Understanding Mechanisms of Water Lead Contamination by Nitrate Spallation Corrosion and Lead Removal by Point-of-Use (POU) Filters

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Abstract

Lead enters drinking water by a process of corrosion, dissolution or particle detachment from lead bearing plumbing materials. Preventing contamination of water from lead-tin solder corrosion and achieving effective removal of particulate lead by point-of-use (POU) filters are important public health goals. These topics are especially timely given forthcoming revisions to the Lead and Copper Rule and ongoing efforts to reduce lead levels at the tap.

Recently a switch from non-corrosive groundwater to a surface water source at a utility in Illinois caused unusual drinking water contamination from the release of large lead solder chunks from plumbing to water. Point-of-use (POU) filters distributed to remove the lead at this utility and elsewhere were not always completely effective. Here, we elucidate the mechanism of lead solder release in two chapters, followed by two more chapters examining lead removal by POU filters.

The lead solder contamination arose after the water utility switched sources from high sulfate and low nitrate groundwater to a surface water with lower sulfate and high nitrate during runoff events. Such problems were unexpected because the surface water with high nitrate was not considered corrosive according to current theory. A chapter entitled *A Novel Mechanism of Lead-Tin Solder Spallation in the Presence of Nitrate* describes how 1) nitrate is extremely corrosive to lead:tin solder galvanically connected to copper, 2) nitrate corrosion can sometimes cause detachment of solder chunks to water, and 3) nitrate corroded the metal by reduction to ammonia and other reaction products.

Another Chapter reports a follow up study, that reproduced the essence of nitrate induced spallation corrosion as observed in homes, using copper pipe with beads of lead-tin solder attached. During a 4-month experiment, the non-corrosive groundwater with high sulfate caused no solder beads to detach and only about 1% of the total lead was released to water. But in the surface water with high nitrate believed to cause the lead problem, 100% of the solder beads detached after just two months, and 80% of the total lead in the solder was released to water after 4 months. In the same surface water that had lower nitrate, with or without zinc orthophosphate or polyphosphate inhibitors, only 8 to 17% of the solder beads detached. Electrochemical studies also found that equimolar concentrations of chloride did not cause the disintegration of tin solder or as much weight loss as nitrate. Moreover, sulfate concentrations as low as 0.75 mM could effectively inhibit tin corrosion caused by 10 mg/L NO_3-N.

Studies focused on efficacy of POU filters have indicated that soluble lead in water is reliably removed, but sometimes particulate lead can escape capture and contaminate the treated water. To better understand this issue and practical limitations of filter use, field studies were performed in occupied and unoccupied homes in Enterprise, LA and New Orleans under both normal and extreme conditions of water lead contamination. For severe lead contamination present after lead pipes were disturbed or when a very long lead service line was present, and filters were tested to 200% of their rated capacity, the treated water occasionally had more than 15 ppb lead even when a very high percentage of the lead was removed. In Enterprise and New Orleans water with more typical levels of influent lead, the treated water was always below 1 ppb lead. But in Enterprise water with high iron and manganese the filters clogged quickly, causing higher costs for filtered water and consumer dissatisfaction.

The occasional problems in removing particulate lead observed in this and prior research gave impetus to a series of bench-scale experiments elucidating particulate lead removal mechanisms by conventional ion-exchange media in sodium (Na^+), strong acid (H^+), chloride (Cl^-) or strong base (OH^-) form. Suspensions of lead phosphate particles of varying sizes and age revealed marked differences in dissolution rates under acidic, circa neutral and basic pHs that are caused by treatment with H^+, Na^+, OH^-, Cl^- form resin. Fresh nanoparticle lead phosphate particles were very labile, and immediately dissolved at pH 4 to form soluble Pb^{+2} ions which were quickly removed by strong acid media. High pHs > 10 and phosphate removal by $OH^–$ form resin could also dissolve the particles, and then remove the anionic soluble lead formed at high pHs. Na^+ and Cl^- resin caused little or no dissolution at the circa neutral pHs associated with their use and had lower rates of lead removal from water as a result. Older lead phosphate particles acquired from a New York City harvested lead pipe loop rig or purposefully synthesized in the laboratory, did not dissolve as readily as fresh nanoparticles which profoundly affected their relative removal efficiency by the different media. Overall, dissolution of lead phosphate particles in the ion-exchange media can sometimes have a range of important effects that can enhance or hinder lead removal dependent on circumstance.

This thesis enhances our understanding of water lead contamination mechanisms by spallation of lead-tin solder and factors affecting lead removal by some POU filters. These novel insights can be helpful in preventing and mitigating future water lead contamination events.

Understanding Mechanisms of Water Lead Contamination by Nitrate Spallation Corrosion and Lead Removal by Point of Use (POU) Filters

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General Audience Abstract

Lead enters drinking water by a process of corrosion, dissolution or particle detachment from lead bearing plumbing materials. Preventing contamination of water from lead-tin solder corrosion and achieving effective removal of particulate lead by point-of-use (POU) filters are important public health goals. These topics are especially timely given forthcoming revisions to the Lead and Copper Rule and ongoing efforts to reduce lead levels at the tap.

Recent studies have revealed that high nitrate sometimes causes severe lead contamination of water in homes with lead soldered copper pipe. This thesis elucidates a novel mechanism of lead solder corrosion from nitrate attack in two chapters, followed by two more chapters examining problems associated with lead removal from water by point-of-use (POU) filters.

In a recent water lead contamination event, nitrate somehow caused large chunks of metallic lead solder to fall off pipes into the drinking water, a novel process that we term “spallation” corrosion. This observation inspired experiments to recreate this problem in the laboratory which found 1) nitrate and its reduced reaction products create a very low pH at the lead or tin anode during the nitrate-accelerated corrosion 2) the corrosion eats at the bond between the lead-tin solder and the copper pipe, cracking the lead:tin solder, causing chunks of metal to completely detach into water, and 3) corrosion of metal via nitrate reduction to ammonia at the tin anode.

