

EVALUATION OF ZINC ORTHOPHOSPHATE TO CONTROL LEAD
SOLDER CORROSION IN WATERS WITH HIGH CHLORIDE TO
SULFATE MASS RATIO

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ABSTRACT

Chloride levels are increasing in some water supplies around the country due to increasing use of road salts and seawater intrusion. This can increase the chloride-to-sulfate mass ratio (CSMR) over a threshold known to trigger serious galvanic corrosion (CSMR > 0.5), and unfortunately, a chemistry modification to stop this problem has never been previously identified. In this work two case studies were conducted in which zinc orthophosphate was used to stop corrosion at two Utility companies, A and B. At each Utility, a simple coupon test was run with 3/8" copper coupons, in which a 1/2" long piece of 50:50 lead: tin solder was melted evenly with a propane torch to create representative galvanic Pb: Sn solder joints. The coupons for Utility A were exposed to orthophosphate, zinc, and zinc orthophosphate at concentrations of 2 mg/L as Phosphate, 400 µg/L as Zn, or 0.650 mg/L as P orthophosphate + 0.400 mg/L zinc, respectively. At Utility B, tests were conducted with a normal level of orthophosphate, high orthophosphate, silicate, and zinc orthophosphate corrosion inhibitors. The dose was 0.5 mg/L as P orthophosphate, 1.0 mg/L as P orthophosphate, 15 mg/L as SiO₂, and 1.0 mg/L as P orthophosphate + 0.3 mg/L zinc, respectively.

A dump-and-fill protocol was applied, in which water was changed Monday, Wednesday, and Friday with samples taken once a week to simulate water moving through pipes. Inductively coupled plasma mass spectrometry (ICP-MS) technology was used to detect concentrations of metals in each coupon. Overall, zinc orthophosphate proved to decrease lead very significantly for both Utility A and B. For A, there was a large difference in lead concentrations in moderate alkalinity conditions (55-60 mg/L as CaCO₃) versus low alkalinity conditions (15-20 mg/L as CaCO₃), with lead decreasing by 51 – 92 % with the dosing of zinc orthophosphate. It also worked very effectively at Utility B (Alkalinity= 200 mg/L as CaCO₃). Orthophosphate alone performed poorly at both Utility A and B, with lead levels higher than that of the control condition, with no inhibitor in the final week of testing. This discovery could have major implications for controlling lead release in high CSMR waters.

EVALUATION OF ZINC ORTHOPHOSPHATE TO CONTROL LEAD SOLDER CORROSION IN WATERS WITH HIGH CHLORIDE TO SULFATE MASS RATIO

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GENERAL AUDIENCE ABSTRACT

Chloride levels are increasing in some water supplies around the country due to use of road salts and seawater intrusion, which can increase the chloride-to-sulfate mass ratio (CSMR) and trigger serious water lead contamination from galvanic lead solder: copper pipe corrosion. Previous attempts to control this problem through simple water chemistry modifications were unsuccessful, but in this work a combination of zinc orthophosphate and moderate alkalinity mitigated lead release in testing at two utilities.

Bench-scale experiments were completed with water from two utilities to look at the effectiveness of zinc orthophosphate, orthophosphate and zinc alone to reduce lead leaching in copper pipes with lead solder. Either zinc alone or phosphate alone were irrelatively ineffective, but the combination of zinc orthophosphate reduced lead leaching by 54-99% (compared to the control without inhibitors) if alkalinity was above about 55 mg/L as CaCO₃. These results may help mitigate future lead in water contamination events.

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ATTRIBUTIONS

Christina Devine - Doctoral candidate, Department of Civil and Environmental Engineering, Virginia Tech. Provided guidance and edits to materials and method section in Chapter 1.

Dr. Jeffrey Parks - Research Scientist, Department of Civil and Environmental Engineering, Virginia Tech. Provided data for Utility B and assisted in writing the results for section Chapter 1, section 3.2.

Dr. Marc Edwards – Professor, Department of Civil and Environmental Engineering, Virginia Tech. Provided funding and guidance on research for Utility. Major contribution to the writing of Chapter 1.

CHAPTER 1: EVALUATION OF ZINC ORTHOPHOSPHATE TO CONTROL LEAD SOLDER CORROSION IN WATERS WITH HIGH CHLORIDE TO SULFATE MASS RATIO

1.0. INTRODUCTION

The 1991 United States Environmental Protection Agency's (EPA) Lead-and-Copper Rule (LCR), set a regulatory standard for lead and copper levels in public drinking water (e-CFR, 2017). Although installation of new lead solder and lead pipes have been banned since 1986, lead service lines are still present in about 3.3 million residences in the U.S., and old solder is often a dominant source of lead in water contamination (Edwards & Triantafyllidou, 2007; Lee, R. G., Becker, W. C., & Collins, D. W., 1989; Oliphant, 1983; Walker, R.J., & Oliphant, R.J., 1982). The LCR presently requires Utility action if more than 10% of first draw samples from high risk homes exceed 15 ppb (e-CFR, 2017).

Galvanic corrosion of lead solder-copper pipe couples in certain waters with a high chloride to sulfate mass ratio (CSMR) can cause serious lead in water contamination events (Dodrill, D.M., & Edwards, M., 1995; Gregory, R. & Gardiner, J., 1985; Gregory, R., 1990; Oliphant, R.J., 1983; Walker, R.J. & Oliphant, R.J., 1982; Willison, H., & Boyer, T.H., 2012). Prior attempts to control this problem with conventional water chemistry modifications were unsuccessful. Specifically, dosing of orthophosphate, proved to be ineffective or even markedly worsened the problem in a few experiments (Nguyen, C.K., et al, 2011). In addition to orthophosphate, zinc orthophosphate has been considered as an option to control solder corrosion, but results have not been consistent (Churchill, D.M., et al, 2000; Edwards & Triantafyllidou, 2007; Gregory, R., & Gardiner, J., 1985; Oliphant, 1983).

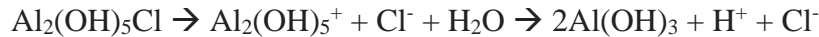
The role of alkalinity and pH adjustments to mitigate problems with galvanic corrosion have also been explored. In general, higher alkalinity somewhat reduced, but did not eliminate, the adverse effect of higher CSMR on lead leaching from galvanic connections (Nguyen, C.K., et al, 2011; Triantafyllidou, S., & Edwards, M., 2011). Mechanistic studies demonstrated that the higher alkalinity maintained higher pH at lead surfaces, which reduced the rate of corrosive attack in high CSMR waters (Dodrill, D.M., & Edwards, M., 1995; Edwards, M., & Triantafyllidou, 2007; Nguyen, C. K., Stone, K. R., Dudi, A., & Edwards, M. A., 2010). But alkalinity and pH adjustments alone have not reduced lead leaching dramatically enough to satisfactorily control lead.

The failure to find simple water chemistry modifications that involve pH, alkalinity or inhibitors, to solve this problem, has resulted in seeking out very unconventional approaches. Since chloride removal is very expensive (Pugh, L., & Lake, K, 2016), the addition of magnesium sulfate can be used to adjust the CSMR below 0.6. In a recent case study with a water that had a CSMR over 1.5, dosing magnesium sulfate to lower CSMR below 0.6 was effective at reducing lead levels (DeLorenzo, S., & Klayman, B., 2013). But in waters with higher initial chloride, very high doses of magnesium sulfate would be required, which is undesirable because of gastrointestinal

concerns, high chemical costs, or role of sulfate in corrosion of other materials such as iron (Heizer, W.D., et al., 1997; Edwards, M., & McNeill, L., 2002).

These issues all came to a head at a recent case study at Utility A, where satisfactory corrosion control was historically achieved by maintaining pH of 8.0 and a moderate alkalinity (≈ 53 mg/L as CaCO_3). For years, this water Utility maintained reported 90th percentile lead levels below 15 ppb, even though the CSMR of > 0.5 has been noted to have a high tendency to cause problems with water lead contamination from solder in some studies. But when the Utility switched from alum to aluminum chlorohydrate (ACH) in 2012, to reduce operating costs and improve performance, the 90th percentile lead levels suddenly rose to 101 ppb and exceeded the LCR (Figure 1). Along with an increase in CSMR from 3.6 to 5.0, the switch in coagulant also decreased alkalinity by about 50%, because although alum produces much more acid than ACH, the utility added lime when alum was used to restore alkalinity (Table 1; Equation 1; Equation 2), and in combination the two changes were believed to have triggered the higher water lead. Testing indicated that the high lead originated with lead: tin solder. A collaboration between the water Utility and Virginia Tech, sought out solutions through a trial and error with experience as a guide, and eventually tested a combination of zinc orthophosphate and moderate alkalinity as a possible solution. Once zinc was added in addition to orthophosphate, and alkalinity was increased, the 90th percentile lead levels decreased back to acceptable levels of 4.5 ppb.

Equation 1. The dissociation of ACH into water:



Equation 2. The dissociation of Alum into water:



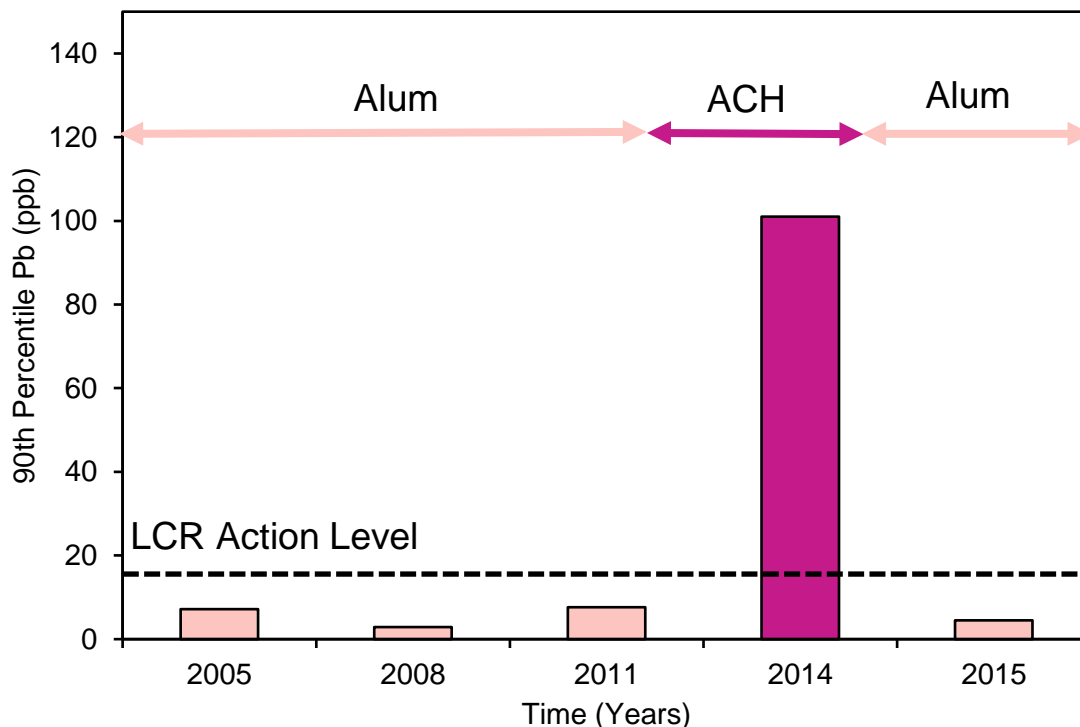


Figure 1. LCR compliance history for Utility A.

In this work we examined the hypothesis, that dosing of zinc orthophosphate in moderate alkalinity water would yield synergistic advantages in mitigating water lead contamination from lead solder. High CSMR water from two utilities (A and B) that had known high potential to cause lead contamination from solder, along with water from utilities nearby Utility A, were used to test this hypothesis at bench scale.

2.0. MATERIALS AND METHODS

Bench-scale experiments were conducted using water from Utility A and Utility B. Utility A was a relatively low alkalinity surface water and Utility B was derived from relatively high alkalinity surface water (Table 1).

Table 1. Baseline water chemistry parameters for representative water from Utility A and B.

Water Parameter	Utility A		Utility B	
	Low Alkalinity	Moderate Alkalinity	Source 1	Source 2
pH	7.5-7.8	7.5-7.8	7.80	8.00
Alkalinity (mg/L as CaCO ₃)	25.0	55.0	180	180
Cl ⁻ (mg/L)	55.0	55.0	50.4	69.4
SO ₄ ⁻² as S (mg/L)	12.0	37.0	45.3	45.5
CSMR	4.6	1.5	1.1	1.5

2.1. Lead Solder-Copper Coupons Preparation

Lead solder-copper coupons were prepared by applying a thin layer of flux to the interior surface of a 7/8", 3/8" diameter copper coupon and melting a 1/2" long piece of 50:50 lead: tin solder evenly using a propane torch. All coupons were chemically cleaned by soaking in a 0.1 M sodium hydroxide solution for 5 minutes, and then rinsing four times with distilled water. The coupons (150) used for Utility A were placed in 50 mL glass jars whereas the coupons for Utility B (74) were placed in 100 mL glass jars.

2.2. Test Water Conditions

Case Study at Utility A. A total of 19 water conditions were tested for the Utility A bench scale case study (Table 2). Sixteen of the target water qualities examined four inhibitor conditions, two alkalinities, and two chloride levels. The inhibitor conditions included a control (no inhibitor), orthophosphate (made with a 1000 mg/L stock of Disodium Hydrogen Phosphate and sodium Dihydrogen Phosphate Dihydrate to maintain desired pH), zinc (made with a 100 mg/L zinc chloride stock), and a zinc orthophosphate provided by Shannon Chemical (SLI-5216, Liquid Zinc Orthophosphate; Table 2). The chloride levels included the current level of 55 mg/L and a forecasted future value of 75 mg/L to represent continued effects of road salt a decade hence.

Another three water conditions examined other conditions of possible interest to the Utility; a low zinc concentration (0.25 mg/L as Zn), a low chloride concentration (30 mg/L as Cl⁻), and a condition with added magnesium sulfate (90 mg/L as S). Test waters were also collected from two nearby partner Utilities which added three additional test water combinations. With 5 replicate samples per condition, 110 (22 total conditions x 5 replicates) were run in total.

To create the waters of interest, 20 L batches of both the treatment plant's combined filter effluent (CFE) and river influent were shipped to Virginia Tech weekly. The raw river water was treated with a process simulating the full-scale plant coagulation, sedimentation and filtration, to the extent possible at lab scale, including dosing of chlorine and ammonia to create a chloramine residual.

Utility B. Two water sources with different chloride levels, Source 1 and Source 2 were shipped to Virginia Tech where they were exposed to five water conditions for seven weeks: a control, medium orthophosphate, high orthophosphate, a zinc orthophosphate and a silicate (Table 2). After the first few weeks, the silicate and medium orthophosphate conditions were eliminated due to a statistically insignificant impact ($p > 0.05$) versus the control condition, and the remaining 3 conditions were tested for an additional 9 weeks (Table 2).

Table 2. Final target Inhibitor doses for each water condition at Utility A and Utility B

Utility A							
Water Condition	pH	Alkalinity mg/L as CaCO ₃	Added mg/L as P	Added mg/L as Zn	mg/L as Cl	mg/L as S	mg/L as SiO ₂
No Inhibitor + Present Chloride	7.5-7.8	20 and 55	----	----	50	12 and 36	N/A
No Inhibitor + High Chloride		20 and 55	----	----	70	12 and 36	
Phosphate + Present Chloride		20 and 55	0.650	----	50	12 and 36	
Phosphate + High Chloride		20 and 55	0.650	----	70	12 and 36	
Zinc + Present Chloride		20 and 55	----	0.400	50	12 and 36	
Zinc + High Chloride		20 and 55	----	0.400	70	12 and 36	
Zinc Phosphate + Present Chloride		20 and 55	0.650	0.400	50	12 and 36	
Zinc Phosphate + High Chloride		20 and 55	0.650	0.400	70	12 and 36	
MgSO ₄ + Present Chloride		20	----	----	50	90.0	
Low Zinc + Current Chloride		55	0.650	0.250	50	36	
No Inhibitor + Low Chloride		55	----	----	35	36	
Partner Utility 1, Site 1		15	0.100	----	280	22	
Partner Utility 1, Site 2		15	----	----	190	15	
Partner Utility 2		25	0.350	0.300	50	19	
Utility B							
Control	7.8-8.2	180-200	----	----	50.0 or 70.0*	45	----
Medium Orthophosphate			0.50	----			----
High Orthophosphate			1.00	----			----
Silicate			----	----			15.0
Zinc Orthophosphate			1.00	0.300			----

Where:

* 50.0 mg/L is for Source 1 and 70.0 mg/L is for Source 2

2.3. Test Protocol

To condition the coupons prior to testing, the solder coupons were rinsed three times with 0.1 M sodium bicarbonate synthetic water solution and a 2 mg/L sodium hypochlorite residual. Pre-testing of each solder coupon was conducted to eliminate outliers and produced sets of solder coupons with statistically similar initial lead release per the method of the National Sanitation Foundation (NSF) and American National Standard's (ANSI) Standard 61, Section 9 (NSF & ANSI, 2007; Parks, J., & Edwards, M., 2014).

2.3.1. Utility A. Coupons in 50 ml jars were placed on a rotary shaker table at 25 rpm. Adjustments to pH were done Monday, Wednesday, and Friday using carbon dioxide and sodium hydroxide to maintain targeted values between 7.5 and 7.8. A dump-and-fill protocol, was used to change water every Monday, Wednesday and Friday. Composite samples were taken on a weekly basis (Friday) for each water condition to track temporal trends in lead release (Edwards & Triantafyllidou, 2007). Once lead concentrations had come to a pseudo steady state, samples from each individual replicate were taken Monday, Wednesday and Friday of week 14 to support statistical analysis of results.

To potentially identify a mechanism by which zinc phosphate is effective, FEI Quanta 600 FEG environmental scanning electron microscope (ESEM) analysis was used to view the surfaces of

the copper and lead solder test specimens. To quantify results, energy-dispersive spectroscopy (EDS) analysis was used to detail the chemical composition of the surface of the samples.

2.3.2. Utility B. Coupons were placed in 100 mL glass jars where water was changed every Monday, Wednesday, and Friday. Water was changed using dump-and-fill protocol every Wednesday where individual coupons were sampled. Lead and copper concentrations were monitored for a duration of 16 weeks. Once lead concentrations came to a pseudo steady state after 16 weeks, a statistical analysis was completed.

2.4. Analytical Methods

Concentration of metals and anions were measured using ICP-MS analysis after at least a 16 h stagnation period after acidification with 2% v/v nitric acid. Prior to analysis, calibration curves were produced to ensure accurate measurements. For statistical analysis, students' t-tests were used to compare inhibitor conditions on a 95% confidence interval and analysis of variance (ANOVA) tests were used to measure the statistical difference between multiple inhibitors. To determine normality, a shapiro-wilks statistical test was completed.

3.0. Results

3.1. Case Study 1: Utility A

3.1.1. Temporal Trends. Representative lead data for composite samples illustrate decreasing lead release during the first 13 weeks of testing as the lead solder coupons passivated (Figure 2). As expected, given the highly variable nature of galvanic corrosion as manifested in lead release to water, lead concentrations over time were very erratic over the first eight weeks. But even considering this variability some trends were clear. Specifically, the 3 inhibitor conditions (No inhibitor, zinc orthophosphate, orthophosphate) with present day moderate alkalinity water, always had lower lead release than the corresponding conditions with low alkalinity water after week 3 ($p < 0.05$; ANOVA). Moreover, the higher alkalinity water showed much faster reductions in lead release, than did the lower alkalinity water (Figure 2).

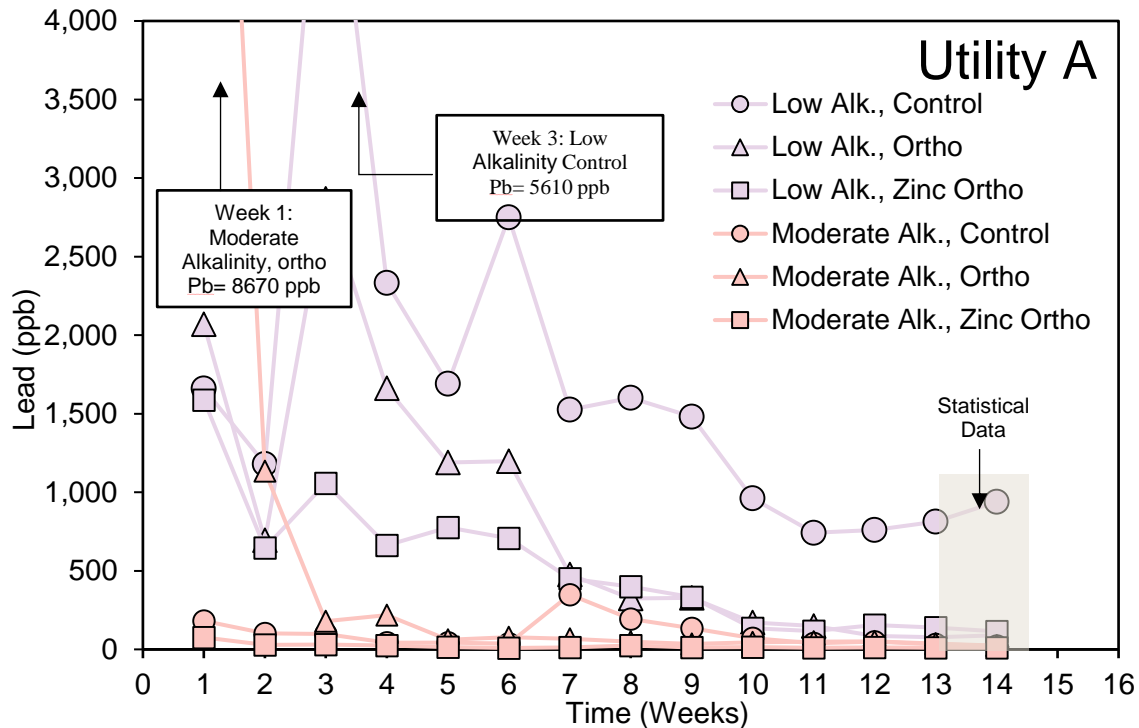


Figure 2. Temporal trends in lead release for low, moderate and high alkalinity conditions with 50 mg/L chloride. Data for other conditions in Appendix D.

3.1.2 The Effect of Alkalinity and Inhibitors. When the week 14 water sample data were collected from individual experimental replicates (3 sampling events of $n = 5$), the overarching role of alkalinity is again apparent (Figure 3). For the control condition without inhibitor at low alkalinity, with both present day and higher chloride, the average lead was 925-940 ppb and standard deviations were 400-530 ppb. For the corresponding conditions at moderate alkalinity, the average lead was at least 15 times lower (22-54 ppb), and the standard deviation was only 6-50 ppb. Hence, from the perspective of average lead and variability as measured by standard deviation, the higher alkalinity alone dramatically improved lead release ($p < 0.05$).

Dosing of orthophosphate alone did not reduce lead significantly compared to the corresponding control condition, with the exception of the case of low alkalinity with present day chloride where the reduction was 90% ($p < 0.05$). The dosing of zinc alone caused no statistically significant differences in lead release (Figure 3), compared to the corresponding control condition without any inhibitor ($p > 0.05$). But dosing of zinc orthophosphate reduced average lead release by 51-92%, compared to the corresponding condition with either no inhibitor or zinc alone (Figure 3). All these results were statistically significant ($p < 0.05$). Generally speaking, zinc orthophosphate was superior in corrosion control compared to orthophosphate ($p < 0.05$), with the exception of the condition with low alkalinity and lower chloride for which the two approaches were not significantly different. The relative advantage of zinc orthophosphate was most apparent in the low alkalinity and high chloride condition, for which average lead was 73 ppb compared to 907 ppb for the corresponding condition with orthophosphate alone.

