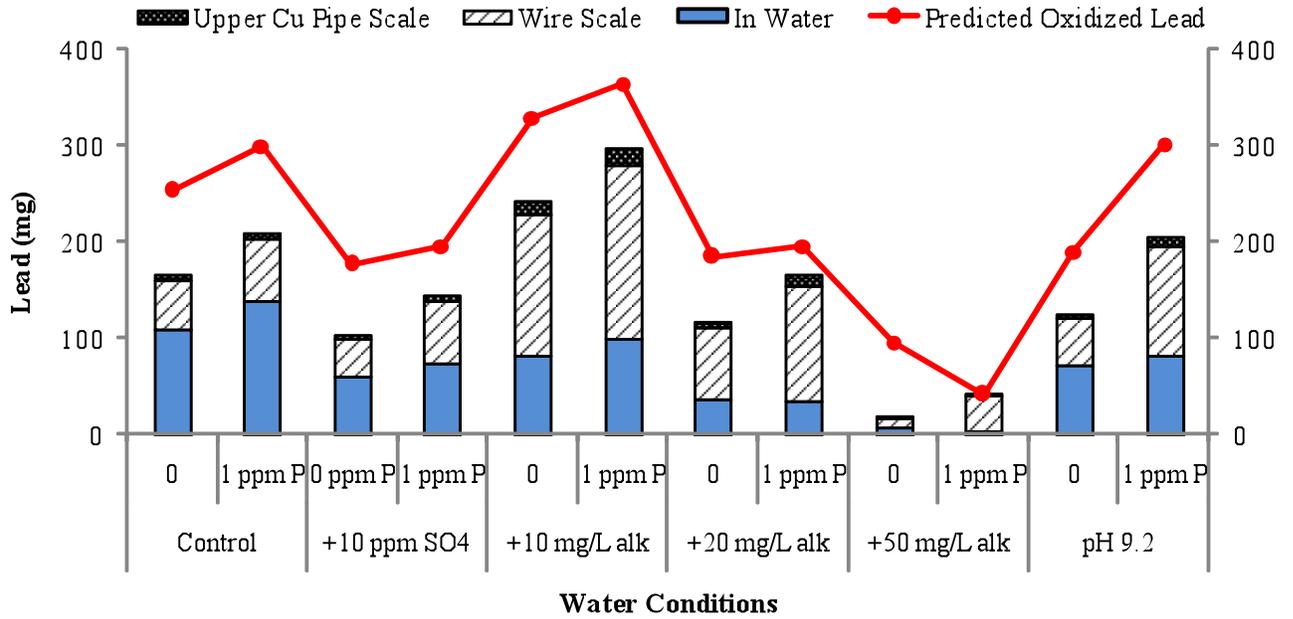


Figure A-2: Mass balance of total released lead from pure lead wires in Case Study 2.

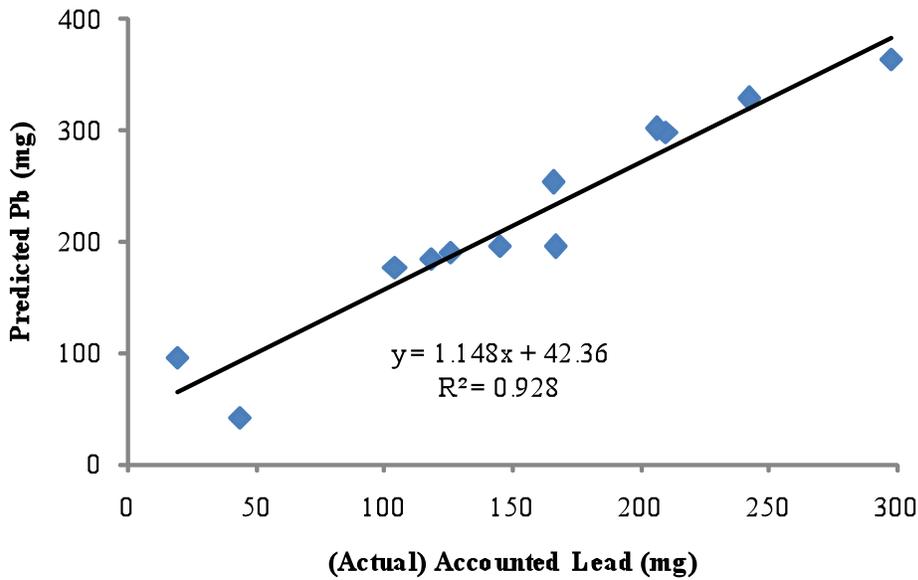


Figure A-3: Comparison of the lead accounted in the water, lead wire scale, and upper copper pipe scale versus the predicted released lead based on Faraday's law.