Follow-up electrochemical studies reproduced the essence of field nitrate induced spallation corrosion as seen in homes using copper pipe with beads of lead-tin solder attached. These beads detached to water during a 4-month experiment in some water chemistries and not others. No solder beads detached, and only about 1% of the total lead in the solder was released to water, during exposure to a non-corrosive groundwater with high sulfate. But all the solder beads detached in just two months, and 80% of the total lead was released to the water in 4 months, in a surface water with high nitrate. Electrochemical studies found that sulfate concentrations as low as 0.75 mM effectively inhibited the extreme tin corrosion caused by 10 mg/L NO_3-N.

Testing of lead certified POU filtration performance under varying conditions offers insight into challenges facing consumers. Field filtration studies were conducted in occupied homes for typical water lead challenges, or in unoccupied homes for testing of potentially dangerous water lead hazards, in Enterprise and New Orleans, LA. Results illustrate the difficulty of always achieving effective lead removal in cases where 1) the

lead service line is very long, or 2) there is high erratic particulate lead after a lead service line is disturbed. Although effective lead removal occurred in other situations, the presence of very high levels of iron caused premature filter clogging and associated consumer frustration.

Problems observed in removing particulate lead informed a series of bench-scale studies evaluating the role of particle age and size on filtration effectiveness by cation and anion form exchange resins (H^+, Na^+, OH^-, Cl^-). Batch tests demonstrated that fresh lead phosphate particles less than 1 micron in size are quickly dissolved at pH less than 4 caused by H^+ form ion-exchange resin and were dissolved moderately fast at pH higher than 10 caused by OH^- form ion-exchange resin. But the particles hardly dissolved at all at the moderate pHs present when Na^+ and Cl^- form resins are used. Dissolved lead was readily removed by H^+, OH^- and Na^+ form resins at the pH range they created during treatment, but not by Cl^- form resins. Lead phosphate particles from New York City did not dissolve as quickly as fresh nanoparticles, which sometimes enhanced or hindered their relative removal efficiency in the range of media tested. Overall, dissolution of lead phosphate particles within the media had important effects on the overall lead removal and could even cause previously removed lead to be released in some cases.

This thesis enhances our understanding of water lead contamination mechanisms by spallation of lead-tin solder and lead removal by some POU filters. These novel insights can be helpful in preventing and mitigating future water lead contamination events.

Acknowledgements

I would like to thank God for inspiring me to take on this work and qualifying me for that call. This thesis is a testament to God's faithfulness, may the glory be to God. Along that line, I'd like to thank my family for their ceaseless prayers which gave me strength, wisdom, and loving kindness throughout this arduous academic journey.

I would like to thank my faculty advisor Dr. Marc Edwards, the Edwards research group, and my committee members for all the assistance they have provided me.

I am forever grateful for the friends I've made along the way that quickly became part of my chosen family and my undergraduate Wellesley College mentors and community for supporting, encouraging, and mentoring me throughout my graduate school years. You all continuously remind me of the importance of mentoring, remaining authentic, and pursuing your curiosities with integrity and fervor.

I dedicate this thesis to my nieces and nephews and all citizen scientists fighting for clean drinking water.

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Attributions

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CHAPTER 1:

Introduction

Lead-tin solder alloys were commonly used in plumbing prior to the lead solder ban of 1986. A galvanic cell is formed when the anodic solder is in electrical contact with cathodic copper pipe. Galvanic corrosion of lead solder can sometimes cause severe water lead contamination because of a large cathode (copper pipe) to anode (solder) surface area ratio (Dodrill, D. and Edwards et al., 1995; Edwards and Triantafyllidou et al., 2007; Nguyen and Stone et al., 2010).

A novel manifestation of lead-tin solder galvanic corrosion was recently identified, in which nitrate disintegrated solder galvanically attached to copper pipe, resulting in spallation of large chunks of metallic solder to water (Lopez et al., 2022). This discovery was worrisome given that lead solder is present in about 80 million U.S. residences, nitrate is not considered a cause of corrosivity in EPA guidance, and seasonal spikes in nitrate during runoff events are increasingly common (Stets et al., 2015; Pennino et al., 2017; Almasri et al., 2004, Dodrill, D. and Edwards et al., 1995; Edwards and Triantafyllidou et al., 2007; Lytle et al., 1996; Nguyen, C, et al., 2011; Nguyen and Stone, et al., 2011a; Oliphant et al., 1983; Schock et al., 1989; Snoeyink et al., 2021; Wilczak et al., 2010). The spallation problem was only detected and diagnosed after a source water switch caused an unexpected water lead contamination event (Lopez et al., 2022).

There is presently no mechanism described for solder spallation corrosion, nor is it understood what water chemistry factors trigger or inhibit the problem. Chapter 2 of this thesis addresses this deficiency by describing “A Novel Mechanism of Lead-Tin Solder Spallation in the Presence of Nitrate,” authored by Dr. Kathryn G. Lopez (experimental design and first authorship), co-authored by Chantaly Villalona (execution of mechanistic experiments), Haley Grubbs (experimental assistance) and Dr. Marc Edwards (conceptualization, methodology, supervision, paper review, advising, editing, funding acquisition). Experimental bench-scale results revealed that high levels of nitrate induced spallation in association with low pH at the anode surface, reduction of nitrate to ammonia, when lead solder was more than 40% tin by weight. Detinning at the copper-solder interface makes the solder susceptible to severe metallic cracking and detachment to water, producing metal weight loss exceeding Faradaic predictions. This manuscript will be submitted to *Environmental Science and Technology Letters*.