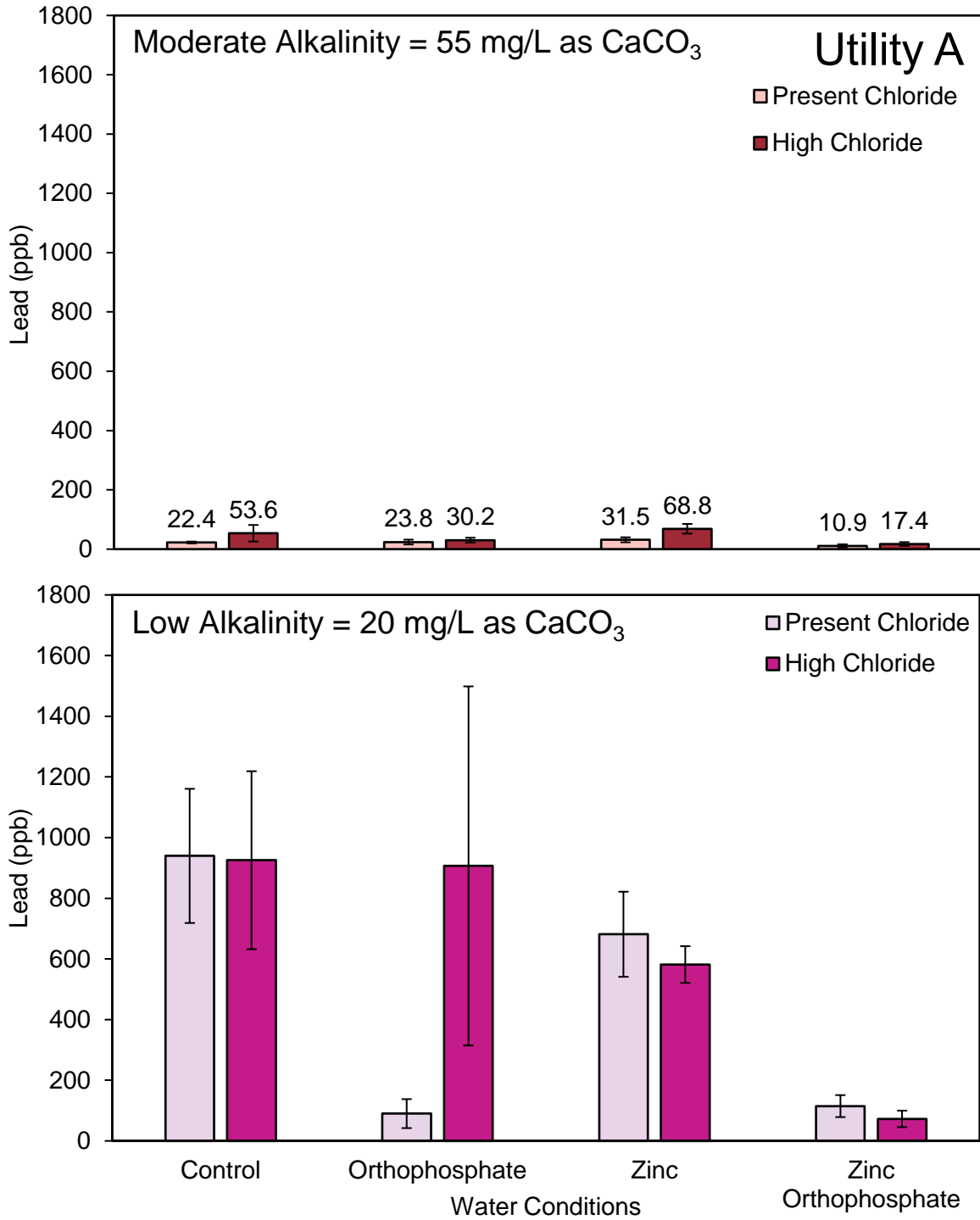
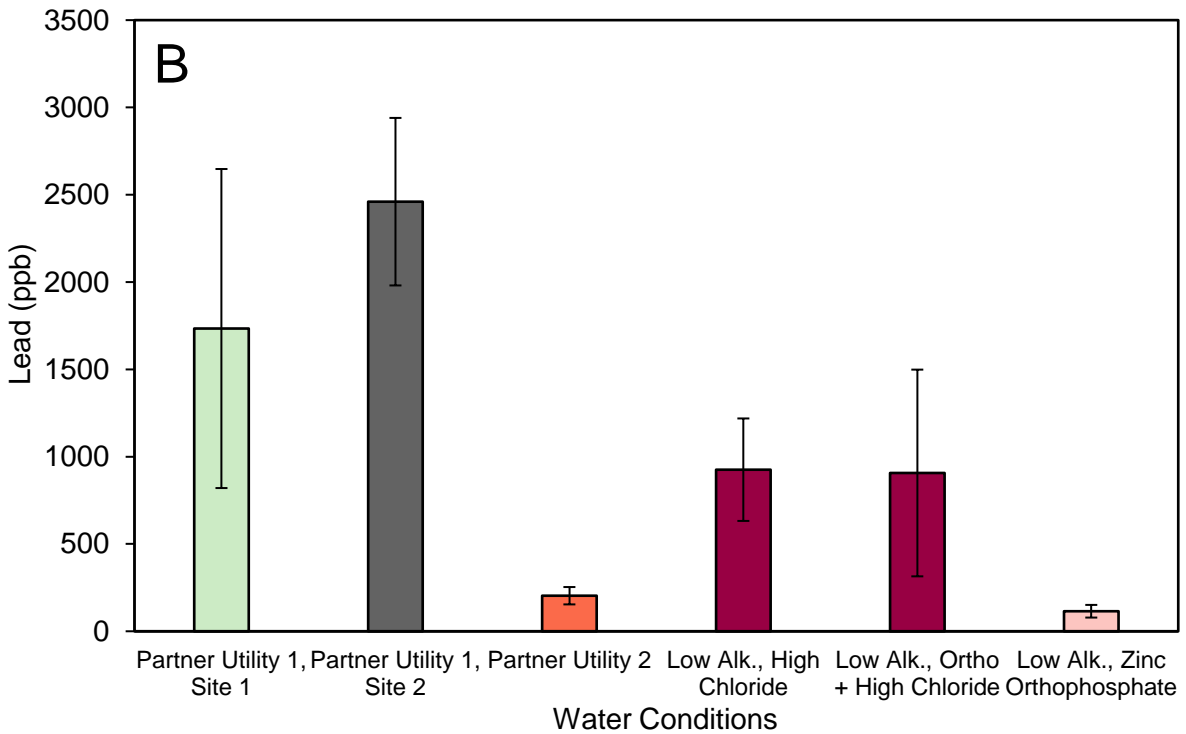
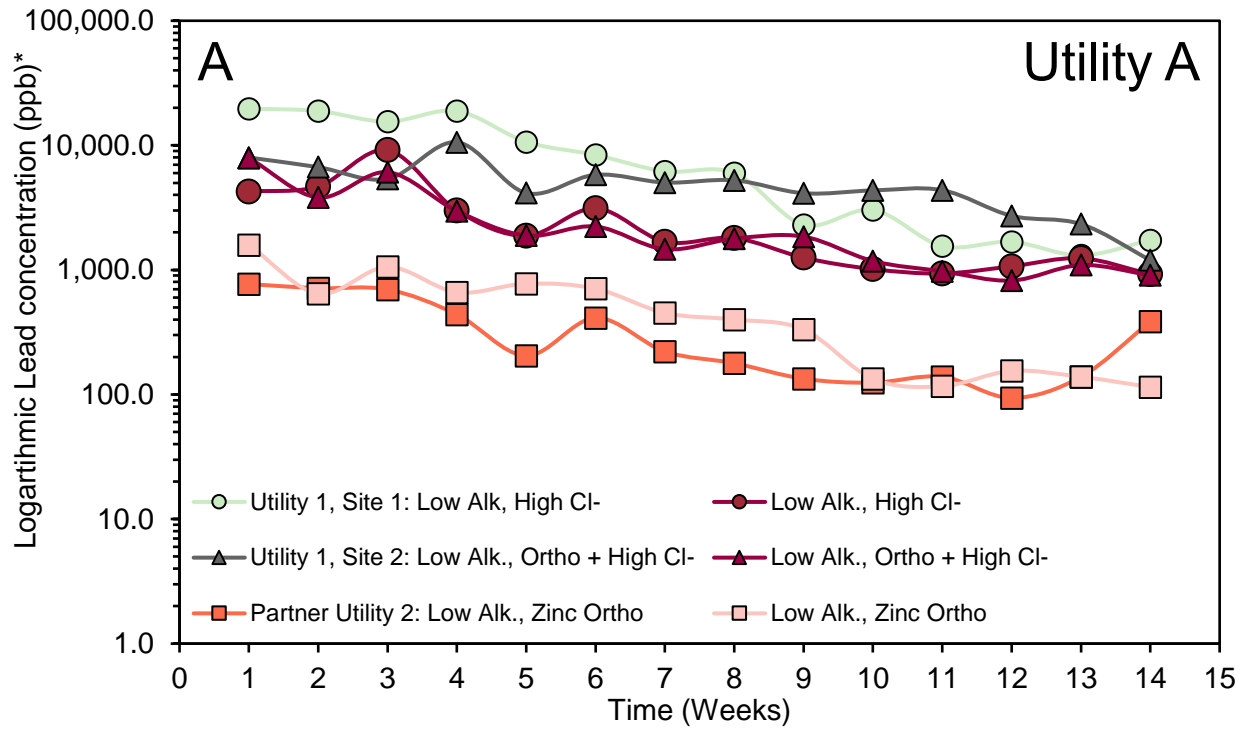


Figure 3. Bar graphs displaying lead concentrations, with 95% confidence intervals, for moderate alkalinity and low alkalinity at present and high chloride. All data presented was collected during the final week of testing (n=15).

3.1.3. Utility A Partner Utility Comparison. Water from two nearby partner utilities was not exceeding the lead action level, despite having relatively low alkalinity and high CSMR levels (Table 2). A key question was “Were these waters somehow less corrosive than similar Water from Utility A that did cause an action level exceedance, when tested head to head?” Utility 1 Site 1 was a groundwater source did not use phosphate corrosion control although chloride levels were at 280 mg/L whereas Utility 1 Site 2 (groundwater) did use orthophosphate at 100 ug/L as P. Partner Utility 2, who used surface water, used zinc at 300 ug/L and orthophosphate at 350 ug/L for corrosion control. As was the case at Utility A, Utility 2 with zinc orthophosphate had the lowest level of lead throughout the study and after the 14th week ($p < 0.05$). Utility 1 site 1 and site 2, with and without orthophosphate, had higher lead than Utility 2 despite having higher alkalinity. Overall, the results from the partner utilities support the contention that zinc orthophosphate can sometimes reduce lead leaching (Figure 4). The partner utilities without zinc orthophosphate had lead levels closer to the range of Utility A with no inhibitor or with zinc orthophosphate.

It is presently unclear why partner Utility 1, site 1 and 2, had no reported problems with the lead action level. It is possible that with years of exposure the high alkalinity water would passivate the lead, even though that did not occur in the 4 months duration of this study. Alternatively, it is possible there is a problem, and the sites that have been selected for testing have soldered joints with relatively little lead surface exposed. The magnitude of the problem is highly dependent on the specifics of every lead solder joint. In contrast, the bench scale testing suggested it was not surprising the Utility with zinc orthophosphate did not have action level exceedances.



* The y-axis has been changed into a logarithmic axis to display all the data on one graph.

Figure 4. A) Average lead release from composite coupon samples for nearby utilities, to Utility A, and their respective comparison condition and B) bar graphs displaying lead concentrations, with 95% confidence intervals, for samples taken at week 14 (n=15) for Utility A and each partner Utility.

3.1.4 Environmental Scanning Electron Microscope Analysis

Table 3. Normalized mass percent of zinc and orthophosphate on the surface of lead solder and copper pipe for coupon samples

Water Combination	Lead		Copper	
	% Zinc	% Phosphate as P	% Zinc	% Phosphate as P
Moderate Alkalinity, Zinc Ortho	0.34	1.33	19.9	2.98
Low Alkalinity, Zinc Ortho	1.83	3.00	1.38	1.03
Moderate Alkalinity, Ortho	0.02	4.41	1.54	0.86

To examine how zinc orthophosphate may have acted to reduce galvanic corrosion, low alkalinity samples and present-day alkalinity coupons were analyzed under the ESEM. According to mixed inhibitor theory, zinc is believed to be a cathodic inhibitor whereas orthophosphate is an anodic inhibitor (Sheffer, G., 2006). If that were the case, zinc would be found at high concentrations on the cathode (copper) surface and orthophosphate would be found at high concentrations on the anode (lead) surface.

Based on chemical analysis from EDS the mass percent of zinc and orthophosphate was obtained on the corresponding cathode and anode surfaces (Table 3). Zinc was indeed present at concentrations up to 20% coating the copper pipe coupon surfaces, when zinc orthophosphate was used at moderate alkalinity. The elevated levels of zinc in this scale, might have therefore reduced the rate of oxygen reduction driving galvanic corrosion, consistent with mixed inhibitor theory. For some reason at the same condition but with lower alkalinity, zinc levels on the copper pipe surface were much reduced. Thus, it is possible that the higher alkalinity, somehow assists the role of zinc in cathodic inhibition, forming a less protective coating at lower alkalinity.

To more intensively examine the theory that zinc acts by depositing at the cathode, a more intensive and detailed investigation of all the copper pieces for the low alkalinity and high alkalinity, zinc orthophosphate conditions with present chloride were examined under ESEM at a magnification of 100X (Figure 5). This more intensive study did not confirm higher levels of zinc on copper surfaces in moderate versus low alkalinity water at greater than 95% confidence—however, the method indicated 27% more zinc on the copper surface at moderate alkalinity on average versus low alkalinity (Figure 6). Moreover, the deposits of zinc and phosphate were much less uniform at moderate alkalinity, as evidenced by standard deviation of ± 1.03 for high alkalinity versus ± 0.29 for lower alkalinity on replicate scans of the surface. It is hypothetically possible that the zinc is preferentially depositing at high activity cathodic sites on the copper surface at moderate alkalinity.

Although this work examining the role of zinc orthophosphate is preliminary and qualitative, it is supported by the hypothesized role of synergistic impacts from zinc orthophosphate according to mixed inhibitor theory. Specifically, consistent with the idea that zinc acts at the cathode and phosphate at the anode, there was more orthophosphate found on the lead surface whereas zinc was found in larger concentrations on the copper surface (Figure 7). Since this is the first time

we have ever documented a possible solution to the lead solder galvanic corrosion problem, future testing of this theory is now warranted.

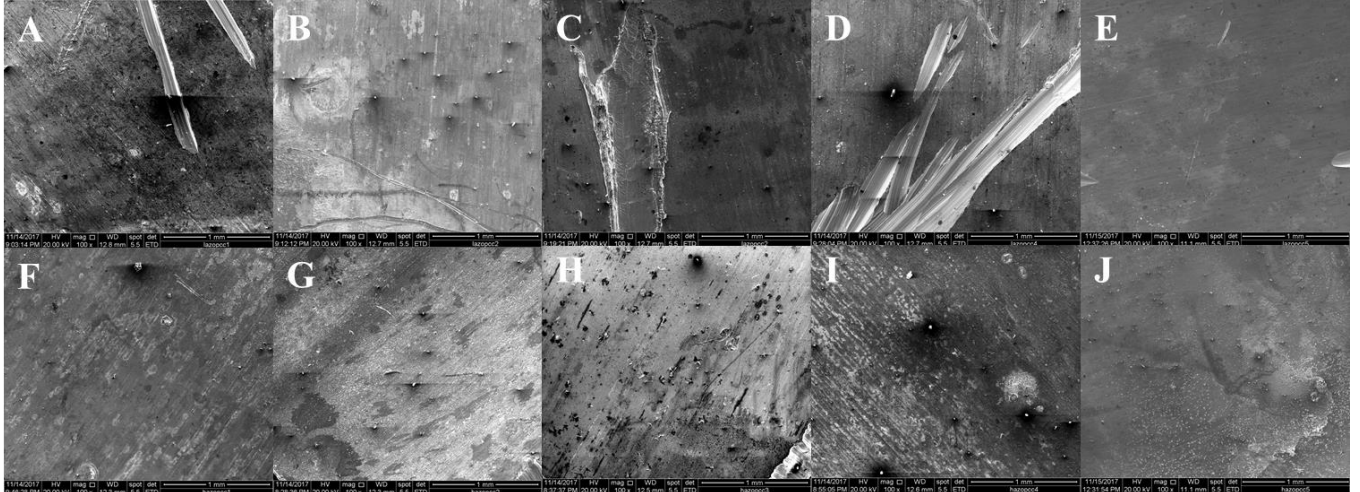


Figure 5. ESEM images of copper coupon pieces. The images show A) low alkalinity, zinc ortho, coupon 1, B) low alkalinity, zinc ortho, coupon 2, C) low alkalinity, zinc ortho, coupon 3, D) low alkalinity, zinc ortho, coupon 4, E) low alkalinity, zinc ortho, coupon 5, F) moderate alkalinity, zinc ortho, coupon 1, G) moderate alkalinity, zinc ortho, coupon 2, H) moderate alkalinity, zinc ortho, coupon 3, I) moderate alkalinity, zinc ortho, coupon 4, and J) moderate alkalinity, zinc ortho, coupon 5.

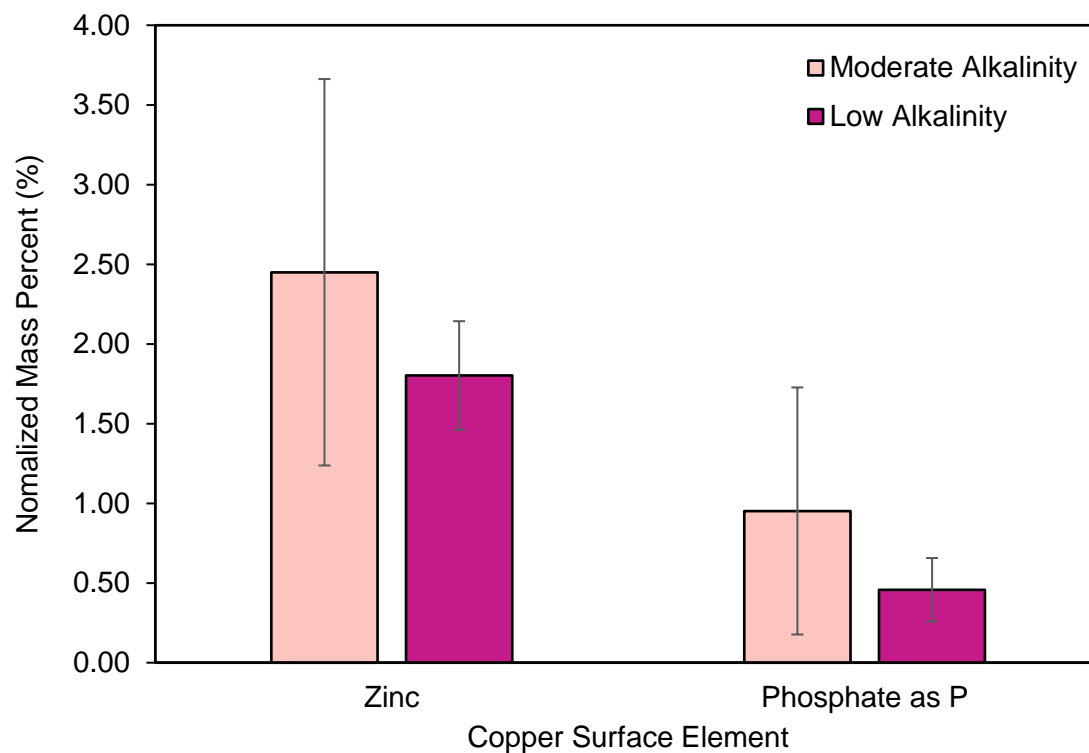


Figure 6. Bar graph of the normalized mass percent of zinc and phosphate as p on the surface of copper coupons with 95% confidence interval error bars (n=5).

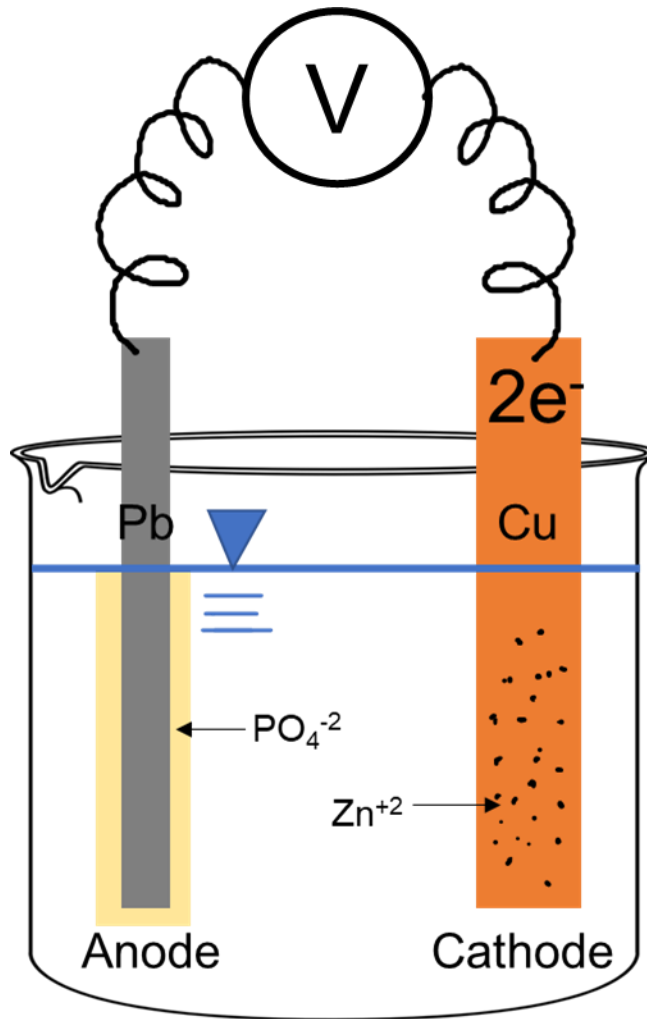


Figure 7. Illustration of the mixed inhibitor theory mechanism, resulting in synergistic action for zinc orthophosphate in a lead solder: copper galvanic cell. According to this theory, the power of the cell is greatly reduced when zinc deposits on the copper surface (cathode) and the orthophosphate deposits and passivates the lead solder surface (anode).

3.2. Case Study 2: Utility B.

Utility B operates using water from two groundwater sources with a finished alkalinity of 180 mg/L as CaCO₃. Source 1 has a CSMR of 1.1 and Source 2 has a CSMR of 1.5 with chloride levels of 50.4 mg/L and 69.4 mg/L, respectively. Prior to the switch from alum to polyaluminum chloride (PACL), the Utility relied on pH and alkalinity for corrosion control. To maintain compliance with the LCR, Utility B wanted to determine which corrosion control approach would be best at controlling lead leaching from galvanic lead solder and copper couples.

As was the case with Utility A, there was very high variability in the two Utility B waters with orthophosphate alone, with a standard deviation of 1480-1720 ppb and an average lead level of 804-1650 ppb (Figure 8). The condition without any orthophosphate had about 8 times lower levels of lead than the condition with orthophosphate (119-203 ppb). But the condition with zinc orthophosphate had average lead levels of just 4-10 ppb. In this case, zinc orthophosphate

reduced lead levels by a factor of about 160-200 times compared to the same condition with orthophosphate alone. The trend was the same when examined from the perspective of the lowest lead release from the replicate samples (lower Figure 4).