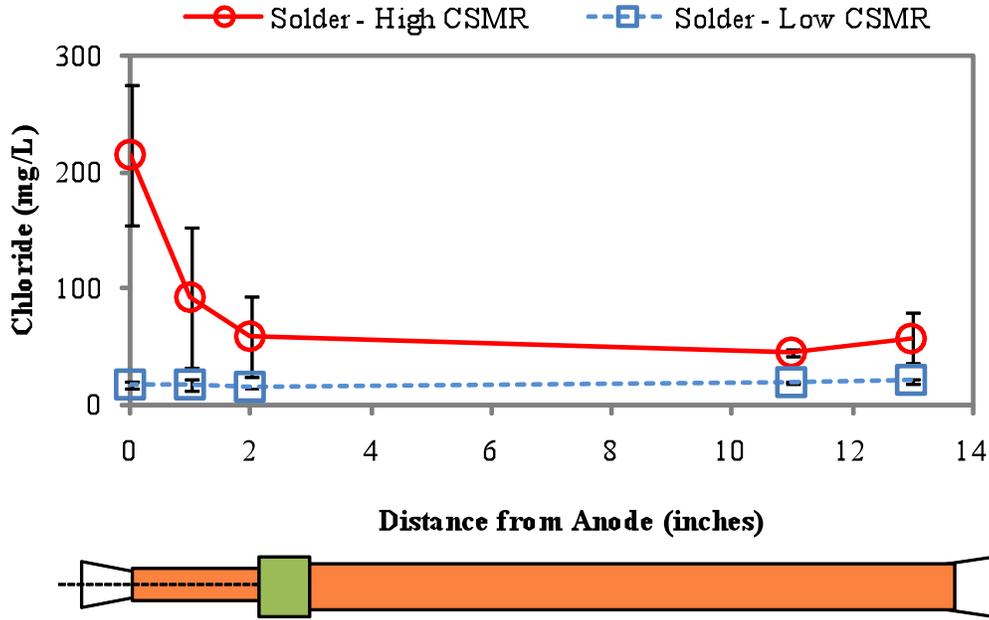


Figure A-4: Chloride microelectrode measurements as a function of distance from the lead solder anode for low and high CSMR waters in Case Study 3. Data are from the 10th week of the study, and error bars represent the 95% confidence intervals.

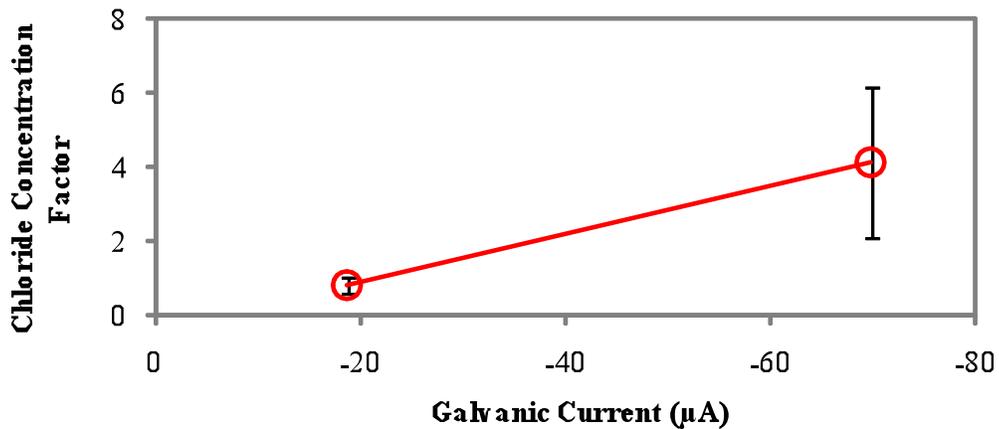


Figure A-5: Chloride concentration factor measured with a chloride microelectrode as a function of galvanic current in Case Study 3 for 50:50 Pb/Sn solder. The two points represent low and high CSMR water conditions at Week 10 of the case study, and error bars represent the 95% confidence intervals.