Chapter 3 of this thesis extends that discovery, by recreating the essence of spallation corrosion in short duration beaker experiments. Additionally, electrochemical studies with separated tin anode and stainless-steel cathode demonstrated that sulfate concentrations as low as 0.75 mM can effectively inhibit the anodic current and suppress weight loss via spallation in the presence of high nitrate, unlike traditional corrosion inhibitors. The manuscript “Sulfate Inhibits Lead-Tin Solder Spallation Caused by Nitrate” was authored by Chantaly Villalona and co-authored by her advisor Dr. Marc Edwards and will be submitted to *Environmental Science and Technology Letters.*

Once lead has contaminated water, lead exposure at the tap may be reduced by implementing corrosion control treatment (CCT), flushing, pipe replacement, and through temporary deployment of point-of-use (POU) filters. Chapter 4 explores "Household Point-of-Use Water Faucet Filters for Lead Removal: Field Performance and User Experiences." It demonstrates the potential for filter challenges (e.g., high effluent lead or reduced efficiency) that occur in the presence of high particulate lead and by clogging when filtering water high in manganese and iron. In cases with high iron and significant filter capacity reduction, it may even be more cost effective to purchase bottled water rather than use filters. This manuscript had co-first authors Dr. Jeannie M. Purchase and Chantaly Villalona, and coauthors Dr. Adrienne Katner, Dr. Kelsey Pieper and Dr. Marc Edwards who helped conceptualize, supervise, review, edit and fund the work. This manuscript will be submitted to *Environmental Science and Technology.*

Reports of POU filter failures in removing lead have prompted testing to explain the varying performance of different filters in removing lead particles (Lytle et al., 2021; Purchase et al., 2020; Masters et al., 2023; Giammar et al., 2022). Chapter 5 examined ion-exchange media in batch and in columns, to elucidate particulate lead phosphate removal mechanisms by a range of ion-exchange media. Experiments revealed that suspensions with fresh lead phosphate nanoparticles had highly labile particles which were readily dissolved and removed by strong acid (H^+ form resin) and/or strong base (OH^- form) resins. Older insoluble particles did not dissolve as readily, nor did fresh lead phosphate at pH 5-8 range caused by Na^+ and Cl^- form resins, causing poor removal of lead by low efficacy particle filtration. The pH and other chemical changes in the resins during stagnation or as water passed through the column, could sometimes cause release of previously removed lead from the filters, at levels which pose a human health concern. These findings can be applied to improve public health protection when POU filters are applied to a range of potable waters and circumstances. The manuscript, "Mechanisms of Lead Phosphate Particle Removal by Ion-Exchange Media Depend on Particle Size and Lability" will be submitted to *Environmental Science and Technology*.

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CHAPTER 2:

A Novel Mechanism of Lead-Tin Solder Spallation in the Presence of Nitrate

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Abstract.

Elevated 90th percentile water lead levels associated with the release of large chunks of lead-tin solder to drinking water was recently attributed to severe, nitrate-accelerated corrosion. A new mechanism of water lead contamination via nitrate-induced spallation of solder was determined using new solder coupons, harvested pipe samples, and galvanic electrochemical tests. Nitrate attack is associated with formation of ammonia and other reduced nitrogen compounds, causing detinning of solder alloys with ≥ 40% tin by weight and eventually complete detachment of solder at the point of adhesion to copper pipe via formation of a corrosive microenvironment. Solder spallation was observed in as little as six weeks and resulted in 1.3 times more metal weight loss than could be explained by Faraday's law for both tin and 50/50 lead-tin solder even after 32 hours. Understanding this mechanism of attack can help explain and predict water lead contamination events and inform the development of optional corrosion control strategies for potable water supplies. These findings raise concerns about the likelihood of joint failures where high tin content solder alloys were used after the 1986 federal ban on leaded solder.

Introduction.

Seasonal fluctuations in source water nitrate recently triggered a major drinking water lead contamination event that was characterized by spallation of large, metallic lead-tin solder particles following a source water change.[1] Although lead-tin solder corrosion is known to be very sensitive to changes in water chemistry parameters, such as the chloride-to-sulfate mass ratio, alkalinity, pH, and corrosion inhibitors, the phenomenon of metallic solder spallation has never previously been reported.[2-10] Prior research on lead-tin solder corrosion has focused almost exclusively on lead corrosion mechanisms since tin does not pose a comparable health threat, which may be a deficiency since tin is half the solder alloy by weight and is susceptible to several unique degradation pathways. For instance, pure tin bars stored in the U.S. National Defense Stockpile that were exposed to air pollution (contaminants unknown) and cold temperatures recently spontaneously crumbled due to "tin pest" degradation.[11] The inclusion of lead in tin alloys can hinder this degradation, although tin pest has also been identified for tin alloys with 37-50% lead by weight at cold temperatures.[12-14]

Unique degradation of metallic tin has also been reported in the presence of nitrate. Tin-plated food cans are susceptible to rapid detinning by 50 mg/L of nitrate at pH <5.0.[15-19] Nitric acid, often in conjunction with hydrochloric acid, has been widely used to enhance recovery of tin metal from scrap printed circuit board solder.[20] Likewise, tin anodes exposed to weak nitric acid have been subject to particulate release and unusually high weight loss.[21] Intergranular cracking was identified in ancient lead-bearing tin museum artifacts exposed to nitric acid[22], and sulfonic acid in laundry detergents (which can contain nitrogen-bearing functional groups) caused detinning and rapid failure of tin solder connections in washing machines[23]. Tin has even been identified as one of the most effective cathodes for the electrochemical reduction of nitrate to nitrogen gas, and many studies have explored its potential to recover valuable resources (NH_4+/NH_3) from wastewater and reduce nitrate pollution in water[24-26]. However, tin's propensity to corrode during the nitrate reduction process is a major hurdle for its use in water treatment practice[27]. Prior work on nitrate's effect on lead-tin solder demonstrated a pattern of non-uniform corrosion that was hypothesized to be intergranular corrosion[28]. All of these observations anticipate unique problems for tin at solder surfaces in potable water, which can contact corrosive microenvironments of acidic pH <2.5 and concentrate anions such as nitrate from the bulk water due to galvanic corrosion[29].

Understanding nitrate's role in lead-tin solder spallation in drinking water is critical to develop effective corrosion control strategies and prevent future water lead events, especially in light of rising nitrate levels and impetus to switch source waters in many areas of the country[30-32]. This study aims to (1) characterize the nitrate solder spallation mechanism through surface analyses of coupons and harvested pipes, (2) recreate the spallation effect in a short-term bench experiment as a function of tin alloy content in leaded solder, and (3) demonstrate that this mechanism of solder spallation is attributable to nitrate.