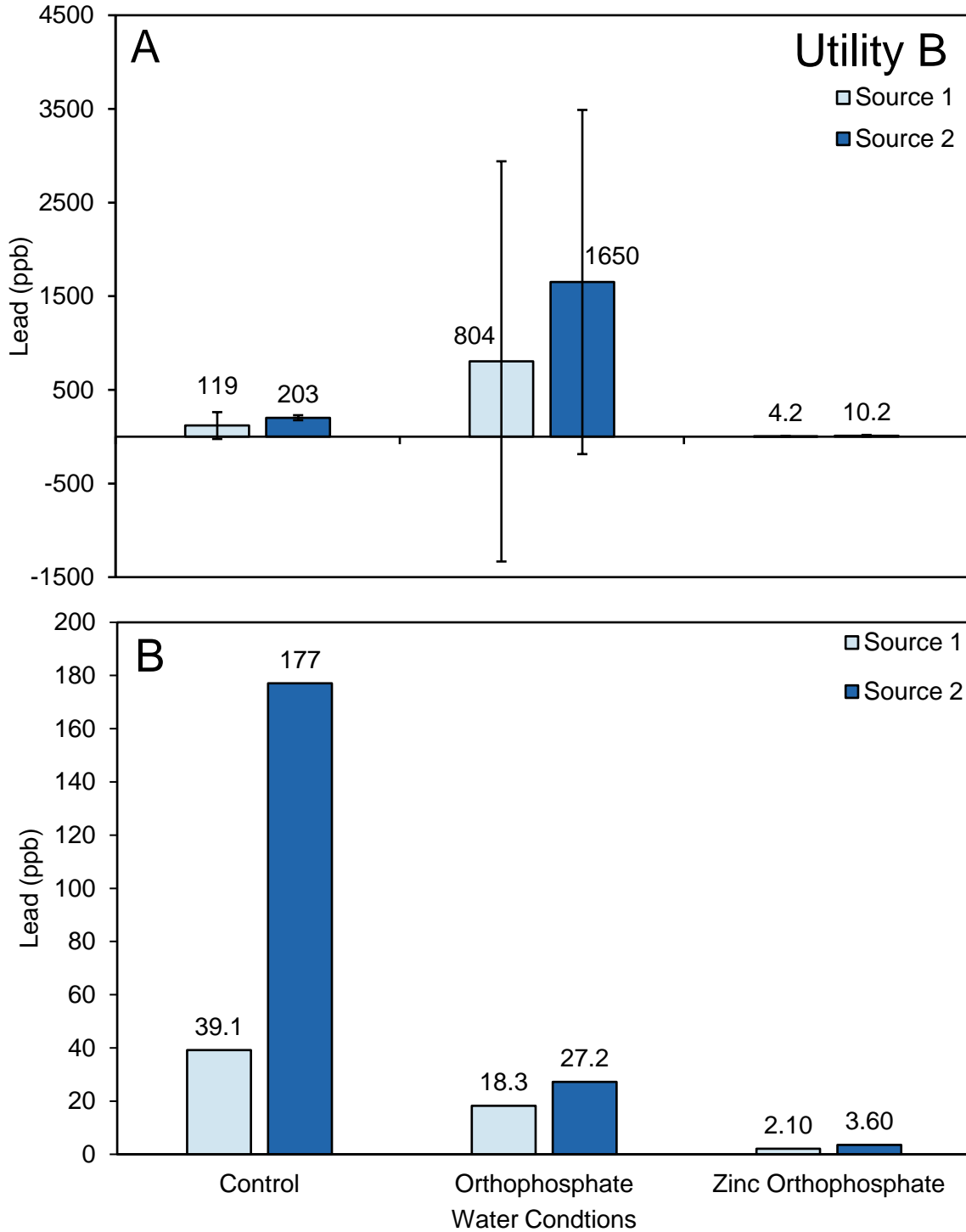


Figure 8. Bar graphs displaying lead data for Utility B with A) 95% confidence interval error bars (n=5) and B) the lowest lead concentration for all inhibitor conditions in week 16.

4.0. Discussion

The bench scale experiments reproduced many of the temporal trends observed in 90%ile lead levels at Utility A which always had high CSMR. Specifically, waters with lower alkalinity without any inhibitors or with orthophosphate alone, had very high levels of lead release. But the combination of zinc orthophosphate with moderate alkalinity had very low levels of lead release. At Utility B with high alkalinity, use of zinc orthophosphate, resulted in dramatic improvements in lead release compared to results obtained with no inhibitor, zinc alone, or orthophosphate alone.

In retrospect, the results of this experiment are somewhat consistent with previous research findings that have sometimes reported profound benefits of zinc orthophosphate in controlling corrosion of lead solder. A few studies have shown that, in low alkalinity (20-30 mg/L as CaCO₃) water, zinc orthophosphate is always more effective in controlling lead release from predominantly solder sources, than pH-alkalinity adjustments alone (Churchill, D.M., et al., 2000; Lee, R. G., Becker, W. C., & Collins, D. W, 1989).

In another study with low alkalinity water (8 and 20 mg/L as CaCO₃) and lead solder-copper coupons, zinc orthophosphate and orthophosphate had no difference when chloride levels were lower. When chloride increased by 5 (CSMR =10), zinc orthophosphate conditions had 90% less lead than when orthophosphate was dosed alone (Schneider, O.D., 2011). In 1990, Gregory found that zinc orthophosphate was superior to zinc or orthophosphate alone at reducing corrosion potential between lead and copper (Gregory, R., 1985). The benefits of zinc orthophosphate were successful at reducing lead in 2 cases tested with alkalinity of 115 and 185 mg/L as CaCO₃.

Experiments have also acknowledged the role of pH in the effectiveness of zinc orthophosphate, suggesting that pH's around 7.5 and ≥ 8.0 work better for passivation of the orthophosphate when coupled with zinc (Churchill, D.M., 2000; Lee, R. G., Becker, W. C., & Collins, D. W, 1989; Schneider, O.D., 2011). Considering zinc orthophosphate had the lowest lead release at higher alkalinity, which also tends to have higher pH, the combination of alkalinity and higher pH may still be influential in determining the magnitude of benefits from zinc phosphate.

While this study did not reveal a mechanism for the role of zinc in mitigating galvanic corrosion, there were differences on the copper surfaces when the zinc is present in either low or high alkalinity water. These differences are somewhat consistent with expectations based on classic mixed inhibitor corrosion theory regarding the action of zinc phosphate. More definitive results must await future research.

5.0. Conclusions

- Zinc orthophosphate proved to be the best inhibitor for control corrosion of lead solder in high CSMR waters at both Utility A and B, with both lower average levels of lead and lower variability from sample to sample.
- If zinc orthophosphate is used in conjunction with a higher alkalinity finished water, the corrosive effects of higher chloride were mitigated, especially for Utility B.
- Alkalinity may play a key role in the effectiveness of inhibiting lead solder corrosion. Although further research is needed to determine exactly how this occurs, zinc orthophosphate appears less effective in low alkalinity waters with high CSMR.
- Although the coupons exposed to lower alkalinity water had higher lead levels when compared to the higher alkalinity in these tests of a few months duration, over much longer periods of time the zinc orthophosphate might eventually passivate to mitigate the high lead release.
- Regardless of the alkalinity, lead release in waters with zinc orthophosphate were equal or lower than any other condition in the coupon testing.
- At moderate alkalinity, more zinc deposited on the cathode, and the deposit was less uniform than at lower alkalinity. This might indicate that zinc is a cathodic inhibitor, slowing the rate of galvanic corrosion by reducing the rate of oxygen reduction.

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APPENDIX A

Final Report: Evaluation of Corrosion Control Alternatives for Lead Corrosion (Utility A)

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1. Introduction

Lead in water is increasingly a public concern given United States Environmental Protection Agency (U.S. EPA) efforts to revise the Lead and Copper Rule (LCR), the 2014-2015 water crisis in Flint MI, and the U.S. Centers for Disease Control (CDC) lowering the blood lead level of concern from 10 to 5 ug/dL (ACCLPP, 2012). The current LCR requires Utility action if 10% of samples collected from high risk homes exceed 15 ppb, including consideration of optimized corrosion control and provision of public education helping consumers avoid lead in water hazards.

For utilities without lead service lines, lead solder installed in homes before 1986 is often a dominant source of water lead (Edwards & Triantafyllidou, 2007; Oliphant, 1983; Walker, R.J., & Oliphant, R.J., 1982). When copper pipes that are connected with lead solder come into contact with a water with a Chloride-to-Sulfate Mass Ratio (CSMR) above the threshold of > 0.6, serious lead in water problems can arise from galvanic corrosion between the lead solder and copper metal (Edwards & Triantafyllidou, 2007; Edwards et al, 1999; Gregory, 1990; Oliphant 1983).

In prior studies of lead solder corrosion with a galvanic connection to copper, unless the CSMR can be adjusted below about 0.6 by simple switching of water treatment chemicals containing chloride to those containing sulfate (e.g., switch ferric chloride to aluminum sulfate coagulant), no other simple and effective solutions to problems with high water lead caused by high CSMR were identified. Normal corrosion control by dosing phosphate proved to be ineffective or sometimes even worsened lead release (Nguyen, Clark, Stone, & Edwards, 2011) and reducing CSMR by removing chloride is very expensive (Pugh, L., & Lake, K, 2016). In one case study in a water with about 8.4 mg/L chloride, 13 mg/L sulfate was added as magnesium sulfate, to successfully adjust the CSMR below 0.6 and reduce lead leaching (DeLorenzo, S., & Klayman, B., 2013), but adding massive amounts of sulfate would be cost prohibitive or holistically undesirable in waters with much higher levels of chloride.

New solutions to reduce water lead caused by high CSMR are needed, because chloride levels (and CSMR) are increasing in many areas of the country due to use of road salts, sea water intrusion in coastal areas and disposal of hydrofracking brine. According to the Salt Institute, from 2013-2014, 17 million tons of salt were applied to highways in the United States (The Salt

Institute, 2014), and this has contributed to a doubling of chloride levels in many rivers from 1990 to 2011 (Corsi, De Cicco, Lutz, & Hirsch, 2015; Kaushal, S., et al, 2005). Salt water intrusion due to declining water tables and sea level rise, can also cause increased chloride levels well over the 250 mg/L secondary MCL in coastal areas (EPA, 2017), as can hydrofracking (EPA, 2015).

The Case of Utility A

Historically effective corrosion control in Utility A was achieved by raising pH to about 8.0, producing 90th percentile lead levels below 8 ppb before about 2011 even when their waters CSMR was well over the 0.6 threshold for problems (**Table A-1**). However, after a switch from aluminum sulfate to aluminum chlorohydrate (ACH), the CSMR increased to above 4.0 and the 90th percentile lead increased to 101 ppb, well over the 15 ppb EPA Lead and Copper Rule (LCR) action level. Intensive follow-up sampling by the Utility demonstrated that the high lead result was not a statistical anomaly. It is believed that the major difference between the 2011 and 2014 LCR testing was the switch from Alum ACH as the coagulant, which not only increased CSMR but also lowered the alkalinity by half. When zinc was added in addition to orthophosphate in 2015, and alkalinity was adjusted back to initial values, by 2016 lead levels had dropped back to 4.5 ppb. Interestingly, although a few prior experiments suggested that zinc orthophosphate could help control galvanic solder corrosion in high CSMR water, in other tests zinc orthophosphate was ineffective (Churchill, D.M., et al, 2000; Edwards & Triantafyllidou, 2007; Gregory, R., & Gardiner, J., 1985; Oliphant, 1983).

In this work the role of zinc orthophosphate in galvanic corrosion of lead solder was evaluated in laboratory studies to answer the following questions:

1. Does Zinc Orthophosphate effectively control lead levels in Utility A water?
2. Will Zinc Orthophosphate continue to work if chloride levels continue to trend higher?
3. How does alkalinity affect the performance of Zinc Orthophosphate?
4. Could Utility A return to using ACH coagulant, without increasing lead levels?

Table A-1. Yearly Historical Data for Utility A

Year	90% Lead ¹ [ppb]	Phosphate [ppb]	Zn [ppb]	Alkalinity [mg/L as CaCO ₃]	Coagulant (ACH ² /Alum)	pH	Chloride [ppm]	Sulfate [ppm]	CSMR ³
2005	7.20		<0.01	61.4	Alum	8.09		11.2	
2006			2.45	57.4	Alum	8.01	28.1	10.4	2.72
2007			4.44	53.4	Alum	7.87	37.2	10.5	3.55
2008	2.92		1.33	58.9	Alum	7.83	32.7	12.0	2.72
2009			1.59	52.2	Alum	7.82	33.7	10.3	3.27
2010		12.4*	2.13	53.3	Alum	7.80	40.7	11.7	3.48
2011	7.64	28.0	1.04	56.8	Alum	8.02	43.0	12.1	3.56
2012		176	1.08	29.5	ACH	7.66	36.6	10.7	3.43
2013		468	1.36	22.9	ACH	7.60	45.7	9.90	4.61
2014	101	758	1.04	20.9	ACH	7.44	52.2	9.80	5.32
1/1/2015- 11/14/2015		472	1.36	56.9	Alum	7.74	55.4	11.3	4.90
11/15/2015- 2/18/2016	4.5	606	307.01	59.0	Alum	7.58		11.8	

*An outlier sample with 84,00 ppb P was excluded from the calculated value.

¹Lead testing was only required every 3 years as per the LCR.

²Aluminum Chlorohydrate (ACH) is a coagulant that is known to have little effect on the pH and Alkalinity of water.

³The chloride-to-sulfate mass ratio (CSMR) is the ratio between the amounts of chloride in a water sample to the amount of sulfate in a water sample.

To evaluate the potential benefits of coupling zinc with orthophosphate and to determine the effects of changing to a sulfate-based coagulant, a bench-top experiment was completed using copper couplings with lead solder, and a galvanic solder and copper pipe macrocell, to observe lead leaching.

2. Materials and Methods

2.1. Apparatus

2.1.1. Preparation of Lead Solder-Copper Couplings

Utility A

To prepare copper couplings for the lead leaching tests, a ½” piece of 50:50 lead: tin solder was evenly melted onto the interior surface of a 7/8”, 3/8” diameter copper pipe couplings. Each coupling was placed in a 100-mL glass jar.

2.1.2. Preparation of Galvanic Pipe Macrocell

In addition to the copper coupling apparatus, 60 simulated copper joints (microcells) were constructed to observe and confirm results in the copper coupling experiment. Six-inch copper pipes (12 mm diameter) were connected with a silicone adhesive (GE Silicone II Household Silicone Adhesive) to 2-inch long polyvinyl chloride (PVC) pipes, creating a 75 mL macrocell (**Figure A-1**). Rubber stoppers sealed with plumbing tape, were used to create a water-tight seal at both ends of the macrocells. To create the lead anode, a 3-inch piece of lead solder was inserted through a hole at the top of the PVC pipe rubber stopper such that 1 ½” inches were exposed to water and 1 ½” inches were left on the outside of the PVC pipe. Between the copper pipe and lead solder was ½” space on the side of the PVC pipe. Copper wire attached to an alligator clip externally connected the lead solder, left on the outside of the PVC pipe, to the copper pipe to form a galvanic connection allowing for ammeter measurements of current and voltage. The macrocell apparatus stood vertically with the PVC section at the top end and the copper pipe at the bottom end.

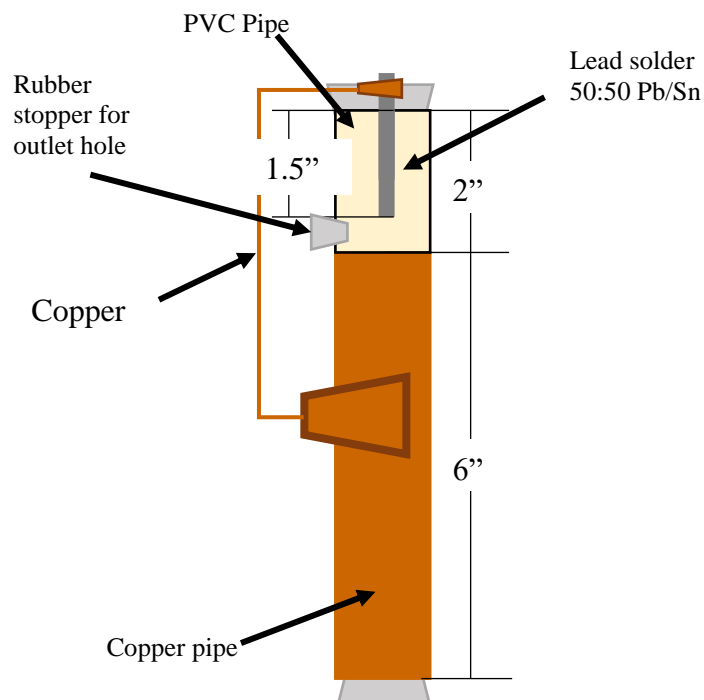


Figure A-1. Pipe macrocell apparatus for mechanistic studies.

2.2 Experimental Methods

To condition both the coupling and macrocell reactors, each apparatus was rinsed three times with 0.1 M sodium bicarbonate (resulting in pH 8 ± 0.5 and alkalinity 500 ± 25 mg/L as CaCO_3) and 2 mg/L free chlorine (dosed from 5000 mg/L sodium hypochlorite stock solution). To identify outliers, a composite sample was collected three times, once after three 24-hour stagnation periods to identical water, for a total composite volume of 150 mL per coupling and 225 mL per macrocell. Each composite sample was preserved with 2% v/v nitric acid and analyzed by a Thermo Electron X-Series ICP-MS for lead and copper concentrations after minimum 16-hour stagnation. Lead concentrations for each coupling and macrocell were organized in ascending order and the lowest and highest concentrations were eliminated as outliers to lower the standard deviation of each sample (coupling and macrocell) used for experiments. This resulted in a total of 110 copper coupling jars and 48 macrocells. The coupling jars were grouped into five replicates whereas the macrocells were sorted into duplicates or triplicates based on a similar average and standard deviation of lead concentration (**Table A-2**).

In an attempt to re-create the historical corrosion control and baseline condition, all 110 couplings and 48 pipes were evaluated for lead and copper leaching in a synthesized low chloride water representing Utility A's water in 2006. For two weeks, water was collected Monday, Wednesday and Friday and at the end of each week, and a composite sample was collected of 150 mL per each coupling and 225 mL from each pipe.

Since a change of coagulant was being explored, 20L samples from both the treatment plant's combined filter effluent (CFE) and river influent was shipped to Virginia Tech on a weekly basis until the end of the project, along with 1L of water from each partner Utility. The river influent water was treated in the lab using Kemira PAX-XL19 polyaluminum chloride (ACH) as the coagulant. Treatment schematics were supplied by the municipality and were used to replicate the treatment process to the extent possible using laboratory simulations. Chloramine was added to the CFE water for use in the experiment, but levels were not monitored for the duration of the project.

Table A-2. Water combinations for coupling and pipe experiments

	Water Combinations	Pipes	Couplings
Low Alkalinity (raw water treated with ACH)	No Inhibitor + Current Chloride	2	5
	No Inhibitor + High Chloride	2	5
	Phosphate + Current Chloride	3	5
	Phosphate + High Chloride	2	5
	Zinc + Current Chloride	3	5
	Zinc + High Chloride	2	5
	Zinc Phosphate + Current Chloride	3	5
	Zinc Phosphate + High Chloride	3	5
	MgSO4+ Current Chloride	2	5
Present alkalinity	No Inhibitor + Current Chloride	2	5
	No Inhibitor + High Chloride	2	5
	Phosphate + Current Chloride	3	5
	Phosphate + High Chloride	2	5
	Zinc + Current Chloride	3	5
	Zinc + High Chloride	2	5
	Zinc Phosphate + Current Chloride	3	5
	Zinc Phosphate + High Chloride	3	5
	Low Zinc + Current Chloride	0	5
	No Inhibitor + Low Chloride	2	5
Partner Utilities	New Jersey Water Supply Authority	0	5
	Southeast Morris County Municipal Utilities Authority- Site 1	0	5
	Southeast Morris County Municipal Utilities Authority- Site 2	0	5
Total		22	44
			110

Once the water was completely treated, a total of 22 water combinations were tested (**Table A-2**). There were 16 main water conditions which were comprised of four inhibitor conditions, two chloride levels and 2 alkalinities. The four inhibitor conditions observed were a control (no inhibitor), zinc (made with a 100 mg/L zinc chloride stock), orthophosphate (made with a 1000 mg/L stock of Disodium Hydrogen Phosphate and Sodium Dihydrogen Phosphate Dihydrate) and a zinc orthophosphate stock provided by Shannon Chemical (SLI-5216, Liquid Zinc Orthophosphate). The two chloride levels included the current level of 55 mg/L and a forecast value of 75 mg/L ten years hence, to test how the inhibitor conditions would respond to projected increased chloride levels. The Utility also wanted to explore the effect a coagulant change from a sulfate coagulant would have on corrosion control, so ACH was used to treat incoming CFE with a finished alkalinity lower than that of the sulfate-based coagulant treated water.

Each inhibitor was dosed at the following concentrations (**Table A-3**):

- a. Zinc- 0.400 mg/L
- b. Orthophosphate- 0.650 mg/L as P
- c. Zinc Orthophosphate- 0.400 mg/L a P + \cong 0.650 mg/L¹

Along with the 16 main water conditions, three unique water conditions were included to represent various points in the historical timeline of the Utility, one of which had a low zinc concentration, one with a low chloride, and one with magnesium sulfate (**Table A-3**). Water was also supplied from two partner Utilities, Utility 1 and Utility 2 which added three additional test water combinations.

¹ The Shannon Chemical zinc orthophosphate solution had a 1:5.5 ratio of zinc to phosphate so to ensure the zinc concentration was at the target concentration of 0.400 mg/L, the zinc orthophosphate was dosed based on the measured Shannon chemical zinc concentration.

Table A-3. Final water chemistry for all 22 water conditions

Water Condition	pH	Alkalinity mg/L as CaCO ₃ (A or B)*	mg/L as P	mg/L as Zn	mg/L as Cl	mg/L as S
No Inhibitor + Present Chloride	7.5-7.8	A and B	----	----	----	----
No Inhibitor + High Chloride		A and B	----	----	75.0	----
Phosphate + Present Chloride		A and B	0.650	----	----	----
Phosphate + High Chloride		A and B	0.650	----	75.0	----
Zinc + Present Chloride		A and B	----	----	0.400	----
Zinc + High Chloride		A and B	----	----	0.400	75.0
Zinc Phosphate + Present Chloride		A and B	0.650	0.400	----	----
Zinc Phosphate + High Chloride		A and B	0.650	0.400	75.0	----
MgSO ₄ + Present Chloride		B	----	----	----	90.0
Low Zinc + Current Chloride		A	0.650	0.250	----	----
No Inhibitor + Low Chloride		A	----	----	35.0	----
Partner Utility A-1 (SMCMUA)			----	----	----	----
Partner Utility A-2 (SMCMUA)			----	----	----	----
Partner Utility B (NJWSA)			25.0	----	0.400	----

For a total of 14 weeks, lead release in both couplings and pipes were measured along with the galvanic potential and current of each Macrocell. The pH of each water condition was maintained between 7.5 and 7.8 by adjusting with carbon dioxide to lower the pH and by adding sodium hydroxide to increase the pH. To simulate the movement of water moving through a pipe, couplings were housed on a shaker table for the duration of the project.

During the first week of experimentation, the pH was measured in the separated cathode and anode compartments using the rubber stopper in the PVC section and the bottom rubber stopper. For the remaining weeks, all samples were taken as composite samples until conditions stabilized. At the end of the 13th week, individual samples were taken Monday, Wednesday and Friday, creating a pool of 15 individual samples for each water type and 9 samples per water condition with triplicates (**Table A-1**). It is important to note that for the first two weeks of sampling, higher doses of Orthophosphate and Zinc were used to speed up the conditioning process for the pipes.

3. RESULTS AND DISCUSSION

Experiments were designed to examine the lead release issue from the perspective of historical, present day and projected future Utility A water qualities in terms of chloride and alkalinity, as well as the effectiveness of various corrosion control options including no inhibitor,

orthophosphate, zinc, and zinc orthophosphate. Two experimental approaches were used including simulated copper and lead solder joints and macrocell experiments.

3.1. Copper and Lead Solder Couplings

3.1.1 Temporal Trends in Composite Samples for No Inhibitor, Zinc Orthophosphate and Phosphate: Low versus Present day (higher) alkalinity

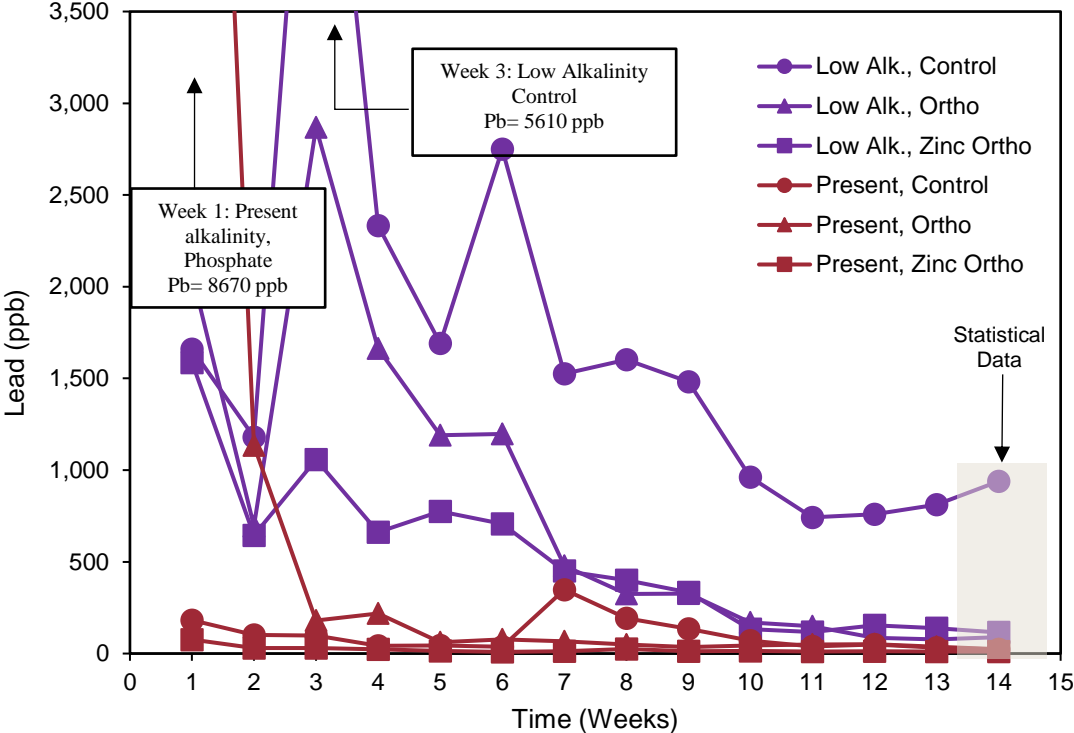


Figure A-2. Composite samples of the control, orthophosphate, and zinc orthophosphate conditions for present day chloride levels. Data for other conditions in Appendix B.

Representative lead data for composite samples from the lead solder coupons illustrate temporal trends in lead release during the first 13 weeks of testing as the coupons passivated (**Figure A-2**). A short-term steady state lead release was achieved by about week 13, at which point testing was conducted of individual replicates to judge statistical rigor of the trends. As expected, given the highly variable nature of galvanic corrosion as manifested by lead release to water, lead levels over time were very erratic during the first eight weeks. But even considering this variability some trends were clear. Specifically, the 3 inhibitor conditions (No inhibitor, zinc orthophosphate, orthophosphate) with present day higher alkalinity water, always had lower lead release than the corresponding conditions with low alkalinity ($p < 0.05$; ANOVA) after week 3. Moreover, the higher alkalinity water showed much faster reductions in lead release, than did the

lower alkalinity water (**Figure A-2**). This result may explain why a switch from higher alkalinity water to lower alkalinity water in 2011-2012, may have triggered a spike in 90%’ile lead at UTILITY A homes.

3.1.2. Statistical analysis of experimental replicate data (week 14)

When the week 14 data were collected from individual experimental replicates ($n = 15$) and summarized with box-plots (**Figure A-3**), the overarching role of alkalinity is again apparent (Figure 3). For the control condition with no inhibitor (**Figure A-3**, upper left), the two conditions at low alkalinity not only had higher average lead, but the lead was also much more variable as indicated by the very wide error bars. From both of these perspectives (average lead, variability in release) the higher present-day alkalinities represent a dramatic improvement in lead corrosion control versus the corresponding condition at lower alkalinities ($p < 0.05$). For the control condition median lead was 20-30 ppb at the present-day alkalinity, with either present day Cl⁻, lower Cl⁻ or high Cl⁻ and results were not statistically different from one another (Figure 3, upper left). But the conditions with lower alkalinity had median lead of 878-889 ppb, which are at least 29 times worse than the results at higher alkalinity (**Figure A-3**, upper left). The dosing of zinc alone caused no statistically significant differences in lead release, compared to the corresponding control condition without any inhibitor (compare upper left to upper right, Figure 3).

The dosing of zinc orthophosphate reduced median lead release by 62-92%, compared to the corresponding condition with either no inhibitor or zinc alone. All of these results are statistically significant ($p < 0.05$). The most dramatic reduction occurred for the low alkalinity condition with high chloride, for which median lead was decreased from 590-890 ppb with no inhibitor or zinc, down to 60 ppb when zinc orthophosphate was dosed ($p < 0.05$). Generally speaking, zinc orthophosphate was superior in corrosion control compared to orthophosphate ($p < 0.05$), with the exception of the condition with low alkalinity and lower chloride for which the two approaches were not significantly different. The relative advantage of zinc orthophosphate was most apparent in the low alkalinity and high chloride condition, for which median lead was 60 ppb compared to 907 ppb for the corresponding condition with orthophosphate alone.

It is important to note the large-scale implications of these results, as they are representative of the historical trends from 2011 to 2015. The week 14 result (median lead concentration) most representative of the water conditions in 2011, is the high alkalinity control with 20.4 ppb lead. The result that best represents the water conditions in 2014, during the time in which the city fell out of compliance with the lead and copper rule is 57.3 ppb for the low alkalinity, orthophosphate condition. The result that best represents the state of the water condition in present day is the high alkalinity, zinc orthophosphate condition with median lead levels at 7.74 ppb. While the lead levels that represent the present condition of the water quality for Utility A are still above 0 ppb, the water is meeting federal regulation with the combination of zinc and orthophosphate.

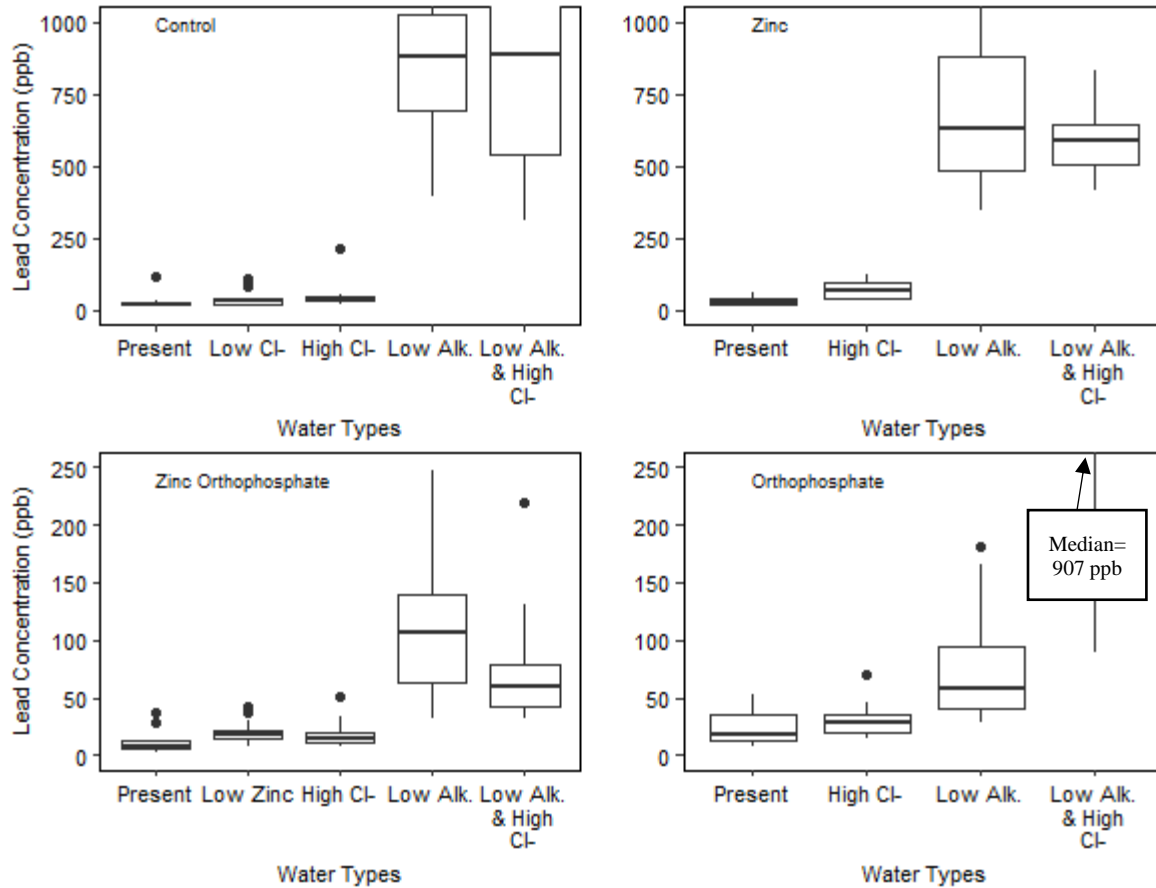


Figure A-3. Boxplots of statistical data based on week 14 replicates (n = 60). Note axis for zinc orthophosphate and orthophosphate is 0-250 ppb whereas those for no inhibitor or zinc is 0-1000 ppb.

3.1.3 Relationship between Lead and Copper

A statistical analysis based on replicate samples during the 14th week of sampling, was used to examine possible relationships between Lead and Copper. During the final week of testing (week 14) individual samples were taken Monday, Wednesday, and Friday. Each inhibitor condition had 4 water conditions and for each of those water conditions were 5 replicate couplings. Individual samples were taken three times in the final week, totaling 15 individual samples per water condition. To show the relationship between lead and copper all of the individual sample data points were graphed creating 60 data points for each inhibitor.

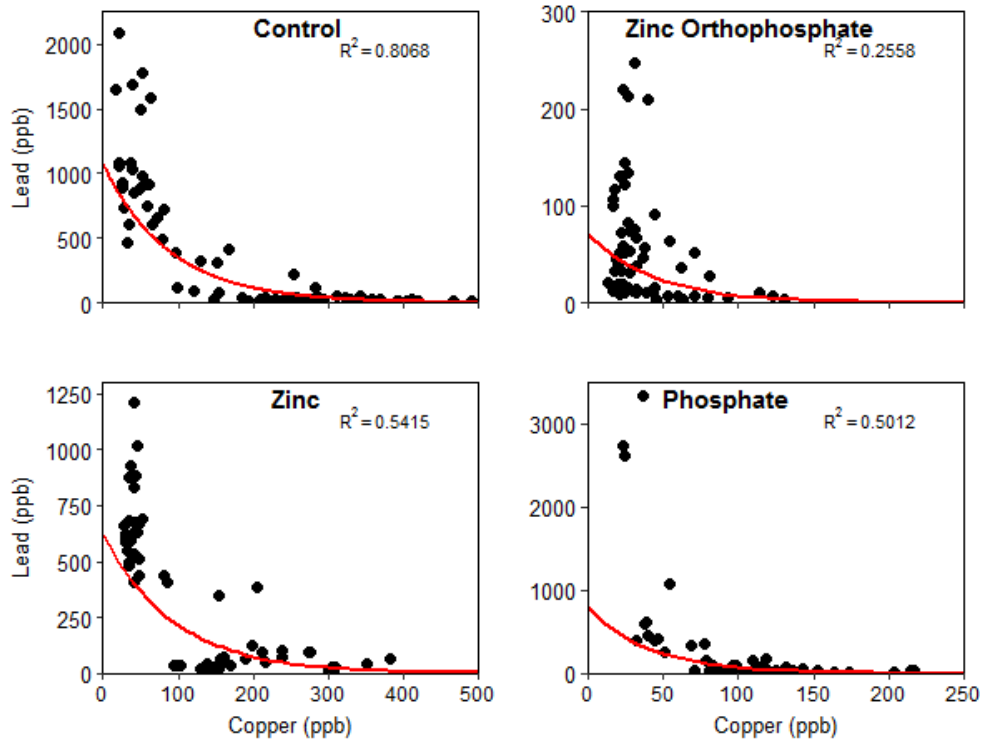


Figure A-4. Galvanic corrosion model of each inhibitor condition.

Equation A-1.

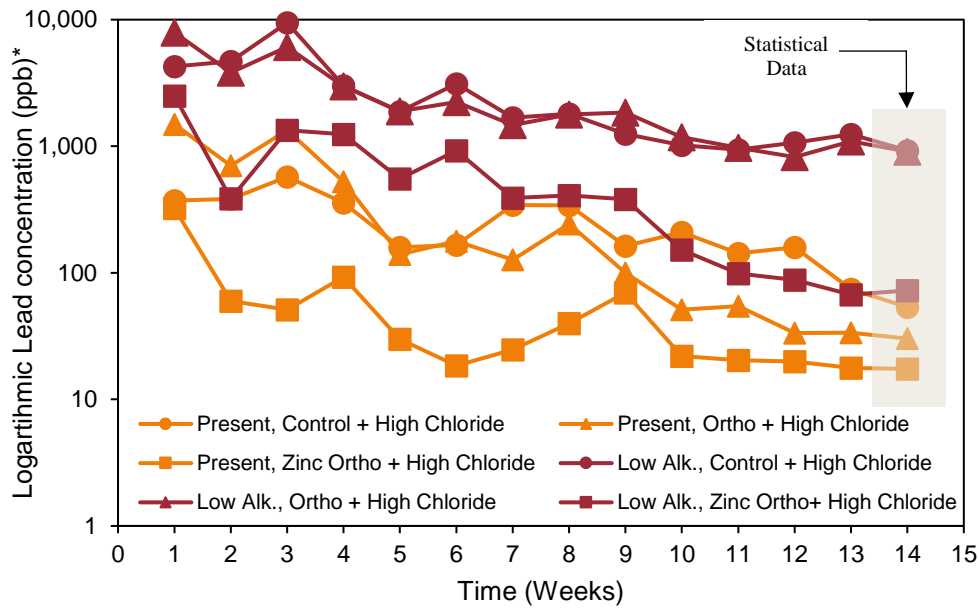
$$Pb=C*\exp^{(-1*B_0)}$$

Table A-4. Exponential decay Shapiro-Wilks statistic values and slopes

Inhibitor	l	W-Statistic	P-Value
Control	-0.0112	0.968	0.0534
Orthophosphate	-0.0239	0.982	0.515
Zinc	-0.0106	0.905	2.26E-04
Zinc Orthophosphate	-0.0222	0.967	0.102

To the extent there is galvanic corrosion, the lead solder is sacrificed, and the copper pipe is protected. Hence, lower copper in the water can be expected to co-occur along with the higher lead. When lead concentration was plotted versus the copper concentration, this possible inverse relationship was confirmed for the waters tested in this work (**Figure A-4**). This provides further evidence that galvanic corrosion was key control on lead release.

3.1.4 High Chloride Analysis for Coupons



* The y-axis has been changed into a logarithmic axis to display all of the data on one graph.

Figure A-5. Average lead release in composite coupling samples in the control, orthophosphate, and zinc orthophosphate conditions for high chloride levels.

Two chloride concentrations were tested during this experiment-- the present-day chloride (55 mg/L) and the 10-year projected future chloride concentration (75 mg/L). For these tests lower alkalinity water always had much higher lead than the corresponding conditions with higher alkalinity waters (**Figure A-5**). For both low and high alkalinity, the zinc orthophosphate inhibitor, always had the lowest lead concentrations averaging at 17.4 ppb for the high alkalinity water and 73.4 ppb for the low alkalinity water.

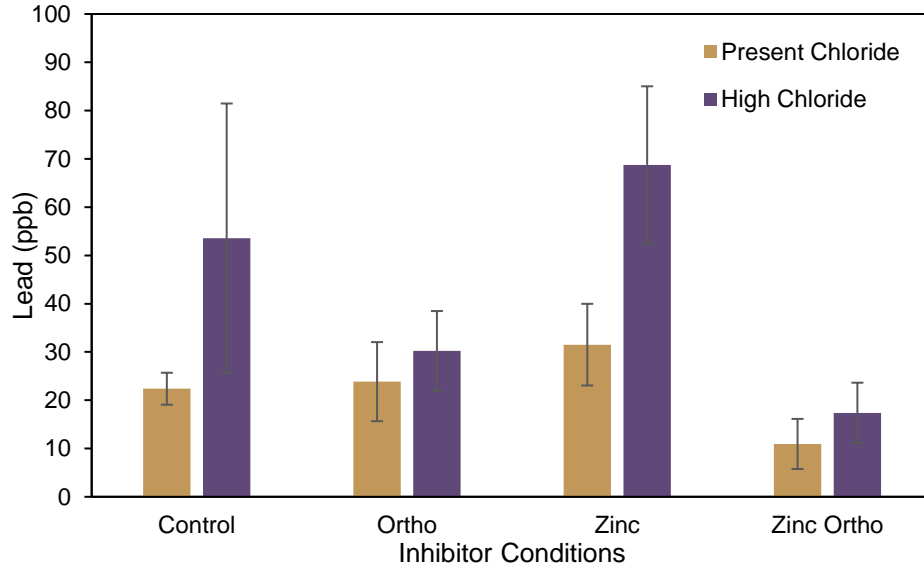


Figure A-6. Bar graph, with 95% confidence interval error bars displaying high chloride and present chloride data for high alkalinity waters in week 14 (n=15).

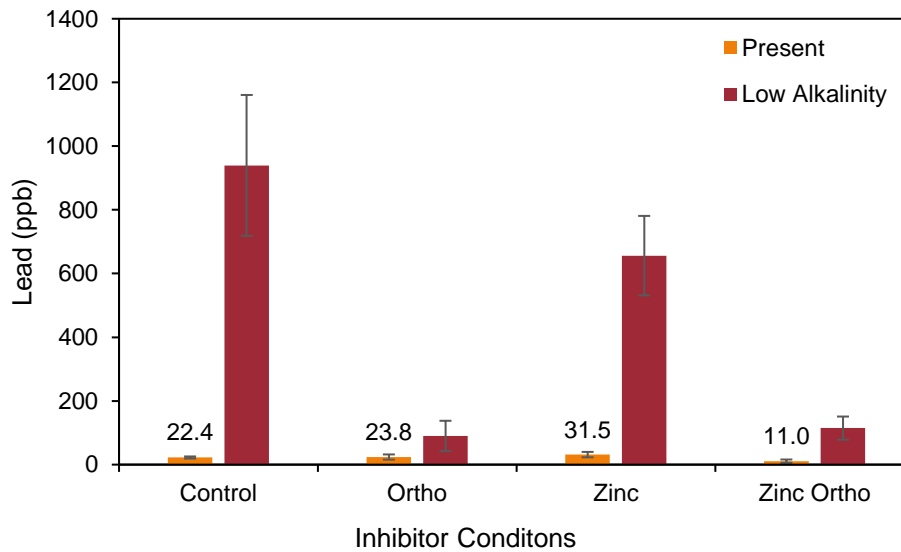
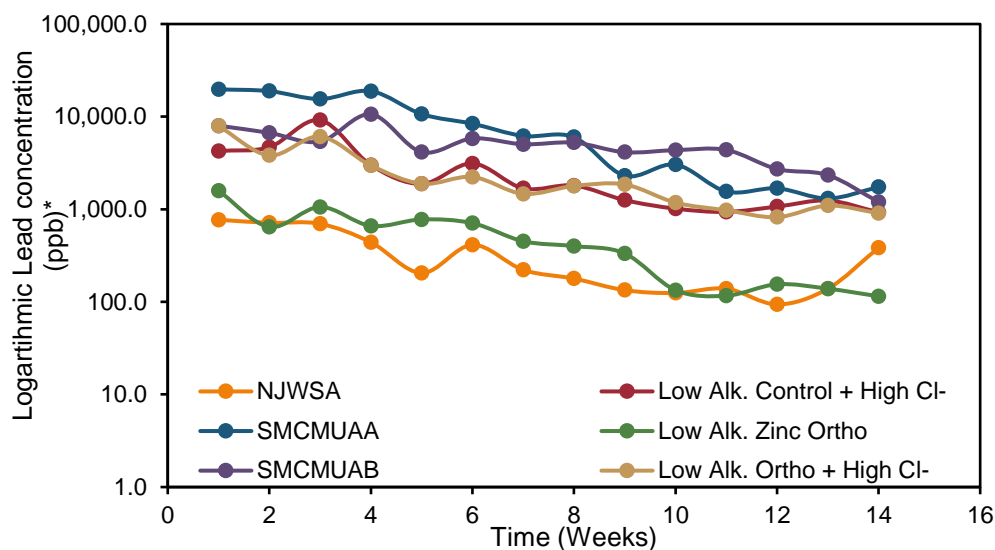


Figure A-7. Bar graph, with 95% confidence interval error bars, displaying high chloride data for the present and low alkalinity inhibitor conditions in week 14 (n=15).

When comparing the performance of the high alkalinity and present chloride waters to high alkalinity and higher chloride waters at 95% confidence, the results were not statistically different with the exception of zinc alone (**Figure A-6**). However, the concentration of lead was the lowest in coupons with zinc orthophosphate, regardless of chloride concentration. Hence,

zinc orthophosphate is mitigating lead release better than the other inhibitors, at both low and high chloride. When comparing high chloride data between low and high alkalinities, it is clear that each high alkalinity sample is statistically lower than the low alkalinity sample (**Figure A-7**). Again, alkalinity is an overarching factor controlling how well each inhibitor reduces corrosion of lead.

3.1.5 Partner Utility Comparison



* The y-axis has been changed into a logarithmic axis to display all of the data on one graph.

Figure A-8. Average lead release in composite coupling samples for nearby utilities and their respective comparison condition.

Water from nearby utilities included in this study were tested to examine how their corrosivity compared to Utility A water under similar test conditions. Utility 2 used zinc at 300 ug/L and orthophosphate at 350 ug/L as their corrosion control, and the chloride levels were about 50 mg/L and the finished water alkalinity measuring was 25 mg/L as CaCO₃. When the Utility A water was treated with zinc orthophosphate, the resulting lead concentrations were comparable (**Figure A-8**), but when only orthophosphate was used the Utility A water produced lead levels that were 2.75 times higher on average (**Figure A-8**).