Methods.

Solder surface analysis. Pipes (cold and hot lines) from 6 homes from the community subjected to nitrate induced spallation corrosion were harvested from homes in spring of 2022 by our utility partners. Lead-tin solder surfaces of new copper coupons derived from a prior laboratory study (Lopez et al., 2022) and the harvested pipes from the affected community in Illinois were analyzed using an FEI Quanta 600 environmental scanning electron microscope with energy-dispersive spectroscopy (SEM-EDS) and an accelerating voltage of 30 kV[1].

Solder droplet study. To recreate the solder spallation effect, droplets of pure lead wire, pure tin wire, and 50/50, 60/40, and 70/30 lead-tin solder wires were soldered onto the surface of copper sheets. The copper sheets were placed in 125-mL glass jars and exposed to pH 2.5±0.1 water with 140 mg/L NO_3-N. The low pH and high nitrate was designed to simulate the microenvironment of water near the solder anode during galvanic corrosion[29]. The jars were subject to weekly water changes for 6 weeks and were otherwise stagnant, and the solder droplets were monitored visually for cracking/detachment and total ammonia production (referred herein as ammonia).

Electrochemical cell study. Electrochemical cells with occluded anodes were designed to track the mechanism driving the spallation effect (Appendix Figure A1). These cells consisted of a 500-mL beaker containing a tube of 25-mL volume with a 2-mm hole in its side. One cm of a pure tin or a 50:50 lead-tin solder wire (anode) was placed in the tube, and 3.4 volts were applied between the anode and a platinum cathode which were 2-in apart. Tests were conducted with constant 0.01 M ionic strength solutions of water: 1) 0.01 M sodium chloride, 2) 0.01 M sodium nitrate, or 3) 0.005 M sodium sulfate. A control with deionized water and an additional test with pure lead wire in 0.01 M sodium nitrate was also run for comparison. After 32-hrs, samples were collected to determine metals release, chemistry of the anode and cathode compartments, and final metal weight loss. Select wires were analyzed with SEM as described above.

Statistical analysis. Statistical analysis used ANOVA to compare weight loss between the conditions of the electrochemical cell study. Statistical significance was determined in R (version 4.1.1) using an alpha (α) value of 0.05.

Results and Discussion.

Solder Surface Analysis.

Spallation in harvested pipes. Eighty-three percent of the cold line pipes and 50% of the hot line pipes with solder joints also had visible, intact metallic solder beads on the interior of the pipe, as often occurs via drips at the joint during installation (Figure 1a). Exposed solder beads as large as 1-cm in diameter were found on the interior of some pipes (Appendix Figure A2a-b). This solder generally remained adhered to the pipes when they were cut open for analysis, but there were instances when corroded chunks of solder would simply fall off the pipe with minor disturbance, demonstrating a weakened bond to the copper pipe. In one case, a dime-sized piece of solder detached from the pipe leaving behind a clear crater in the pipe scale (Figure 1b). Many of the pipes had these visible craters where spallation had previously occurred, contributing large particles that clogged the aerators of consumers' homes (Figure 1c, Appendix Figure A2c-d). Analysis with SEM-EDS showed a clear pattern of detinning, as evidenced by much higher proportions of lead than was present in the original solder (Figure 1d). This detinning is hypothesized to play a critical role in spallation, since de-alloying creates internal stresses that can cause cracking and spallation[33-36].

Spallation from new solder. Cutting open copper coupons coated with new lead-tin solder that were exposed to the affected community's water supply with supplemental nitrate for over 13 months also revealed visible craters up to 2.5-mm in length in the solder surfaces where particles spalled off. The craters most often occurred at the interfaces between the solder and copper pipe, where the most intense galvanic activity occurs (Figure 1e).

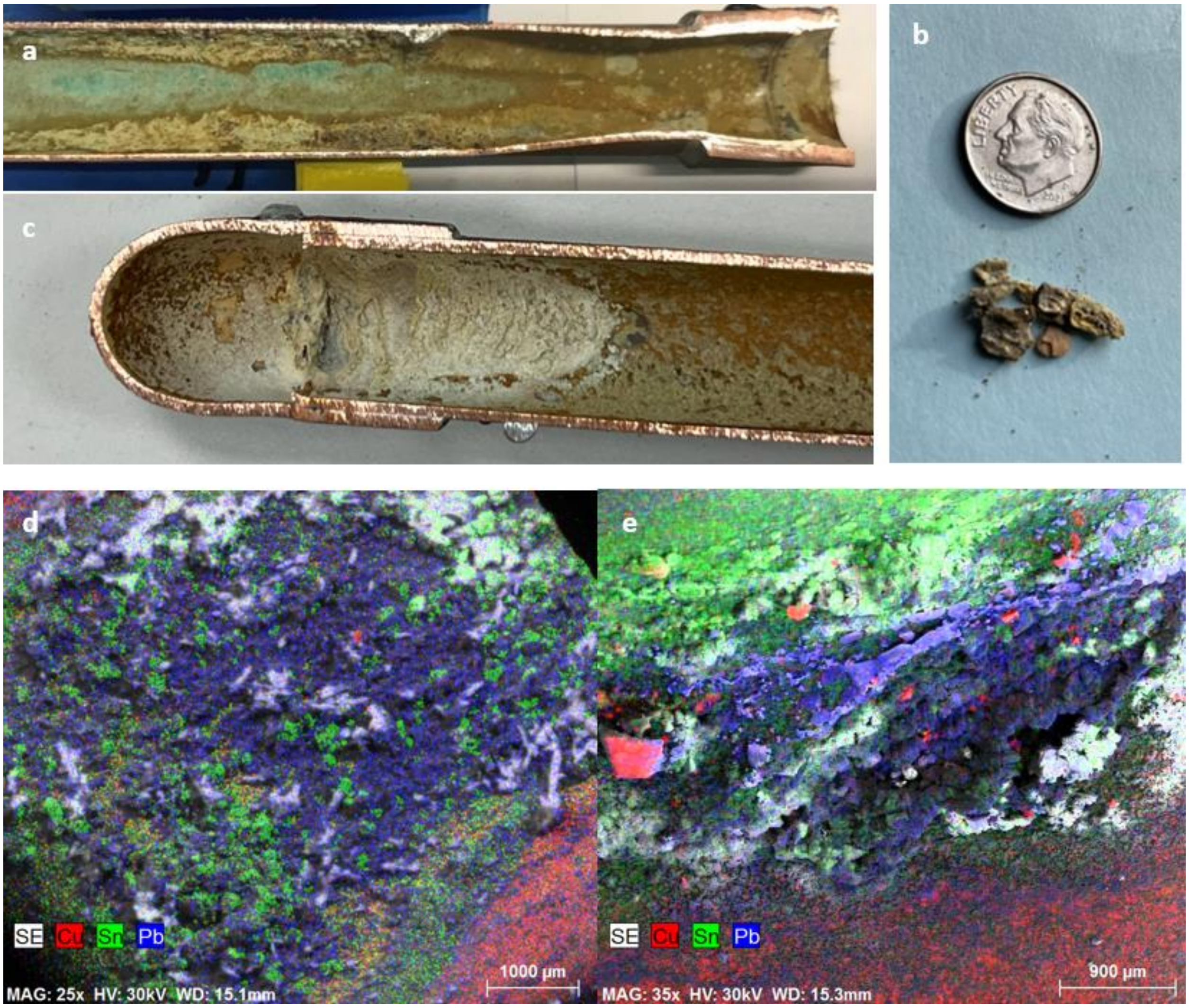

Figure 1. a) Image of an exposed bead of solder below a solder joint on the interior of a hot supply pipe from the affected community. b) Dime-sized piece of solder that completely detached from pipe while cutting. c) Crater on the interior of a pipe where solder once was, covered in a brittle, porous white precipitate. SEM-EDS images of detinning and non-uniform corrosion on lead-tin solder surfaces from d) harvested pipe exposed to source water with natural levels of nitrate, and e) new copper coupon treated with source water that contained natural levels of nitrate. These craters occurred at the interface between solder and copper pipe. Areas with higher surface concentrations of copper, tin, and lead are highlighted in red, green, and blue, respectively.

Solder Droplet Study.

Solder spallation and detachment recreated in solder alloys with 40% or more tin. Corrosion of the solder droplets with 40% or more tin in the 140 mg/L NO_3-N and pH 2.5 water proceeded rapidly, and pure tin was most affected (Figure 2a-e). On the fifth day of the experiment, a thick, white ring of scale was observed at the copper-solder droplet interface. By day 11, there was visible separation at the copper-solder interface and small particles were observed in the jars. Significant cracking was first identified on day 18: after interfacial attack began, very large cracks visible to the naked eye began to cover the surfaces of the 60/40, 50/50, and pure tin droplets. Two days later, the 50/50 droplets' surface cracks began to separate, and large chunks spalled off into the water without any flow disturbance whatsoever. This trend continued through the end of the 6-week experiment. While the 60/40 and 50/50 metallic droplets remained partially intact after they completely detached from the pipe, the pure tin droplets appeared as if they had exploded into fragments (Figure 2f-g).

Before fragmentation of the pure tin droplets began, their volume seemed to increase by about 25%. Such expansion has been reported during tin pest transformations, wherein volumes increased by up to 27% due to internal restructuring of the crystal lattice[14]. Tin is also one of a handful of elements known to be particularly susceptible to hydrogen embrittlement, which can cause irregular volume expansion, separation of grain boundaries, and associated cracking[37]. Detectable ammonia, which has been shown promote hydrogen production during anaerobic iron corrosion, was a reaction product of nitrate in all of the droplet jars during the experiment[38]. Ammonia decreased over time for pure lead and the alloys but remained highest for pure tin (4.6 mg/L total NH_3-N, Appendix Table A1).

Pure lead and the 70/30 lead-tin solder alloy did not exhibit spallation. In contrast with the other alloys, the 70/30 lead-tin solder droplets did not exhibit cracking or spalling and, although they formed the same ring of white scale at the copper-solder interface remained completely adhered to the copper sheet through the end of the study. Likewise, the pure lead droplets did not exhibit spallation, cracking, or detachment. Instead, these droplets turned black by day 5 and began to uniformly dissolve, leaving behind a white powder (Appendix Figure A3).