Two waters were received at Virginia Tech from Utility 1 during the testing. Site 1 didn't use corrosion control although chloride levels were at 280 mg/L whereas site 2 (did use orthophosphate at 100 ug/L as P with chloride levels at 180 mg/L. Since the test alkalinity for each site was 15 mg/L, site 1 was compared to Utility A's low alkalinity, control condition with

high chloride while site 2 was compared to the low alkalinity, orthophosphate condition with high chloride (**Figure A-8**).

Site 1 from Utility 1 was the most aggressive. Compared to the low alkalinity condition with high chloride, Site 1 and 2 performed poorly with lead levels significantly higher than those in Utility A water ($p < 0.05$). While Utility 2 had the lowest lead levels in week 14 at 385 ug/L (44% decrease), the lead was still significantly higher than that of the Utility A water low alkalinity condition ($p < 0.05$).

Although corrosion control was used for Utility 2 and Site 2 at Utility 1, the aggressive nature of the water is due to the high levels of chloride and low alkalinity. A key hypothesis of this work, is that there might have been chemical constituents in the Utility 2 water, that rendered it less corrosive than the Utility 1 water. However, that does not appear to be the case.

3.2 Galvanic Solder Macrocell

3.2.1 Phosphate vs. Zinc Orthophosphate

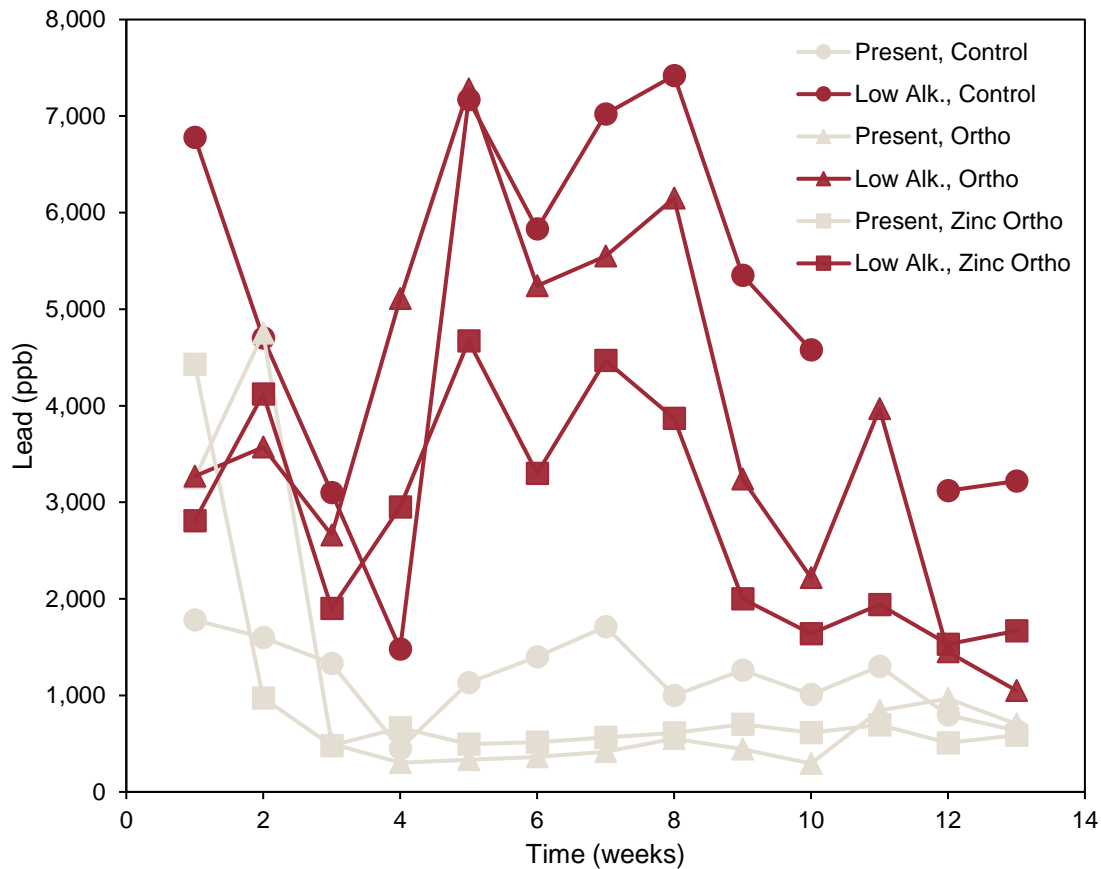


Figure A-9. Average lead release in composite macrocell samples for orthophosphate and zinc orthophosphate for present chloride levels.

Compared to the couplings data (**Figure A-3**) which reproduced the expected trends observed in the field data, the macrocell data indicated a different trend in lead over time and did not give results consistent with expectations. The lead levels for low alkalinity conditions increased and then decreased again, making overall reduction in lead release over time very slight. The present alkalinity conditions appeared to stay the same over time and were not that different from each other. The low alkalinity, phosphate condition had the highest decrease in lead from the first week of testing to the last week at 61% lower lead levels. For the present alkalinity conditions, the control had a 49% decrease in lead which was the largest for that alkalinity. While the low alkalinity conditions for zinc orthophosphate and orthophosphate decreased in lead over time, there was a 42% increase for the present, orthophosphate condition from week 3 to week 14 and a 22% increase for zinc orthophosphate in the present condition. Although zinc orthophosphate did not decrease the lead levels, it did stop them from increasing as much as was observed in the system with orthophosphate (**Figure A-9**).

For the low alkalinity conditions, zinc orthophosphate performed poorly in comparison to the orthophosphate ($p=0.014$). As seen in the coupling testing, the inhibitors did not do well to decrease lead and that is confirmed in the macrocells. As to why the orthophosphate performed better than the zinc orthophosphate, that cannot be explained, but in any event, it is not consistent with the coupling testing or the trends in the field data. We speculate that the failure of this test, was due to the spatial separation between the anode and cathode, which has not been an impediment in past studies but may have been problematic in this work.

3.2.2 Relationship between Lead and Current

Table A-5. Properties of the line of best-fit for the present and low alkalinity macrocells of lead vs. current.

Inhibitor	Low Alkalinity		Present alkalinity	
	Slope	R ²	Slope	R ²
Control	375	0.389	391	0.858
Orthophosphate	353	0.693	246	0.618
Zinc	1053	0.828	455	0.828
Zinc Orthophosphate	152	0.411	170	0.527

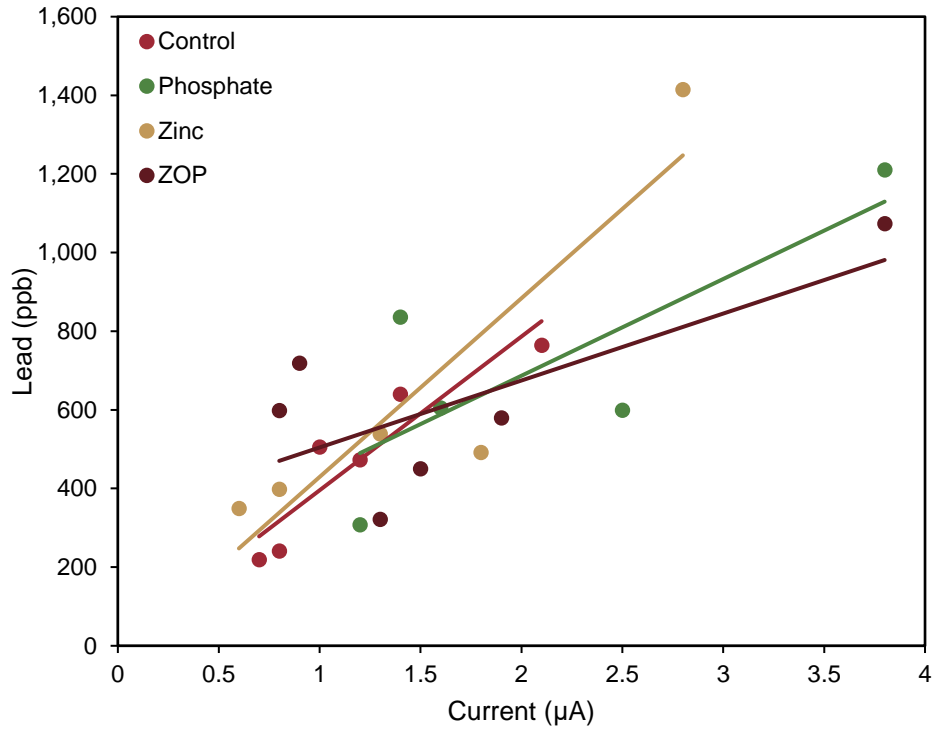


Figure A-10. Lead vs. current for present alkalinity inhibitor conditions.

Statistical data collected in the last week of testing was used to explore a relationship between lead and galvanic current using the macrocells. Based on the R^2 values in **Table A-5**, a moderate to high correlation is shown for all the inhibitor conditions. This is also displayed in **Figure A-10**, where the regression lines show linear relationships. According to **Table A-5**, the slope of each line varies for each condition, consistent with expectations given that a varying percentage of lead goes into the scale dependent on the condition studied. The correlation was high for both zinc and orthophosphate showing that the current caused the lead release for those conditions.

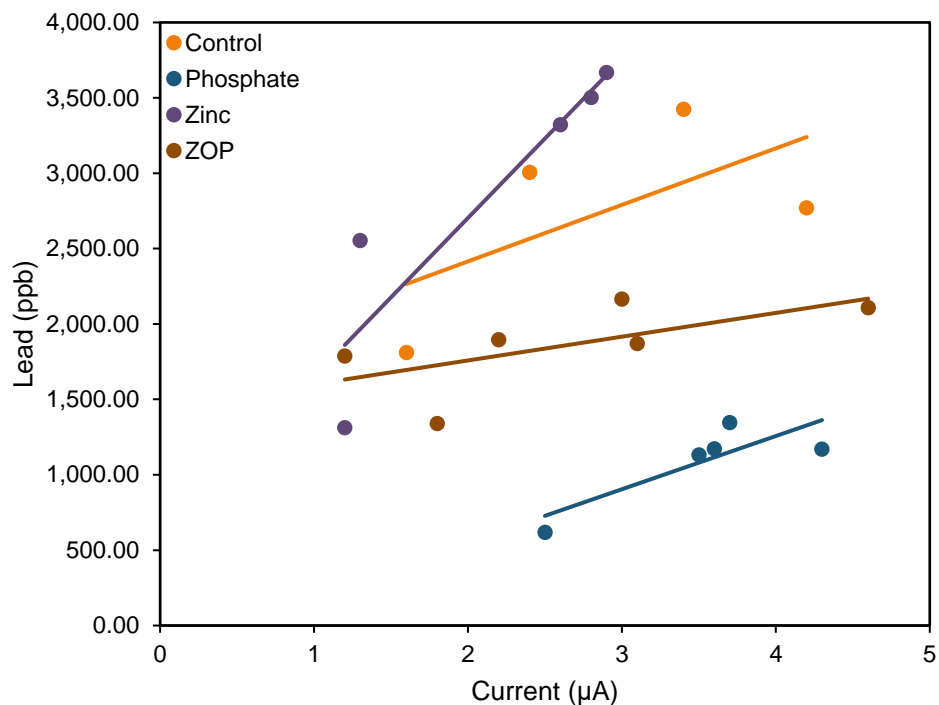


Figure A-11. Lead vs. Current for low alkalinity inhibitor conditions.

Interestingly, zinc orthophosphate had a slope less than half that of the orthophosphate in the low alkalinity conditions ($p=0.014$), suggesting that the galvanic corrosion did not cause as much problem with higher lead (**Table A-3, Figure A-11**). Essentially, a given amount of galvanic current, contributes half the lead to water if the zinc was present. Following up on this trend may reveal the mechanism by which zinc works.

It should be noted that zinc orthophosphate had the lowest slope for both alkalinities which suggests the current doesn't have a large effect on lead release when zinc is used with orthophosphate.

3.2.3 Anode and Cathode Analysis

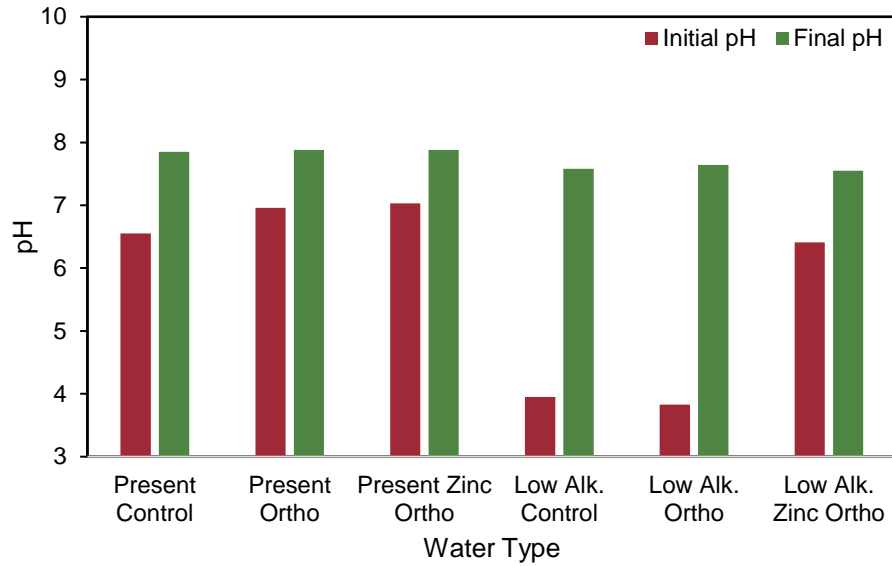


Figure A-12. pH change in Anode (Pb)

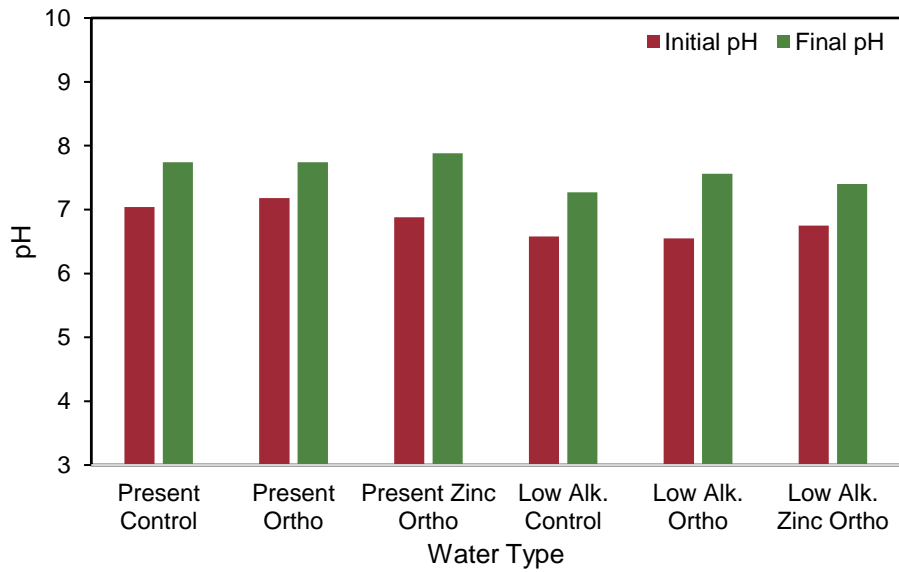


Figure A-13. pH change in Cathode (Cu)

The pH was measured at the anode and cathode during the first and final week of water changes (**Figure A-12**, **Figure A-13**). Overall the pH at the anode and the cathode, in the final week, was not very different between conditions. However, in the earlier part of the experiment, **Figure A-12** shows that there was a big change in pH at the anode for the low alkalinity control and ortho conditions. In particular, the waters at low alkalinity, had extremely low pH at the anode, which

is consistent with the adverse effects of galvanic corrosion on lead release from solder (**Figure A-12**; Dudi, A., 2004). Again, it is speculated that the distance between the anode and cathode, somehow reduced the influence from galvanic corrosion in the macro-cells with time, relative to what would occur in practice and in the parallel testing with the coupons.

3.3. Environmental Scanning Electron Microscope Analysis

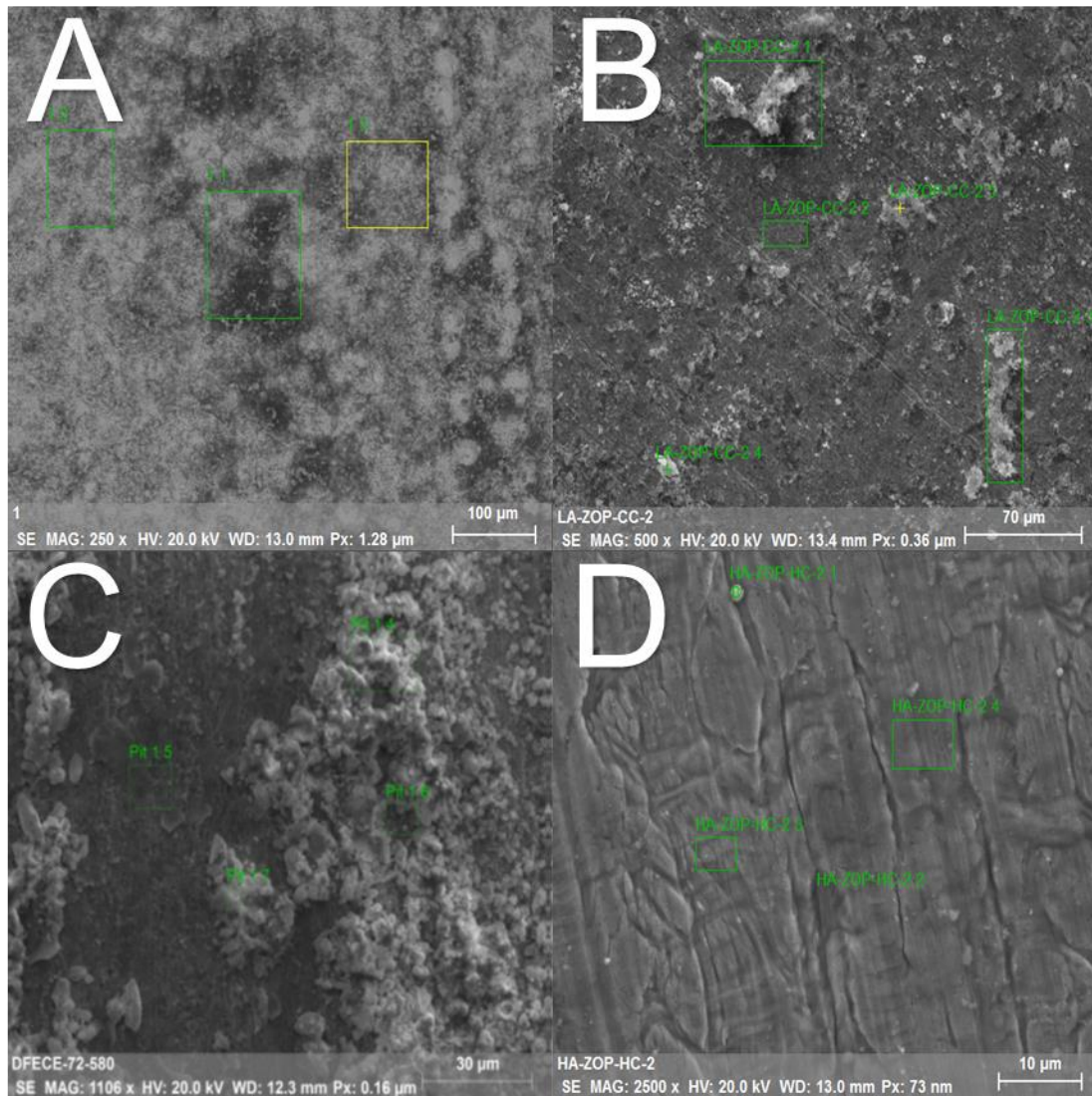


Figure A-14. ESEM images of copper and lead surfaces in the macrocell. The images show A) low alkalinity, zinc ortho lead solder, B) low alkalinity, zinc ortho copper pipe, C) high alkalinity, zinc ortho lead solder, and D) high alkalinity, zinc ortho copper pipe.

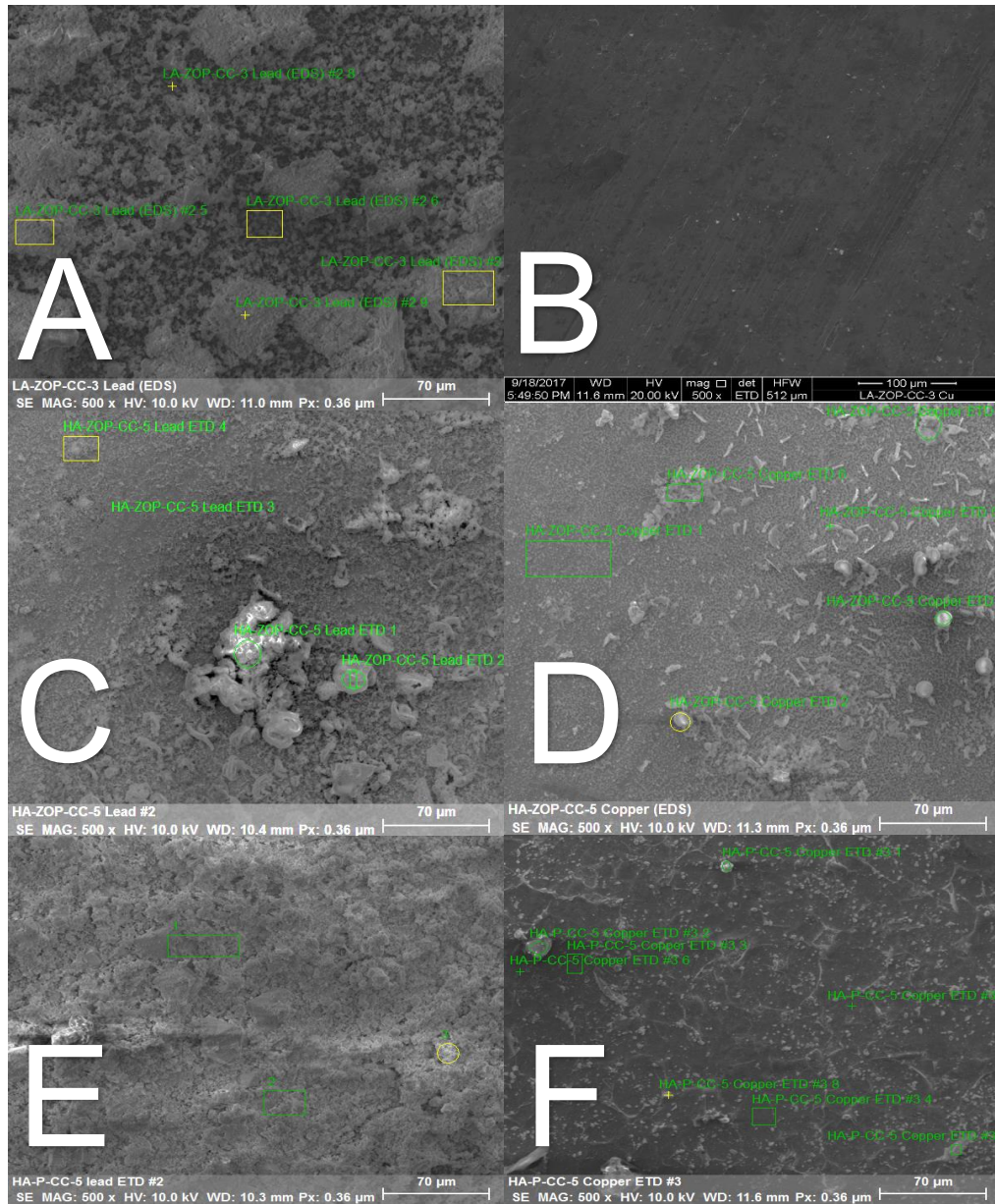


Figure A-15. ESEM images of lead solder and copper surfaces from the coupon testing. The images show A) low alkalinity, zinc ortho lead solder, B) low alkalinity, zinc ortho copper coupling, C) high alkalinity, zinc ortho lead solder, D) high alkalinity, zinc ortho copper coupling, E) high alkalinity, ortho lead solder, and F) high alkalinity, ortho copper coupling.