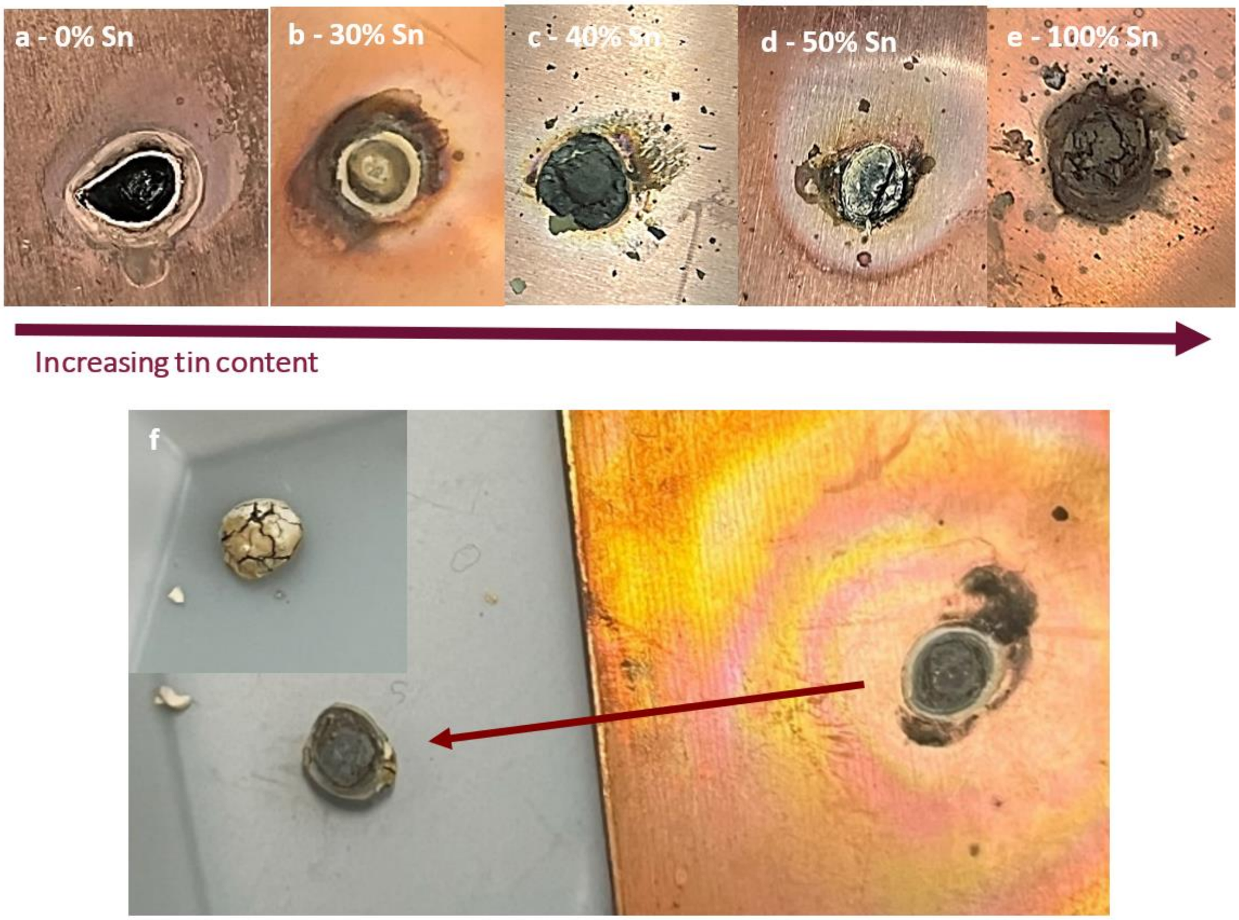

Figure 2. Pictures of droplet surfaces on copper sheets on day 20 shown in order of increasing tin content: a) pure lead, b) 70/30 lead-tin solder, c) 60/40 lead-tin solder, d) 50/50 lead-tin solder, and e) pure tin. Cracking and spallation of large metallic solder particles is visible on droplets with 40% or more tin. f) Picture of surface cracks on a 50/50 lead-tin solder droplet after spalling, and the underside of the droplet and detachment site.

Surface analysis shows nitrogen at the copper-solder interface. Surface analysis of the detachment site where a 50/50 lead-tin solder droplet spalled off showed detectable levels of nitrogen (up to 17 atomic %) in the remaining scale where the copper-solder interface used to be (Appendix Figure A4). These spots with detectable nitrogen had less tin than other areas of the detachment site. Minimal lead (<1 atomic %) was detected at the detachment site, presumably because any exposed lead dissolved in the acidic environment (pH 2.5) by the end of the study. This likely explains the absence of the characteristic white, brittle precipitate that was found at solder spallation sites in the pipes. Detectable nitrogen was not found using SEM on other studies of solder surfaces without nitrate in the water.

Electrochemical Cell Study.

Nitrate solution triggered spallation of both tin and 50/50 lead-tin solder. Disintegration of the tin anode occurred within 32 hours of exposure to nitrate in the electrochemical cell. Weight loss from the tin wire in the control solution with and without sulfate was always less than 0.16% and these sulfate conditions were not significantly different from the control ($p=0.54$, ANOVA). Chloride was significantly corrosive to tin and caused 0.86% weight loss ($p=3.0*10^{-6}$). However, nitrate caused the greatest weight loss from tin with 1.7% weight loss ($p<1*10^{-7}$), significantly higher than chloride ($p=9.2*10^{-6}$). Surface analysis with SEM confirmed that the tin wires exposed to nitrate had been more severely corroded relative to other conditions, and cracks and craters were evident on the surface from which particles spalled (Appendix Figure A5a-e). In contrast, the tin wires exposed to chloride and sulfate had no craters or cracks.

The 50/50 lead-tin solder wires behaved similarly to tin. The control and sulfate solutions had minimal effects on weight loss (<0.08%) and were not significantly different from each other ($p=0.94$). Chloride, which is well-known to exacerbate lead solder corrosion, caused a weight loss of 0.97% ($p=1.0*10^{-6}$). Yet, nitrate caused more weight loss (1.5%, $p<1*10^{-7}$) than chloride ($p=6.0*10^{-4}$). Only nitrate caused spallation of the lead-tin solder, but it was not as severe as observed for pure tin (Appendix Figure A6a-e), consistent with expectations that higher lead content reduces susceptibility of the alloy to acidic attack[22]. Pure lead wire exposed to the same nitrate solution did not produce significantly different weight loss (1.8%) than lead-tin solder (1.5%, $p=0.20$) in 32 hours. However, pure lead's corrosion mechanism was visibly different: while lead-tin solder spalled chunks of metal, the pure lead wire uniformly corroded consistent with classic mechanisms (Appendix Figure A7).

Weight loss from wires exposed to nitrate exceeds Faraday's law. Currents for the pure tin wires in all treatment conditions increased throughout the 32-hr period (Figure 3a). Despite the fact that nitrate caused significantly greater weight tin loss than chloride (1.7% versus 0.86%), currents for both of these treatments followed very similar trends and at the end, were effectively the same (144 versus 142 μA, respectively). A predicted weight loss was calculated by integrating the currents and applying Faraday's law assuming a 2-electron transfer. The actual weight loss values for both sulfate and chloride were below this predicted value, which is an understandable deviation because some corroded metal remains attached to the anode after light cleaning (Figure 3c). However, metal weight loss values for nitrate exceeded the Faradaic predicted value by 1.3 times, consistent with the "chunk effect," in which there is anomalously high metal weight loss relative to Faradaic current predictions[21,39].