Environmental Scanning Electron Microscope (ESEM) analysis is used to capture images of environmental samples under pressure (Knowles, W.R., 2005). To possibly determine the mechanism of how zinc orthophosphate acted to reduce galvanic corrosion, low alkalinity samples and present-day alkalinity macrocells and couplings were analyzed under the ESEM. According to theory of how zinc phosphate acts, zinc is believed to be a cathodic inhibitor whereas orthophosphate is an anodic inhibitor. If that were the case, zinc would be found at high

concentrations on the cathode (copper) surface and orthophosphate would be found at high concentrations on the anode (lead) surface.

Table A-6. Mass percent of zinc and orthophosphate on the surface of lead solder and copper pipe for couplings and macrocells.

	Combination	Lead		Copper	
		% Zinc	% Phosphate	% Zinc	% Phosphate
Couplings	Present, Zinc Ortho	0.34	1.33	19.89	2.98
	Low Alk., Zinc Ortho	1.83	3.00	1.38	1.03
	Present, Ortho	0.02	4.41	1.54	0.86
Macrocells	Present, Zinc Ortho + High Chloride	0.28	0.95	0.53	0.03
	Low Alk., Zinc Ortho	1.23	6.14	1.08	2.41

Based on chemical analysis from EDS (**Figure A-14; Figure A-15**), the mass percent of zinc and orthophosphate was obtained for the corresponding cathode and anode surfaces. (**Table A-6**). Zinc was indeed present at concentrations up to 20% coating the copper pipe coupon surfaces, when zinc orthophosphate was used at relatively high alkalinity. The elevated levels of zinc in this scale, might have therefore reduced the rate of oxygen reduction, consistent with classic theory regarding action of mixed inhibitors. For some reason at the same condition but with lower alkalinity, zinc levels on the copper pipe surface were much reduced.

To more intensively examine the theory that zinc acts by depositing at the cathode, a more intensive and detailed investigation of all the copper pieces for the low alkalinity and high alkalinity, zinc orthophosphate conditions with present chloride were examined under ESEM at a magnification of 100X (**Figure A-16**).

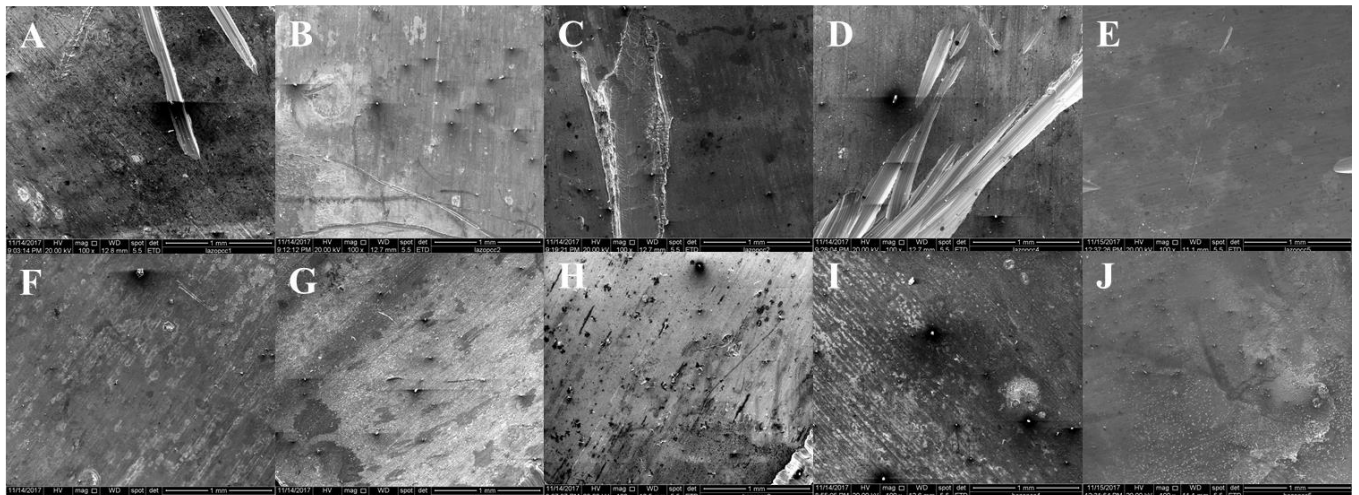


Figure A-16. ESEM images of coupon copper pieces. The images show A) low alkalinity, zinc ortho, coupon 1, B) low alkalinity, zinc ortho, coupon 2, C) low alkalinity, zinc ortho, coupon 3, D) low alkalinity, zinc ortho, coupon 4, E) low alkalinity, zinc ortho, coupon 5, F) high alkalinity, zinc ortho, coupon 1, G) high alkalinity, zinc ortho, coupon 2, H) high alkalinity, zinc ortho, coupon 3, I) high alkalinity, zinc ortho, coupon 4, J) high alkalinity, zinc ortho, coupon 5.

ortho, coupon 3, I) high alkalinity, zinc ortho, coupon 4, and J) high alkalinity, zinc ortho, coupon 5.

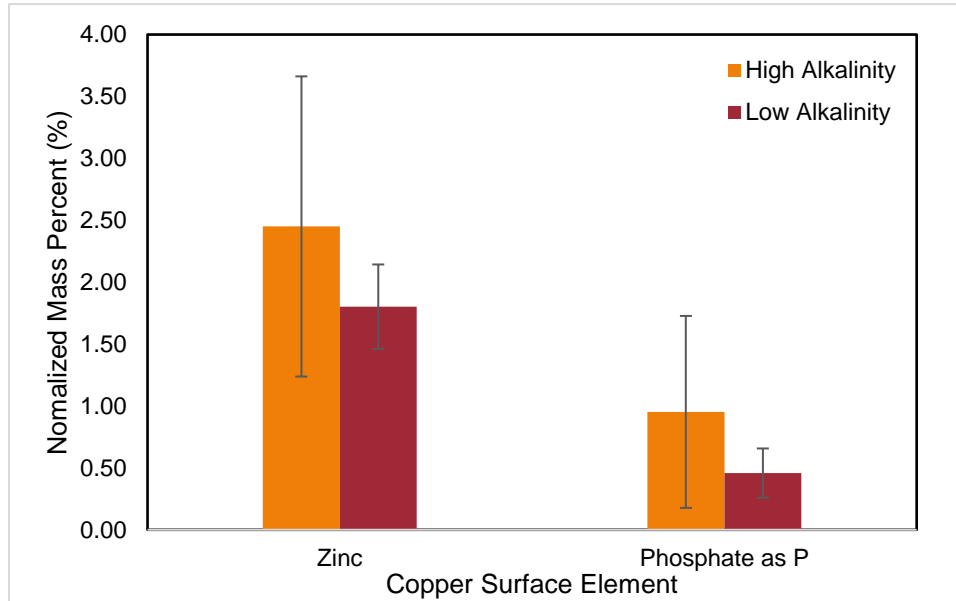


Figure A-17. Bar graph of the normalized mass percent of zinc and phosphate as p on the surface of copper coupons with 95% confidence interval error bars (n=5).

Although the more intensive study did not confirm higher levels of zinc on the surfaces of the low alkalinity and high alkalinity copper surfaces at greater than 95% confidence, there was 27% more zinc on the copper surface at high alkalinity on average versus low alkalinity (**Figure A-17**). Moreover, the deposits of zinc and phosphate were much less uniform at high alkalinity, as evidenced by standard deviation of ± 1.03 for high alkalinity versus ± 0.29 for lower alkalinity. Clearly, while this study did not confirm a mechanism for the role of zinc in mitigating galvanic corrosion due to the failure of the macro-cells to replicate the phenomenon, there are differences on the copper surfaces when the zinc is present in either low or high alkalinity water. These differences are somewhat consistent with expectations based on classic corrosion theory regarding the action of zinc phosphate. More definitive results must await future research.

4. CONCLUSIONS

- For the coupon testing, zinc orthophosphate proved to be the best inhibitor to control corrosion.
- At levels exceeding the critical CSMR threshold of 0.6, higher chloride levels do not make a significant difference in lead levels. If zinc orthophosphate is used in conjunction with a higher alkalinity finished water, the corrosive effects of higher chloride were mitigated in Utility A water.

- Alkalinity plays a key role in the effectiveness of inhibiting lead solder corrosion. Although further research is needed to determine exactly how this occurs, a switch back to ACH without also increasing alkalinity is not recommended.
- Although the couplings exposed to lower alkalinity water had higher lead levels when compared to the higher alkalinity, over much longer periods of time the zinc orthophosphate might eventually act to mitigate the high lead release. It just did not do so in the time period of this study.
- Chloride levels do not have a significant effect on the performance of the corrosion inhibitors unlike alkalinity. Zinc orthophosphate is the best corrosion inhibitor to remediate lead at a higher chloride level.
- Based on the relationship between lead and copper in the coupon testing, the control appeared to experience the most galvanic corrosion (lead sacrificed, and the copper protected), and the zinc orthophosphate was relatively unimpacted by galvanic effects
- At higher alkalinity, more zinc deposited on the cathode, and the deposit was less uniform than at lower alkalinity. This might indicate that zinc is a cathodic inhibitor, slowing the rate of galvanic corrosion by reducing the rate of oxygen reduction.
- Regardless of the alkalinity, lead release in waters with zinc orthophosphate were equal or lower than any other condition in the coupling testing.
- Initially, consistent with adverse consequences of galvanic corrosion, there was a large drop in pH at the lead solder anode surface, consistent with the extremely aggressive conditions and very high lead leaching to water. In the macrocell, this effect gradually dissipated, but in the coupon study the effects of galvanic corrosion were much more persistent.

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APPENDIX B

Final Report – Evaluation of Corrosion Control Alternatives for Lead and Copper Corrosion for Utility B

INTRODUCTION

In this bench-top study Virginia Tech tested whether the addition of orthophosphate, zinc orthophosphate, or silicate would reduce lead or copper leaching relative to the current corrosion control technique already being used by Utility B. The two water sources used to run experiments were supplied by Utility B from Source 1 and Source 2 treatment facilities.

MATERIALS AND METHODS

Prior to testing water from Utility B, (74) 3/8" copper couplings were obtained. A thin layer of flux was applied to the inner surface of each coupling and a 1/2" long piece of 50:50 lead: tin solder was melted evenly using a propane torch. All couplings were chemically cleaned by soaking in a 0.1 M sodium hydroxide solution for 5 minutes and then rinsed four times with distilled water. Each coupling was then placed in a 100 mL glass bottle. All 74 couplings were evaluated for lead and copper leaching in a synthetically formulated water chemistry. Twenty-five milliliters of 0.4 M sodium bicarbonate were added to each liter of distilled water required for the test. This resulted in a water chemistry of pH 8 (± 0.5) and alkalinity 500 mg/L as CaCO₃ (± 25). Sodium hypochlorite was added so that the free chlorine concentration was 2 mg/L (± 0.5). The couplings were rinsed three times with this water and then each glass jar was filled. Water was dumped after 24 hours and then the jars were refilled. After 24 hours the water was collected from each jar, and fresh water was refilled. Water was collected (as a composite sample) and refilled twice more after two more 24-hour stagnation periods, so that a final volume of 300 mL was collected from each coupling. Each composite sample was preserved with 2% v/v nitric acid and analyzed by a Thermo Electron X-Series ICP-MS for lead and copper concentrations after a minimum 16-hour stagnation.

Fifty of the copper couplings with the most reproducible lead leaching concentrations were selected for the test with the two Citizens Water waters. The 50 couplings were randomly placed into ten sets of five. Five sets were used to test water from Source 2 and five sets were used to test water from Source 1. Fresh water from each water source was shipped to Virginia Tech weekly for seven weeks. Alkalinity and pH were measured periodically throughout the study.

For the first seven weeks of testing, five corrosion control conditions were tested for each water, which included five replicates each. The corrosion control conditions are listed below:

- 1- Control (water as received)
- 2- Medium orthophosphate (0.5 mg/L as P orthophosphate)
- 3- High orthophosphate (1.0 mg/L as P orthophosphate)
- 4- High orthophosphate plus zinc (1.0 mg/L as P orthophosphate + 0.3 mg/L zinc)
- 5- Silicate (as specified by supplier)

After the initial seven weeks of testing, the testing program was placed on hold for two weeks to evaluate data. Following this evaluation, conditions 1, 3 and 4 from above were continued for nine additional weeks with the same coupons. This additional testing resulted in a total testing period of 16 weeks for those conditions.

Each of the 50 glass jars were filled with the appropriate water and a ‘dump-and-fill’ protocol was followed. Water was collected, and glass jars were refilled with fresh water three times during the week. Water was collected as a composite sample, and at the end of the week it was preserved with 2% v/v nitric acid and analyzed for lead, copper, and tin by ICP-MS. Student’s t-tests were used to evaluate whether there was a difference in lead or copper leaching between each inhibitor condition and the control for each water type.

RESULTS AND DISCUSSION

Lead and copper leaching from the 74 copper/solder coupons exhibited significant variability. The average lead leaching was 12.2 ppb with a standard deviation of 3.1 ppb (25% relative standard deviation (RSD); **Figure B-1**). Copper leaching was 117 ppb with an RSD of 24%.

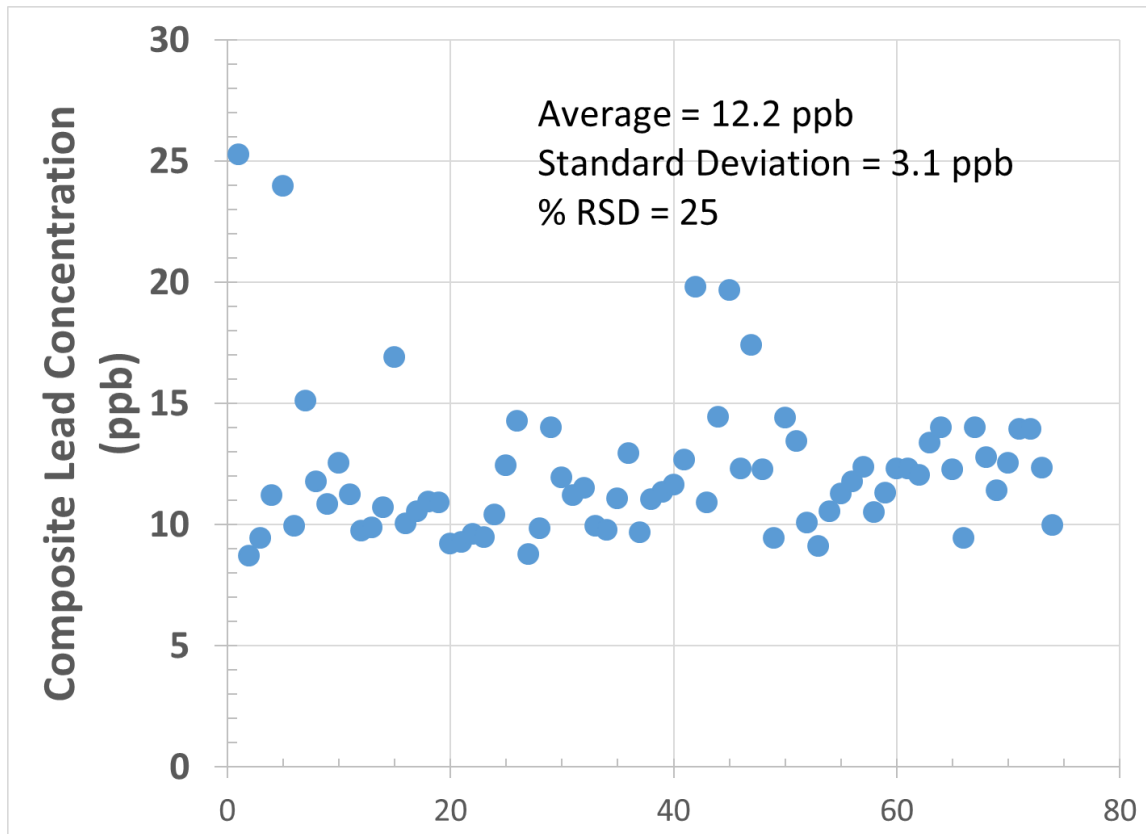


Figure B-1. Lead concentration in composite samples from the 74 copper/solder coupons

Since 50 coupons were needed for the bench-scale testing, the 24 most variable with regards to lead concentration were discarded. This resulted in 50 coupons with an average lead leaching of

11.6 ppb and an RSD of 10%. The copper concentration RSD decreased to 18% for these same coupons.

Results for All Inhibitors from First Seven Weeks

Lead and copper data for the first seven weeks of testing for each water and inhibitor condition are shown in **Tables B1-4**. None of the inhibitor conditions showed significant statistical differences in lead concentrations compared to the Control for either source water, while all the inhibitors except silicate in the Source 1 water had statistically significant lower copper concentrations when compared to the control (as opposed to none of the inhibitor conditions with the Source 2 water; see **Table B-5** for statistical comparisons).

When comparing lead leaching in Week 7 to Week 1, the only condition that showed a significant decrease in lead concentration was the Zinc Orthophosphate in Source 1 water ($p=0.00053$). When comparing copper leaching in Week 7 to Week 1, for Source 2 water surprisingly the Control, Medium Orthophosphate, and Silicate conditions showed statistical improvement in copper leaching over the seven weeks, while for Source 1 water only the Medium Orthophosphate condition showed statistical improvement ($p=0.007$, although the High Orthophosphate and Zinc Orthophosphate conditions were close ($p=0.073$ and $p=0.053$, respectively)).

Table B-1. Source 1 lead release – first seven weeks

Water/Inhibitor/ Replicate	Lead (ppb)							Week 1 to Week 7 reduction (%)
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	
FC C-1	26.3	20.6	17.1	15.7	36.0	16.7	12.9	51
FC C-2	16.6	18.7	14.3	13.9	27.8	16.0	14.5	13
FC C-3	20.2	38.6	19.5	775.9	474.6	99.0	552.5	-
FC C-4	21.2	25.9	15.5	14.8	34.8	20.4	14.1	34
FC C-5	45.2	26.3	20.4	20.8	35.2	48.6	2,976.0	-
FC MO-1	12.1	7.3	5.1	4.3	4.6	3.7	2.8	77
FC MO-2	22.0	1,170.0	1,204.0	396.0	829.0	535.2	147.2	-
FC MO-3	14.5	9.6	6.3	5.4	5.4	3,039.0	363.8	-
FC MO-4	18.7	14.2	9.6	7.5	9.7	8.8	5.5	71
FC MO-5	13.0	7.7	7.1	4.7	4.5	5.4	3.3	75
FC HO-1	772.9	3,237.0	5,883.0	2,417.0	3,150.0	3,534.0	2,075.0	-
FC HO-2	18.4	11.6	6.3	5.3	9.2	1,552.0	128.1	-
FC HO-3	9.7	49.6	11.9	8.0	16.3	10.6	5.2	47
FC HO-4	17.3	12.3	6.2	5.2	5.2	4.2	3,771.0	-
FC HO-5	16.2	8,020.0	3,162.0	4,628.0	5,435.0	1,472.0	249.7	-
FC ZO-1	15.2	9.2	5.3	3.0	8.6	7.0	4.3	71
FC ZO-2	10.4	5.8	3.1	2.5	3.2	2.0	1.3	87
FC ZO-3	18.1	10.0	6.8	4.9	7.7	4.7	2.8	84
FC ZO-4	11.5	8.0	3.5	2.0	2.4	1.4	0.7	94
FC ZO-5	17.4	12.1	6.6	4.7	10.4	6.2	2.8	84
FC S-1	33.0	22.6	16.4	13.7	118.5	15.6	12.5	62
FC S-2	2,198.0	8,304.0	2,340.0	1,037.0	1,119.0	526.0	288.7	87
FC S-3	2,414.0	9,550.0	2,477.0	2,059.0	2,857.0	2,954.0	1,315.0	46
FC S-4	24.5	22.1	14.9	13.5	47.0	22.2	21.2	13
FC S-5	15.3	13.5	10.2	10.3	25.9	9.9	7.7	50

Table B-2. Source 2 lead release – first seven weeks

Water/Inhibitor/ Replicate	Lead (ppb)							Week 1 to Week 7 reduction (%)
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	
WR C-1	26.6	30.2	21.1	20.5	41.8	17.7	1,272.0	-
WR C-2	19.8	18.3	12.8	12.6	176.1	120.3	26.3	-
WR C-3	14,930.0	6,795.0	3,024.0	3,382.0	4,266.0	763.6	544.5	96
WR C-4	7,494.0	6,056.0	2,624.0	1,542.0	5,097.0	2,706.0	2,448.0	67
WR C-5	20.5	18.3	170.7	473.7	289.3	2,758.0	407.7	-
WR MO-1	5,313.0	9,540.0	4,980.0	1,792.0	2,122.0	7,132.0	4,783.0	10
WR MO-2	18.6	17.4	12.7	10.2	17.2	11.1	9.6	48
WR MO-3	60.5	18.2	9.1	6.5	11.4	8.2	5,009.0	-
WR MO-4	20.6	15.8	9.6	7.7	18.3	10.1	7.0	66
WR MO-5	6,357.0	4,285.0	1,125.0	342.0	1,176.0	5,294.0	4,427.0	30
WR HO-1	14.8	8.4	7.0	5.5	13.6	21.6	2,364.0	-
WR HO-2	10.0	8.9	5.4	4.5	7.1	5.2	7.7	23
WR HO-3	12.0	8.6	5.6	4.7	2,967.0	5,229.0	3,339.0	-
WR HO-4	9,070.0	7,904.0	3,842.0	4,245.0	2,538.0	690.7	3,799.0	58
WR HO-5	6,784.0	6,523.0	3,883.0	5,662.0	5,361.0	4,945.0	2,730.0	60
WR ZO-1	3,924.0	3,253.0	1,610.0	1,149.0	1,338.0	824.9	85.9	98
WR ZO-2	21.7	13.4	9.4	7.9	57.1	429.9	20.0	8
WR ZO-3	8,959.0	3,006.0	1,097.0	1,238.0	1,159.0	413.4	69.3	99
WR ZO-4	4,070.0	2,611.0	1,386.0	438.4	555.6	42.6	51.9	99
WR ZO-5	12.9	6.7	3.6	4.2	4.2	2.1	1.7	87
WR S-1	13.5	10.6	9.0	10.6	18.7	9.9	9.6	29
WR S-2	2,128.0	373.3	163.0	387.5	6,591.0	4,189.0	2,286.0	-
WR S-3	11,950.0	8,699.0	2,430.0	1,977.0	2,997.0	1,300.0	674.5	94
WR S-4	23.5	16.1	12.1	12.6	34.3	48.6	818.4	-
WR S-5	19.4	11.4	8.0	9.0	11.2	8.5	3,249.0	-

Table B-3. Source 1 copper release – first seven weeks

Water/Inhibitor/ Replicate	Copper (ppb)							Week 1 to Week 7 reduction (%)
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	
FC C-1	579.1	526.6	750.0	641.8	668.3	646.1	484.9	16
FC C-2	687.8	582.2	601.0	552.4	695.3	785.2	582.6	15
FC C-3	1,139.0	881.5	960.2	667.5	1,136.0	872.6	677.7	41
FC C-4	646.2	516.7	491.5	506.5	640.1	529.0	466.4	28
FC C-5	1,540.0	665.8	678.6	712.3	1,151.0	782.6	195.8	87
FC MO-1	601.6	369.3	367.5	284.3	363.3	454.4	239.2	60
FC MO-2	352.9	196.1	245.6	249.5	320.1	355.1	210.3	40
FC MO-3	387.1	291.3	259.4	243.9	305.4	278.1	246.1	36
FC MO-4	512.7	320.4	361.1	310.3	440.3	405.5	286.5	44
FC MO-5	627.7	405.2	413.4	331.1	401.7	524.4	288.0	54
FC HO-1	268.8	180.0	96.2	64.5	268.1	138.8	51.4	81
FC HO-2	253.1	253.4	205.6	186.2	428.9	316.6	222.1	12
FC HO-3	182.4	172.5	185.6	154.3	229.8	213.8	140.0	23
FC HO-4	392.2	216.5	185.0	153.4	295.7	297.8	143.7	63
FC HO-5	283.3	218.1	70.7	60.4	1,178.0	284.9	242.2	15
FC ZO-1	580.8	355.8	195.2	118.7	240.2	258.6	116.8	80
FC ZO-2	223.5	132.0	102.3	103.3	230.5	211.3	98.6	56
FC ZO-3	197.9	116.6	87.7	88.2	236.9	160.5	85.3	57
FC ZO-4	219.6	131.6	89.0	75.9	188.6	180.8	63.7	71
FC ZO-5	192.9	139.4	86.4	69.7	277.4	185.8	104.6	46
FC S-1	431.7	459.5	333.0	307.5	522.9	364.7	296.2	31
FC S-2	252.4	140.9	149.1	388.3	600.5	483.5	370.9	-
FC S-3	216.6	104.6	36.0	29.8	68.8	42.4	27.9	87
FC S-4	614.5	538.7	381.2	335.9	570.4	419.3	320.5	48
FC S-5	661.6	604.4	484.8	484.1	608.0	501.4	394.5	40

Table B-4. Source 2 copper release – first seven weeks

Water/Inhibitor/ Replicate	Copper (ppb)							Week 1 to Week 7 reduction (%)
	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	
WR C-1	517.2	441.2	438.2	400.1	734.2	434.0	357.5	31
WR C-2	861.5	867.3	742.6	688.1	1,211.0	543.6	483.5	44
WR C-3	371.9	103.9	54.6	54.6	175.6	93.4	74.4	80
WR C-4	351.9	92.5	47.3	31.7	420.7	130.6	55.3	84
WR C-5	548.4	458.7	384.5	404.0	866.4	413.3	429.7	22
WR MO-1	168.1	72.3	36.6	29.3	256.6	136.1	47.1	72
WR MO-2	378.2	336.3	309.4	270.4	600.0	321.7	236.8	37
WR MO-3	394.5	324.1	287.6	286.0	633.7	412.2	196.2	50
WR MO-4	419.7	327.6	273.7	229.5	826.0	444.3	311.4	26
WR MO-5	115.6	70.4	282.4	318.8	502.0	281.1	74.5	36
WR HO-1	545.5	222.2	274.3	184.8	454.9	367.0	146.7	73
WR HO-2	218.2	333.3	294.5	240.3	574.2	355.2	245.8	-
WR HO-3	182.8	184.2	179.3	156.1	367.4	140.4	78.3	57
WR HO-4	103.2	63.8	30.4	41.8	185.0	173.6	141.5	-
WR HO-5	92.3	39.5	31.2	38.4	113.8	62.0	36.4	61
WR ZO-1	131.2	72.6	31.5	17.9	145.5	77.7	47.4	64
WR ZO-2	131.2	72.7	41.4	64.3	261.6	111.8	20.5	84
WR ZO-3	121.0	32.0	30.1	24.8	235.5	89.8	57.0	53
WR ZO-4	175.3	64.4	62.2	64.3	190.7	188.9	75.7	57
WR ZO-5	905.4	339.5	223.0	141.9	523.0	233.0	97.6	89
WR S-1	241.8	240.9	199.3	212.9	601.5	261.6	194.0	20
WR S-2	200.2	274.1	284.9	263.0	246.4	126.8	65.9	67
WR S-3	108.8	52.8	19.5	34.4	143.7	39.1	25.2	77
WR S-4	267.3	243.6	191.4	235.0	461.6	312.4	190.6	29
WR S-5	239.8	255.7	212.4	210.7	306.4	243.2	186.4	22

In many instances, the lead leaching was visibly observed, likely a result of galvanic corrosion. **Figure 2** shows copper couplings from Source 1 and Source 2 with Medium Orthophosphate and Silicate as the corrosion inhibitors with visible white corrosion deposits. These deposits slough off into the water, resulting in high levels of lead.

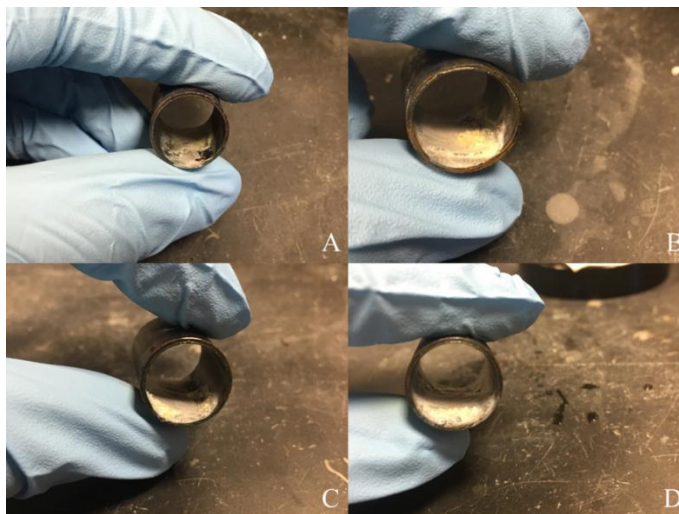


Figure B-2. Photograph of Copper Couplings with lead solder showing corrosion deposits A) Source 1- medium orthophosphate B) Source 1- Silicate C) Source 2- medium orthophosphate D) Source 2- Silicate

Lead and copper concentrations continued to decrease for the most part from Weeks 1 to 7 in the Zinc Orthophosphate condition in both Source 1 (**Tables B-1 and B-3**) and Source 2 (**Tables B-2 and B-4**). This was also consistent visually; no deposits were observed on the copper couplings that were exposed to Zinc Orthophosphate (**Figure B-3**). Lead concentrations in other inhibitors also decreased with time in several instances, but in some cases the corrosion process seemed to initiate at random times (e.g., Source 1 control coupon #5 in Week 7, **Table B-1**). For this reason, it was determined that the Zinc Orthophosphate condition deserved further testing to observe whether these corrosion deposits would initiate after further aging. The experiments were then run for nine additional weeks with only the Control, High Orthophosphate and Zinc Orthophosphate inhibitor conditions. Although lead levels for several of the High Orthophosphate coupons increased throughout the first 7 weeks (as the galvanic corrosion mechanism was somehow initiated), we included these in the final phase of testing because the orthophosphate dosing was the same as that for the Zinc Orthophosphate condition.

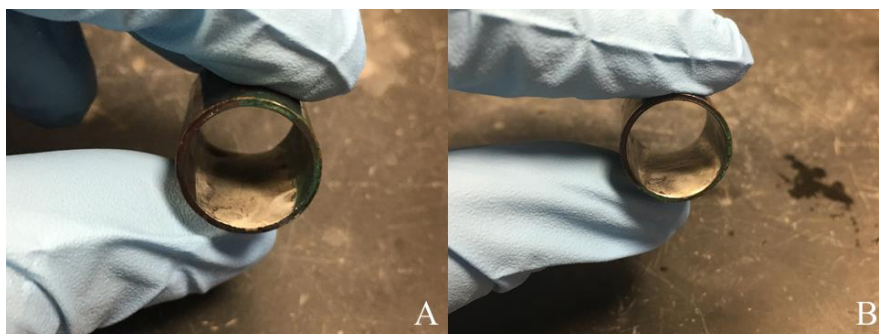


Figure B-3. Photograph of Copper couplings with lead solder depicting no visible corrosion A) Source 1- zinc orthophosphate B) Source 2- zinc orthophosphate

Table B-5. Student's T-Test Results and Conclusions for Weeks 1-7 (Lead Release only)

Condition Comparison	p-value	Conclusion
FC - MO vs Control	0.35	no significant difference
FC - HO vs Control	0.59	no significant difference
FC - ZO vs Control	0.28	no significant difference
FC - S vs Control	0.56	no significant difference
WR - MO vs Control	0.18	no significant difference
WR - HO vs Control	0.10	no significant difference
WR - ZO vs Control	0.10	no significant difference
WR - S vs Control	0.54	no significant difference
FC - Control Wk 7 vs Wk 1	0.29	no significant difference
FC - MO Wk 7 vs Wk 1	0.28	no significant difference
FC - HO Wk 7 vs Wk 1	0.20	no significant difference
FC - ZO Wk 7 vs Wk 1	5.3E-04	Wk 7 lead release lower than Wk 1 lead release
FC - Silicate Wk 7 vs Wk 1	0.19	no significant difference
WR - Control Wk 7 vs Wk 1	0.29	no significant difference
WR - MO Wk 7 vs Wk 1	0.69	no significant difference
WR - HO Wk 7 vs Wk 1	0.69	no significant difference
WR - ZO Wk 7 vs Wk 1	0.11	no significant difference
WR - Silicate Wk 7 vs Wk 1	0.60	no significant difference

*Note: Statistical significance determined based on p-value <0.05, representing a 95% confidence in a difference between results based on an assumed normal distribution of data

Results for Extended Testing of Control, High Orthophosphate, and Zinc Orthophosphate Conditions

Lead and copper data for the final nine weeks of testing for each water for the Control, High Orthophosphate, and Zinc Orthophosphate inhibitor conditions are shown in **Tables 6-9**.

Table B-6. Source 1 lead release – final nine weeks

Water/Inhibitor/ Replicate	Lead (ppb)									Week 8 to Week 16 reduction (%)
	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15	Week 16	
FC C-1	69.1	33.8	187.5	70.5	242.6	41.1	29.0	31.0	40.4	41
FC C-2	5,552.0	2,002.0	498.6	839.1	2,330.0	402.8	2,331.0	1,193.0	318.2	94
FC C-3	4,714.0	498.4	1,473.0	177.9	94.5	71.1	65.6	65.5	39.1	99
FC C-4	36.5	410.8	526.8	454.8	224.7	181.9	138.3	117.2	103.0	-
FC C-5	1,386.0	289.2	364.6	251.5	315.1	235.9	142.2	186.2	93.8	93
FC HO-1	3,496.0	218.1	4,082.0	735.0	267.9	119.7	74.7	98.2	39.5	99
FC HO-2	3,337.0	218.7	71.7	338.3	38.9	27.9	17.1	104.2	18.3	99
FC HO-3	7,130.0	3,887.0	8,349.0	7,715.0	7,325.0	7,561.0	5,334.0	9,256.0	3,878.0	46
FC HO-4	1,679.0	171.7	180.4	102.1	97.6	241.8	84.6	61.1	37.8	98
FC HO-5	6,742.0	1,510.0	431.7	398.5	213.7	126.3	74.9	89.7	45.1	99
FC ZO-1	1,801.0	170.0	108.5	25.8	45.7	28.7	8.5	9.4	6.9	100
FC ZO-2	632.4	24.0	40.2	21.1	16.8	7.4	4.5	6.1	4.2	99
FC ZO-3	124.8	8.5	9.8	11.8	8.1	5.5	6.9	6.6	5.1	96
FC ZO-4	1,007.0	120.5	63.2	33.8	16.5	13.0	7.6	11.1	2.8	100
FC ZO-5	16.6	5.2	7.1	8.0	5.4	5.0	4.2	2.6	2.1	87

Table B-7. Source 2 lead release – final nine weeks

Water/Inhibitor/ Replicate	Lead (ppb)									Week 8 to Week 16 reduction (%)
	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15	Week 16	
WR C-1	1,641.0	206.9	147.0	277.7	75.0	59.7	131.9	80.7	190.2	88
WR C-2	8,571.0	2,607.0	4,124.0	2,779.0	854.9	514.0	316.8	256.7	177.1	98
WR C-3	8,401.0	912.3	2,793.0	1,758.0	1,522.0	1,186.0	383.6	1,458.0	230.9	97
WR C-4	2,620.0	1,810.0	1,371.0	1,123.0	984.8	363.5	1,099.0	1,131.0	198.1	92
WR C-5	4,295.0	4,092.0	3,723.0	5,452.0	3,257.0	1,714.0	1,527.0	616.2	216.6	95
WR HO-1	1,053.0	1,149.0	238.1	229.8	91.6	63.9	156.2	124.9	27.2	97
WR HO-2	5,947.0	4,354.0	6,680.0	4,626.0	3,018.0	5,273.0	3,612.0	4,163.0	2,633.0	56
WR HO-3	3,204.0	1,911.0	1,182.0	900.3	2,047.0	655.2	676.6	318.2	92.9	97
WR HO-4	6,742.0	4,081.0	4,596.0	4,780.0	3,762.0	3,727.0	4,015.0	2,247.0	2,374.0	65
WR HO-5	5,479.0	2,886.0	4,334.0	3,819.0	2,621.0	847.5	948.6	6,714.0	3,130.0	43
WR ZO-1	1,754.0	577.6	276.4	184.6	250.8	62.0	63.0	45.2	10.9	99
WR ZO-2	392.7	139.3	65.6	210.3	33.3	17.3	103.4	45.3	9.8	97
WR ZO-3	337.7	57.1	66.2	29.5	41.2	26.1	18.1	9.5	5.6	98
WR ZO-4	1,282.0	500.6	321.3	482.6	464.3	532.6	289.0	79.5	21.1	98
WR ZO-5	1,080.0	383.8	120.7	33.3	14.4	85.5	13.0	6.2	3.6	100

Table B-8. Source 1 copper release – final nine weeks

Water/Inhibitor/ Replicate	Copper (ppb)									Week 8 to Week 16 reduction (%)
	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15	Week 16	
FC C-1	621.0	478.1	514.7	781.9	762.3	721.2	607.5	797.2	673.6	-
FC C-2	236.2	259.0	737.0	836.2	468.6	849.3	398.9	668.8	633.2	-
FC C-3	259.6	449.6	298.1	797.4	760.4	666.9	697.2	837.1	696.5	-
FC C-4	588.9	428.6	544.1	868.4	800.2	667.7	624.9	834.9	613.7	-
FC C-5	727.5	538.8	690.2	877.3	931.2	820.2	809.5	932.5	890.0	-
FC HO-1	267.6	218.1	165.0	288.1	345.8	272.3	271.3	248.5	234.4	12
FC HO-2	365.3	330.0	424.5	434.9	420.5	409.8	348.0	306.1	270.4	26
FC HO-3	204.4	84.0	121.0	132.9	103.1	83.6	58.0	71.6	37.8	81
FC HO-4	333.7	285.1	391.7	347.5	325.4	303.1	295.3	292.2	239.9	28
FC HO-5	246.9	234.1	382.0	386.6	384.3	324.2	313.8	304.4	263.6	-
FC ZO-1	194.3	107.1	174.6	181.9	221.4	191.6	169.7	106.8	131.6	32
FC ZO-2	229.4	65.4	167.2	252.9	210.5	167.0	170.6	120.2	151.1	34
FC ZO-3	240.3	93.6	184.1	202.6	235.4	182.9	199.8	133.1	168.1	30
FC ZO-4	159.2	87.1	143.3	155.2	159.5	128.7	151.6	92.3	116.5	27
FC ZO-5	226.6	115.8	200.4	216.3	181.7	191.7	199.7	95.2	88.7	61

Table B-9. Source 2 copper release – final nine weeks

Water/Inhibitor/ Replicate	Copper (ppb)									Week 8 to Week 16 reduction (%)
	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15	Week 16	
WR C-1	408.9	279.7	251.7	361.0	297.1	313.5	281.4	373.9	178.8	56
WR C-2	228.8	84.4	158.7	101.6	335.5	384.5	350.6	412.0	294.5	-
WR C-3	121.1	84.6	68.0	76.4	52.5	42.9	50.1	62.5	37.0	69
WR C-4	120.7	65.6	79.0	85.2	70.4	85.4	55.3	83.2	59.2	51
WR C-5	235.3	88.9	97.5	140.4	73.8	103.2	102.2	294.0	272.5	-
WR HO-1	218.7	142.2	210.8	313.4	259.7	221.4	179.9	180.8	159.1	27
WR HO-2	293.7	90.8	116.1	131.1	81.8	107.2	54.6	62.7	27.8	91
WR HO-3	212.3	163.9	194.9	300.7	180.9	177.4	156.2	177.6	169.8	20
WR HO-4	119.3	49.0	48.6	75.9	51.3	55.1	35.0	75.3	61.2	49
WR HO-5	93.5	60.0	51.1	83.8	47.4	85.4	134.7	82.5	31.0	67
WR ZO-1	80.3	34.8	62.1	120.3	81.1	62.0	82.6	63.0	33.8	58
WR ZO-2	113.1	50.9	60.9	70.1	82.0	77.6	92.4	53.9	34.6	69
WR ZO-3	84.4	31.1	41.0	84.3	55.9	61.6	73.4	32.1	10.3	88
WR ZO-4	111.9	42.3	52.5	129.5	72.0	39.5	49.2	50.5	27.7	75
WR ZO-5	129.0	76.5	110.1	146.8	121.5	147.6	130.3	53.1	42.9	67

Neither High Orthophosphate nor Zinc Orthophosphate showed significant statistical differences in lead concentrations compared to the Control for Source 1; however, Zinc Orthophosphate inhibitor resulted in a dramatic improvement in the Source 2 water ($p=1 \times 10^{-5}$). You can see from **Tables B-2 and B-7** that the two weeks between the two test phases resulted in some significant lead release in the WR-ZO coupons, but that after nine weeks of exposure to additional Zinc Orthophosphate the lead release was much improved. In fact, only one of the five coupons exceeded the EPA action level of 15 ppb even though nine weeks earlier 300-1,800 ppb lead was being released.

Similar to the first seven weeks of testing, the copper release for the High Orthophosphate and Zinc Orthophosphate conditions was statistically lower than the Control in the Source 1 water but there was no statistical difference in the Source 2 water (although the Zinc Orthophosphate was very close, $p=0.053$).

Once again, the higher corrosion under the HO conditions in comparison to the ZO conditions can be observed by comparison of visual corrosion deposits as indicated in **Figure B-4** and **Figure B-5**. No corrosion deposits are visually apparent in the ZO coupon for Source 1 (Figure 4, picture D). There are some visually apparent corrosion deposits in the ZO coupon for Source 2 sample (**Figure B-5**, picture D).

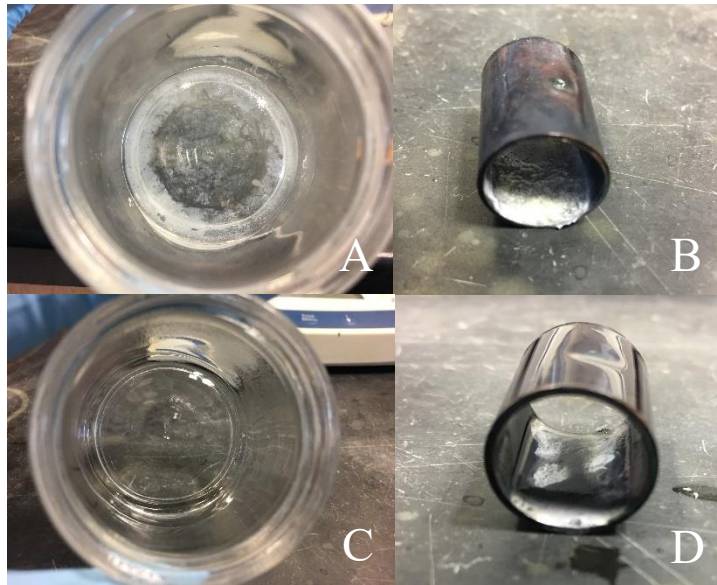


Figure B-4. A) Jar of a Source 1-HO coupon with residual lead on base B) Source 1-HO coupon with lead solder and corrosion deposits C) Jar of a Source 1- ZO Coupon with no residual lead D) Source 1- ZO coupon with lead solder and no visible corrosion deposits.

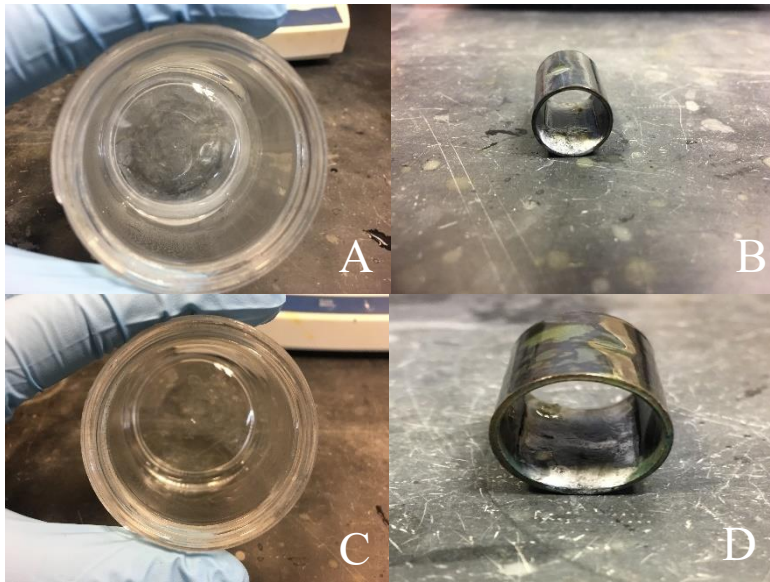


Figure B- 5. A) Jar of a Source 2-HO coupon with residual lead on base B) Source 2-HO coupon with lead solder and corrosion deposits C) Jar of a Source 2- ZO Coupon with no residual lead D) Source 2- ZO coupon with lead solder and minimal visible corrosion deposits.

While pictures also support the observation that lead levels are lower for both Source 1 and Source 2 in the Zinc Orthophosphate condition, it is important to discuss the relationship between lead and copper over the last nine weeks of testing. **Figure B-6** depicts what happened to lead concentrations over the last nine weeks of the study. Likewise, copper concentrations are shown in **Figure B-7**. Lead concentrations started out quite high in the Source 2 coupons for each inhibitor, but there was a steady improvement over the nine weeks (**Figure B-6**). Somewhat surprisingly, the High Orthophosphate condition appeared to be the worst. Similar trends were observed in the Source 1 waters but at a lower magnitude (**Figure B-6**).

Copper concentration trends were markedly different than those for lead (**Figure B-7**). Copper concentrations were fairly constant over the nine-week period in each inhibitor condition for each water. The Source 1 control condition had the greatest amount of copper leaching (**Figure B-7**).