Similarly, currents for the 50/50 lead-tin solder wire increased over time with the exception of sulfate (Figure 3b), which has previously been shown to passivate lead solder corrosion[40]. Nitrate had the greatest final current (125 μA) compared to the other conditions (chloride had a final current of 100 μA). Weight loss from the solder wires followed a similar pattern as tin (1.3 times the predicted value in the nitrate solution), with the exception that chloride also caused greater weight loss than predicted based on Faraday's law for this condition (Figure 3c). The test was repeated at a much lower level of nitrate (10 mg/L NO_3-N) and similar severe degradation of pure tin wires occurred.

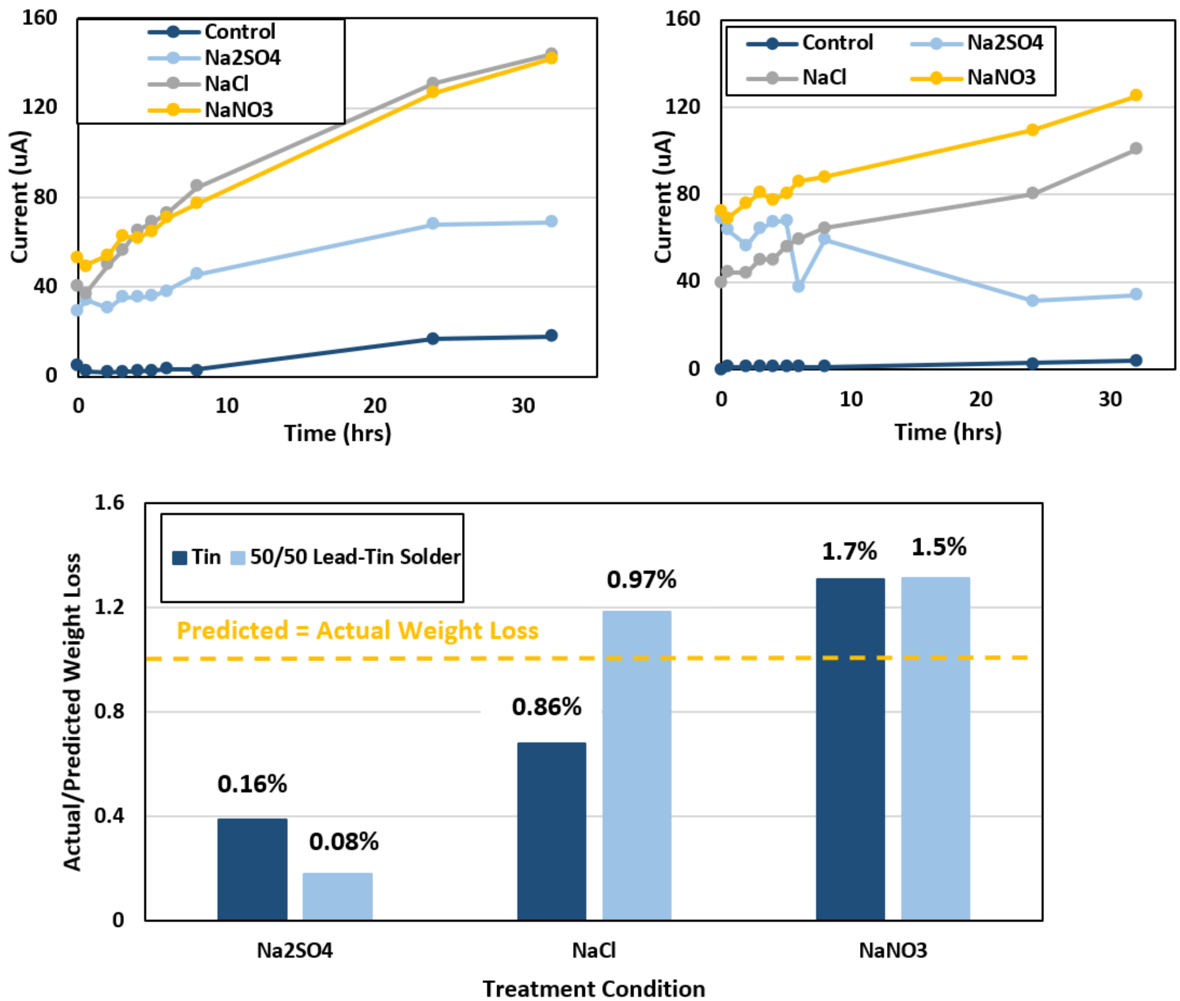

Figure 3. a) Current over time in the electrochemical cell with a tin anode for all 4 treatment conditions: control, sulfate, chloride, and nitrate (n=1). b) Current over time in the electrochemical cell with a 50/50 lead-tin solder anode for the same conditions (n=1). c) Fraction of actual versus predicted weight loss for both tin and 50/50 lead-tin solder wires in the 3 anion solutions (n=5). The yellow line indicates where actual weight loss equated predicted weight loss. Actual percent weight loss measurements are shown above the bars. The control group was omitted from this figure because weight loss measurements were within the range of error for analytical equipment.

Chemical reactions at the anode.

In all of the electrochemical cells, a pH drop in the anode compartment was observed relative to the original pH (approximately 5.9) as expected (Appendix Table A2). For tin, chloride produced the lowest anode compartment pH (2.87), followed by nitrate (3.11), sulfate (3.40), and the control (4.11). For 50/50 lead-tin solder, sulfate produced the lowest anode pH (3.28), followed by chloride (3.53), nitrate (4.61), and the control (4.92). Lead wire in nitrate solution had the highest pH in the anode compartment at 6.00. Tin, and alloys with higher tin contents, can create lower anode compartment pH levels because tin is a stronger Lewis acid than lead, which may be key to creating the corrosive galvanic microenvironment that makes nitrate attack possible. An increase in pH to 6.06-9.00 was observed in the cathodic compartment of the electrochemical cell for all conditions. Chloride was 38% lower at the tin anode and 34% lower at the solder anode when compared to the bulk water. Likewise, sulfate was conserved at the cathode for both tin and solder but was 32% lower at the tin anode and 23% lower at the solder anode. This is contrary to expectations since anions are expected to migrate to the anode.