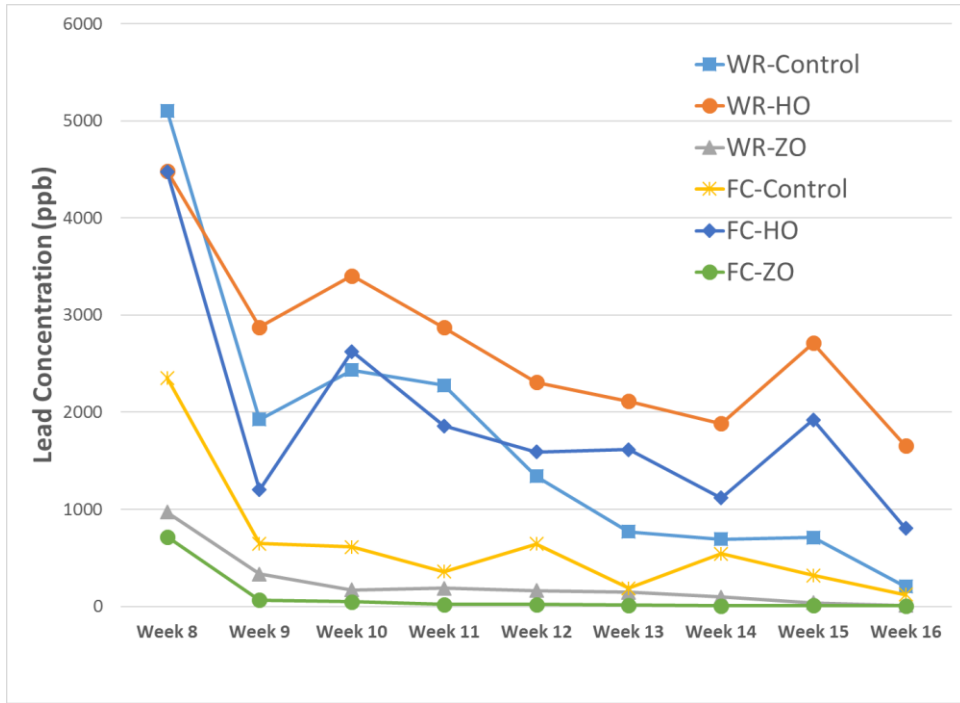


Figure B-6. Average Lead Release over Final 9 Weeks in Source 2 and Source 1 waters.

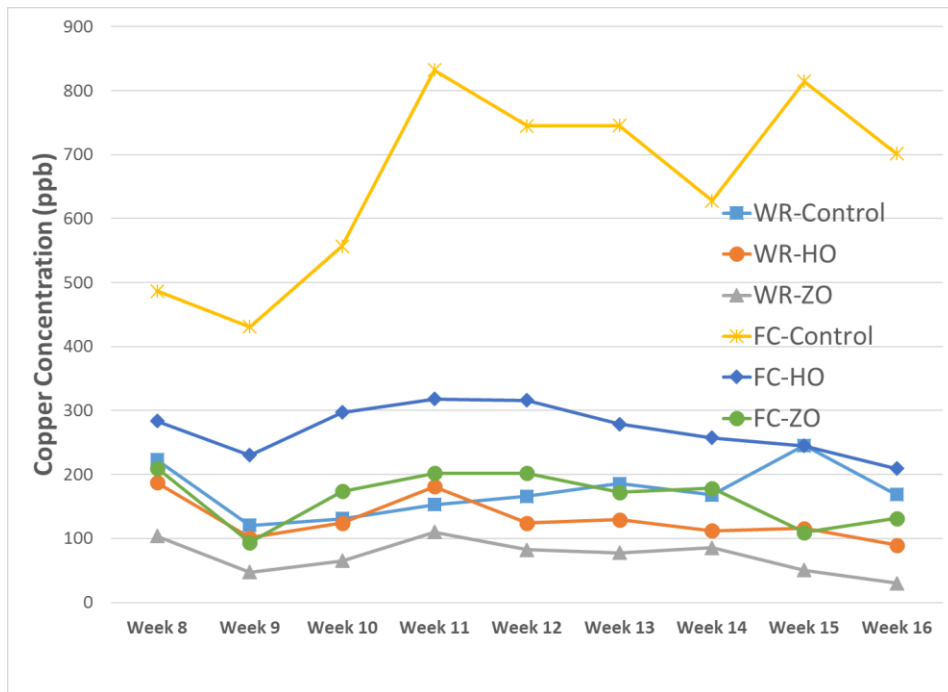


Figure B-7. Average Copper Release over Final 9 Weeks in Source 2 and Source 1 waters.

Statistical Analysis

Student's t-tests were conducted with a 95% confidence interval to statistically determine if there were differences between the mean values of lead and copper in each inhibitor compared to the control. After comparing the inhibitor conditions to the control, the Zinc Orthophosphate was then compared to the other inhibitors. Each inhibitor was also evaluated to compare its performance in the final week to the initial week of testing. It should be noted that the Student t-test allows comparison of datasets based on the assumption that the data is normally distributed. Given the variability in results, likely caused by galvanic corrosion, the standard deviations of results for each condition were generally quite broad, resulting in only a few conditions that exhibited a statistically significant difference using the normal distribution assumption.

Compared to the Control, only the Zinc Orthophosphate inhibitor in Source 2 water had a significantly different mean for lead than that of the Control ($p=9.9E-6$). Compared to the three other inhibitor conditions for Source 2, there was no significant statistical difference in lead release with a 95 % confidence interval. Concerning copper, no conditions were statistically different from the Control.

For Source 1 water, there was no significant difference in lead release with any of the four inhibitors and the Control at the 95% confidence level. However, the Zinc Orthophosphate inhibitor did show an improvement in comparison to the control at a 90% confidence level ($p=0.09$). For copper, the Medium Orthophosphate and Zinc Orthophosphate inhibitors indicated a significant reduction in release in comparison to the control ($p=0.01$ and $p=0.005$, respectively).

In order to determine how well each inhibitor individually reduced lead and copper concentrations, the first week of testing was compared to the final week of testing. For the Medium Orthophosphate and Silicate conditions, Week 7 was compared to Week 1. For the Control, High Orthophosphate and Zinc Orthophosphate, Week 16 was compared to Week 8 (the first week of the second phase of the study). When compared to its concentration in Week 8, Zinc Orthophosphate did not show a significant decrease in lead in Source 1 ($p=0.093$) but did in Source 2 ($p=0.023$). The Zinc Orthophosphate showed a significant decrease in copper in both waters (**Table B-10 and Table B-11**).

Table B-10 and Table B-11 show summaries of the t-test results for Source 1 and Source 2.

Table B-10. Student's T-Test Results for Source 1

T-Test Samples	Probability	
	Lead	Copper
MO vs. C	0.350	0.047
HO vs. C	0.423	7.61E-05
ZO vs. C	0.090	1.65E-04
S vs. C	0.564	0.094
C (Week 8 vs. Week 16)	0.122	0.104
MO (Week 1 vs. Week 7)	0.277	0.010
HO (Week 8 vs. Week 16)	0.011	0.198
ZO (Week 8 vs. Week 16)	0.093	0.005
S (Week 1 vs. Week7)	0.191	0.212
ZO Vs. MO (Compared at Week 7)	0.221	5.13E-05
ZO Vs. HO (Compared at Week 16)	0.357	0.150
ZO Vs. S (Compared at Week 7)	0.265	0.045

Table B-11. Student's T-Test Results for Source 2

T-Test Samples	Probability	
	Lead	Copper
MO vs. C	0.183	0.338
HO vs. C	0.094	0.244
ZO vs. C	9.91E-06	0.059
S vs. C	0.541	0.186
C (Week 8 vs. Week 16)	0.027	0.355
MO (Week 1 vs. Week 7)	0.694	0.009
HO (Week 8 vs. Week 16)	0.007	0.081
ZO (Week 8 vs. Week 16)	0.023	4.99E-04
S (Week 1 vs. Week7)	0.604	0.007
ZO Vs. MO	0.074	0.083
ZO Vs. HO	0.068	0.126
ZO Vs. S	0.083	0.116

CONCLUSIONS

- The five coupons used for each condition tested indicated a high degree of variability in lead and copper release. This high variability was most likely due to the occurrence of galvanic corrosion between the lead solder and copper coupling. Galvanic corrosion is known to be highly variable and specific timing triggers for metal release are highly uncertain.
- The addition of silicates did not indicate a statistically significant reduction in lead release in comparison to the control based on seven weeks of testing.
- Both the control samples and the samples with inhibitors continued to provide indications of downward trends in lead release rates after 16 weeks of testing, and that trend is likely to continue as the metal passivates.
- Throughout the testing period, samples with ZO exhibited the lowest lead release in comparison to the Control and to the other inhibitors. Of the conditions tested, the optimal condition for minimizing lead release in both the Source 1 and Source 2 water was with the addition of Zinc Orthophosphate (0.300 mg/L as Zn and 1.0 mg/L as P).
- The HO coupons exhibited higher lead release rates than the Control coupons. This is a counter-intuitive result and more testing would be required to attempt to explain this. From this study it does appear zinc is a necessary component to slow or stop the galvanic corrosion, so maybe without zinc the orthophosphate alone at such a high concentration may actually enhance the galvanic corrosion.

APPENDIX C

Table C-1. Low Chloride Synthetic Water Recipe¹ (Utility A)

	Stock solution	Amount per 1 L	Amount for 10 L
1	MgSO ₄ (1M)	0.1 mL	1 mL
2	Na ₂ SO ₄ (1M)	0.9 mL	9 mL
3	CaHCO ₃	75 mL	750 mL
4	K ₂ SiO ₃	15.4 mg (0.0154g)	154 mg (0.145 g)

¹Ten liters of synthetic water was added to 10L of moderate alkalinity Utility A water to create a low chloride water with half the amount of chloride.

Table C-2. Water type labeling system used in grouping coupons and pipes (Utility A)

A	No Inhibitor + Current Chloride	Low Alk Water
B	No Inhibitor + High Chloride	
C	Phosphate + Current Chloride	
D	Phosphate + High Chloride	
E	Zinc + Current Chloride	
F	Zinc + High Chloride	
G	Zinc Phosphate + Current Chloride	
H	Zinc Phosphate + High Chloride	
I	No Inhibitor + Low Chloride	
J	MgSO ₄ + Current Chloride	
K	No Inhibitor + Current Chloride	Moderate Alk Water
L	No Inhibitor + High Chloride	
M	Phosphate + Current Chloride	
N	Phosphate + High Chloride	
O	Zinc + Current Chloride	
P	Zinc + High Chloride	
Q	Zinc Phosphate + Current Chloride	
R	Zinc Phosphate + High Chloride	
S	Low ZOP + Current Chloride	Partner Utilities
T	Utility 1, Site 1	
U	Utility 1, Site 2	
V	Utility 2	

Table C-3. Baseline testing results and Groupings for Coupons (Utility A)

Water	Coupon #	Lead (ppb)	Average	St. Dev.
A	B112	228.0		
A	B86	152.2		
A	B84	92.1		
A	B110	68.1		
A	B43	42.0	116.5	74.4882721
B	B34	227.4		
B	B146	151.6		
B	B39	92.8		
B	B66	70.5		
B	B58	42.5	116.95	73.63269349
C	B30	220.3		
C	B62	148.0		
C	B108	93.1		
C	B45	70.9		
C	B72	43.8	115.226	70.12237931
D	B4	213.4		
D	B125	146.0		
D	B107	93.7		
D	B28	71.1		
D	B60	45.4	113.93	66.82051631
E	B120	206.3		
E	B8	139.7		
E	B137	94.4		
E	B54	72.0		
E	B131	47.6	111.986	62.69015537
F	B22	197.8		
F	B149	136.4		
F	B133	94.8		
F	B103	73.1		
F	B91	48.2	110.078	58.75881738
G	B23	192.1		
G	B102	131.5		
G	B48	96.9		
G	B12	73.8		
G	B75	51.4	109.148	55.03485232
H	B106	191.6		
H	B74	129.4		
H	B52	97.5		

H	B109	74.2		
H	B145	52.0	108.926	54.39764499
I	B31	188.2		
I	B17	129.0		
I	B119	99.5		
I	B118	76.8		
I	B81	52.0	109.088	52.56802897
J	B73	183.3		
J	B140	127.5		
J	B90	100.1		
J	B80	77.9		
J	B37	52.3	108.22	50.30161031
K	B16	182.9		
K	B96	127.1		
K	B116	100.2		
K	B77	78.0		
K	B87	53.0	108.238	49.90109538
L	B15	182.8		
L	B27	127.0		
L	B69	100.2		
L	B71	78.5		
L	B57	54.5	108.582	49.38350048
M	B63	176.4		
M	B53	126.7		
M	B21	101.0		
M	B61	80.1		
M	B104	55.2	107.89	46.47487171
N	B79	172.0		
N	B32	125.7		
N	B33	101.4		
N	B83	81.9		
N	B26	58.2	107.836	43.63880991
O	B36	170.8		
O	B143	122.6		
O	B65	103.1		
O	B117	82.7		
O	B11	60.7	107.986	41.99866641
P	B114	165.0		
P	B20	122.2		
P	B10	105.6		
P	B123	86.1		
P	B18	61.5	108.086	39.04135602
Q	B2	163.3		
Q	B35	118.3		
Q	B128	106.0		

Q	B88	87.7		
Q	B50	62.7	107.6	37.52019523
R	B82	160.4		
R	B76	117.4		
R	B70	108.2		
R	B67	89.5		
R	B56	62.8	107.664	36.1165188
S	B127	159.7		
S	B144	117.2		
S	B105	108.8		
S	B38	90.3		
S	B138	64.3	108.048	35.29796411
T	B44	158.7		
T	B7	114.1		
T	B129	109.9		
T	B147	90.7		
T	B122	64.5	107.584	34.64190064
U	B148	156.3		
U	B111	114.1		
U	B95	111.9		
U	B134	91.6		
U	B85	66.3	108.04	33.14233773
V	B141	155.2		
V	B46	113.5		
V	B130	112.2		
V	B142	92.0		
V	B41	68.1	108.186	32.1236732

Table C-4. Baseline testing results and Groupings for Pipes (Utility A)

Pipe #	Water Type	Lead (ppb)	Average
P9	A	429.5	
P12	A	1165.0	797.3
P4	B	442.1	
P27	B	1162.0	802.1
P1	C	466.5	
P25	C	781.4	
P29	C	1051.0	766.3
P53	D	472.6	
P40	D	1026.0	749.3
P60	E	495.2	
P15	E	679.8	
P57	E	1010.0	728.3

P30	F	536.4	
P23	F	998.0	767.2
P33	G	543.3	
P45	G	765.5	
P31	G	991.1	766.6
P41	H	549.4	
P46	H	680.7	
P16	H	952.0	727.4
P54	I	552.1	
P24	I	938.7	745.4
P55	J	593.7	
P10	J	907.1	750.4
P48	K	601.9	
P13	K	904.4	753.2
P58	L	603.9	
P35	L	887.9	745.9
P56	M	607.8	
P22	M	756.1	
P49	M	877.3	747.1
P51	N	624.7	
P50	N	869.5	747.1
P11	O	643.9	
P43	O	694.2	
P47	O	846.9	728.3
P37	P	624.9	
P44	P	818.9	721.9
P14	Q	665.2	
P42	Q	720.5	
P26	Q	808.8	731.5
P6	R	677.7	
P39	R	699.3	
P17	R	782.6	719.9

Table C-5. Baseline Results for Coupons (Utility A)

Water Type	Lead (ppb)	Water Type	Lead (ppb)	Water Type	Lead (ppb)	Water Type	Lead (ppb)
Present-1	39.35	Present- 1	8.972	Present-1	56.89	Present-1	55.28
Present-2	27.96	Present- 2	11.09	Present-2	53.45	Present-2	12.79
Present-3	124.5	Present- 3	40.03	Present-3	34.89	Present-3	426.3
Present-4	30.95	Present- 4	66.49	Present-4	45.56	Present-4	45.89
Present-5	10.38	Present- 5	15.71	Present-5	24.15	Present-5	7.634
High Chloride-1	33.91	High Chloride-1	388.7	High Chloride-1	20.88	High Chloride- 1	30.12
High Chloride-2	8.781	High Chloride-2	36.58	High Chloride-2	9.015	High Chloride- 2	34.96
High Chloride-3	24.71	High Chloride-3	49.49	High Chloride-3	47.39	High Chloride- 3	313.8
High Chloride-4	50.5	High Chloride-4	15.44	High Chloride-4	32.91	High Chloride- 4	58.99
High Chloride-5	11.48	High Chloride-5	20.79	High Chloride-5	6.57	High Chloride- 5	50.24
Low Alkalinity-1	35.82	Low Alkalinity- 1	46.9	Low Alkalinity- 1	41.97	Low Alkalinity- 1	15.88
Low Alkalinity-2	33.35	Low Alkalinity- 2	318.1	Low Alkalinity- 2	48.55	Low Alkalinity- 2	12.73
Low Alkalinity-3	15.87	Low Alkalinity- 3	37.36	Low Alkalinity- 3	12.66	Low Alkalinity- 3	23.23
Low Alkalinity-4	8.388	Low Alkalinity- 4	163.2	Low Alkalinity- 4	8.717	Low Alkalinity- 4	15.17
Low Alkalinity-5	14.37	Low Alkalinity- 5	35.05	Low Alkalinity- 5	6.213	Low Alkalinity- 5	11.84
Low Alk. + High Chloride- 1	22.68	Low Alk. + High Chloride- 1	40.09	Low Alk. + High Chloride- 1	30.14	Low Alk. + High Chloride -1	44.7
Low Alk. + High Chloride- 2	53.88	Low Alk. + High Chloride- 2	72.78	Low Alk. + High Chloride- 2	41.48	Low Alk. + High Chloride -2	554.6
Low Alk. + High Chloride- 3	430.4	Low Alk. + High Chloride- 3	13.62	Low Alk. + High Chloride- 3	32.76	Low Alk. + High Chloride -3	40.55
Low Alk. + High Chloride- 4	17.76	Low Alk. + High Chloride- 4	31.22	Low Alk. + High Chloride- 4	38.93	Low Alk. + High Chloride -4	31.25
Low Alk. + High Chloride- 5	12.2	Low Alk. + High Chloride- 5	7.011	Low Alk. + High Chloride- 5	693.7	Low Alk. + High Chloride -5	72.52
Low Chloride- 1	17.7			Low Zinc- 1	168.8		
Low Chloride- 2	59.68			Low Zinc- 2	320.4		
Low Chloride- 3	10.71			Low Zinc- 3	27.28		
Low Chloride- 4	118.1			Low Zinc- 4	46.48		
Low Chloride- 5	9.948			Low Zinc- 5	12.66		
Low Alk. + MgSO4-1	13.78	NJWSA-1	46.68	SMCMUAA-1	37.68	SMCMUAB-1	31.14
Low Alk. + MgSO4-2	17.51	NJWSA-2	19.92	SMCMUAA-2	9.596	SMCMUAB-2	27.17
Low Alk. + MgSO4-3	46.08	NJWSA-3	588.9	SMCMUAA-3	18.25	SMCMUAB-3	14.44
Low Alk. + MgSO4-4	11.35	NJWSA-4	62.5	SMCMUAA-4	323.6	SMCMUAB-4	42.66
Low Alk. + MgSO4-5	15.81	NJWSA-5	47.66	SMCMUAA-5	264.6	SMCMUAB-5	27.22

APPENDIX D

Table D-1. Raw coupon data (Utility A)

Coupons	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	% Decrease	% Difference ¹
Low Chloride	874	217	68.2	62.4	49.5	49.8	37.1	56.0	44.4	43.1	34.4	30.9	33.9	39.4	42.2	N/A
High Chloride	371	384	573	358	159	166	342	342	163	210	142	159	74.4	53.6	90.6	N/A
Present	182	102	98.6	42.9	43.5	37.0	348	193	135	70.8	39.4	49.5	31.8	22.4	77.3	N/A
Low Alk. + High Chloride	4,260	4,680	9,450	3000	1880	3120	1680	1800	1250	1020	940.0	1070	1240	925	90.2	N/A
Low Alkalinity	1,660	1,180	5,610	2330	1690	2750	1530	1600	1480	962	743	760	812	940	83.3	N/A
High Chloride	1,490	703	1,340	525	140	177	127	244	100	51.1	54.6	33.4	33.7	30.2	97.7	7.54
Present	8,670	1,140	180	218	62.1	77.6	66.8	48.9	34.9	44.3	49.0	50.2	37.0	23.8	86.7	11.5
Low Alk. + High Chloride	7,920	3,820	6,090	2970	1890	2230	1470	1780	1850	1180	974	821	1090	907	85.1	5.45
Low Alkalinity	2,070	695	2,870	1660	1190	1200	478	324	327	170	149	85.1	77.0	90.0	96.9	15.1
Low Zinc	145	60.3	43.4	56.0	25.5	26.1	24.2	19.5	18.7	19.2	19.1	37.9	24.3	19.4	55.4	33.0
High Chloride	2,280	1,330	695	561	286	287	268	651	269	189	159	358	135	68.8	90.1	0.594
Present	874	519	279	109	83.4	54.5	83.6	94.7	53.8	48.4	39.8	62.6	43.9	31.5	88.7	13.7
Low Alk. + High Chloride	2,100	1,280	1,860	1510	1430	2110	1240	1450	1240	718	608	775	774	581	68.7	26.7
Low Alkalinity	1,700	963.3	2,855.00	1854	1723	2225	1201	1275	1236	777.5	670.2	884.8	703.8	681	76.1	8.92
High Chloride	324	59.9	51.0	92.5	29.9	18.4	24.7	39.8	69.6	22.0	20.4	20.0	17.8	17.4	65.9	31.6
Present	76.2	29.3	30.2	23.7	14.9	8.92	12.9	24.3	13.0	13.5	10.2	12.2	10.8	10.9	63.8	19.2
Low Alk. + High Chloride	2,500	385	1,340	1240	552	925	390	410	381	152	98.6	87.8	67.2	72.7	94.6	5.09
Low Alkalinity	1,590.0	645	1,060	661	776	707	451	400	333	134	116	155	139	115	89.2	6.84
Low Alk. + MgSO4	3,730	2,480	2,180	2160	1970	2100	1510	1830	1780	1920	1520	1550	1640	1750	19.7	123
Partner Utility 2	769	713	696	439	205	412	221	178	134	125	139	93.8	139	385	44.7	0.621
Partner Utility 1, Site 1	19,700	18,900	15,500	18900	10700	8380	6180	6000	2300	3030	1550	1680	1310	1730	88.8	0.000120
Partner Utility 1, Site 2	7,980	6,680	5,380	10600	4140	5810	5030	5240	4130	4350	4360	2720	2330	1300	75.8	16.9

A)

Legend:

	Control		Zinc Orthophosphate
	Orthophosphate		Partner Utilities
	Zinc		Magnesium

APPENDIX E

Table E-1. Student's T-Test Data for Coupons (Utility A)

Coupon Conditions	Probability
Present, Control VS. Present, Zinc Ortho	0.000553
High Cl-, Control VS. High Cl-, Zinc Ortho	0.0158
Low Alk, Control VS. Low Alk, Zinc Ortho	1.13E-06
Low Alk. + High Cl-, Control VS. Low Alk. + High Cl-, Zinc Ortho	0.0174
Present, Control VS Present, Ortho	0.726
High Cl-, Control VS. High Cl-, Ortho	0.104
Low Alk, Control VS. Low Alk, Ortho	6.92E-07
Low Alk. + High Cl-, Control VS. Low Alk. + High Cl-, Ortho	0.952
Present, Zinc Ortho VS Present, Ortho	0.00885
High Cl-, Zinc Ortho VS. High Cl-, Ortho	0.0135
Low Alk., Zinc Ortho VS. Low Alk, Ortho	0.383
Low Alk. + High Cl-, Zinc Ortho VS. Low Alk. + High Cl-, Ortho	0.00917