On average, 18% of the original nitrate was consumed during this testing, accounted for by an increase in ammonia nitrogen to 1% and the remainder presumably lost due to N_2 and other gases (Appendix Table A3). Prior work has found that during the electrochemical reduction of nitrate on tin cathodes, the production of N_2 increases with concentrations of nitrate in solution (100 to 62,000 mg/L $NaNO_3$ tested) and cathodic potentials (<-1.8 V vs Ag/AgCl) while ammonia is the main by-product[24,41]. Conditions more analogous to environmental systems have not yet been well explored. While no detectable nitrite was found in the presence of the tin anodes, it was the dominant detectable reaction by-product for 50/50 lead-tin solder. Specifically, for the 50/50 solder, 16% of the original nitrate was consumed, forming 1.2% nitrite, 0.73% ammonia, and the 13.8% remainder of nitrogen unaccounted for was probably converted to N_2 or NO gas.[25]

Conclusions.

Nitrate has recently been identified as an important corrosion factor that can aggressively accelerate lead-tin solder corrosion and cause the spallation of lead-bearing particles that pose acute health risks. While most solder research has emphasized controlling lead corrosion mechanisms, this study highlighted the importance of understanding how the tin in the alloy plays a role in corrosion mechanisms. Specifically, this work identified a nitrate spallation mechanism in which:

1. Tin corrosion in the solder alloy creates a sufficiently low galvanic microenvironment pH that makes nitrate-accelerated corrosion possible.
2. Detinning of the alloy coupled with other factors renders the solder susceptible to severe cracking and spalling. This spallation results in metal weight loss that exceeds expectations based on Faraday’s Law because much of the released metal has not been oxidized.
3. The attack is concentrated at the copper-solder interface where galvanic activity is greatest, which in some cases causes complete detachment of the solder.
4. Nitrate is reduced to ammonia and other products at the anode.

Understanding this mechanism can help inform treatment strategies for lead-tin solder corrosion, which have focused on controlling lead corrosion, and prevent similar lead release events from occurring in the future as nitrate contamination of source waters continues increase in some areas and many utilities are changing source waters[31]. Additionally, these findings raise concerns about the likelihood of joint failures where high tin content solders (typically 95-97% tin) were used after the 1986 federal ban on leaded solder.

Acknowledgements.

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CHAPTER 3:

Sulfate Inhibits Lead-Tin Solder Spallation Caused by Nitrate

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Sulfate Inhibits Lead-Tin Solder Spallation Caused by Nitrate

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Abstract.

Nitrate-induced spallation (i.e., chunk) corrosion of lead:tin (Pb/Sn) solder causes weight loss in excess of Faraday's law. The essence of spallation corrosion was recreated in jar tests, that revealed that up to 79% of the lead weight in soldered beads detached into potable water after just 2 months when exposed to 10 mg/L of nitrate. In potentiostatic testing with a tin anode and separated stainless steel cathode, conventional corrosion control by orthophosphate or zinc orthophosphate, at low or high alkalinity, had little inhibitory effect on nitrate attack. But the presence of high levels of sulfate relative to nitrate reduced the current and weight loss by up to 93.2%, while preventing chunk corrosion and the reduction of nitrate. Sulfate was not significantly present in the pipe scale, suggesting it may inhibit corrosion, by displacing nitrate at the anode or cathode surface.

Introduction.

A novel mechanism of lead-tin solder corrosion was recently identified, in which nitrate disintegrates lead-tin solder in galvanic contact with copper pipe, resulting in spallation of large chunks of metallic solder to potable water (Lopez et al., 2023). This discovery is worrisome given that lead solder is present in about 80 million U.S. residences, nitrate is not presently considered to be a corrosive agent in EPA guidance, and seasonal spikes in nitrate during runoff events are increasingly common (Stets et al., 2015; Pennino et al., 2017; Almasri et al., 2004; Dodrill, D.; Edwards et al., 1995; Edwards & Triantafyllidou et al., 2007; Lytle et al., 1996; Caroline K. Nguyen, Clark, et al., 2011; Caroline K. Nguyen, Stone, et al., 2011a; Oliphant, 1983; Schock, 1989; Snoeyink et al., 2021; Wilczak et al., 2010). The spallation corrosion was detected during an unexpected water lead contamination event, triggered by a utility switching from a groundwater source with very high sulfate and very low nitrate, to a new surface water source with seasonally high nitrate (Lopez et al., 2023).

It was recently demonstrated that spallation can occur (Lopez et al., 2024), when anodic tin is oxidized by nitrate with the production of ammonia or other nitrogenous reaction products (e.g. NH_4, NO_2):

$$2\ Sn^{\circ} + NO_3^- + 7H_2O \rightarrow NH_4^+ + 2\ Sn(OH)_4\ (solid) + 2OH^-$$

This attack is unusual, because chunks of metal are released to water, far exceeding predictions based on Faraday's law. At the affected utility, this type of attack was also not sufficiently mitigated by orthophosphate inhibitors alone but required months of dosing zinc orthophosphate before lead levels in the water supply dropped below the Federal action level (Lopez et al., 2023).

This disconcerting incident of solder contamination prompted an investigation into other factors that can promote or inhibit solder spallation attack. Here, we attempt to recreate the essence of lead-tin solder spallation corrosion in a simple jar-test bench scale study. We also examine the effects of sulfate, orthophosphate, and bicarbonate on tin spallation.

Methods.

Lead-Tin Solder Bead Bench-Scale Study. To illustrate the essence of the solder spallation effect, four 50/50 lead-tin solder beads of 0.02 ± 0.005 g were soldered onto 3.3 cm copper pipe couplings (Figure 1). Such droplets of solder with a small surface adhering to copper pipe are occasionally found inside plumbing near soldered joints. Firm adherence was confirmed by applying a sideways force of about 0.98 Newtons to each solder bead without causing detachment. Each coupon was placed in completely filled 125-mL glass jars and exposed to one of six different water chemistries in triplicate, creating 12 solder beads total per condition (Table 1). During the bench-scale study the water was stagnant between water changes to represent what was believed to be the worst case for concentration cell corrosion in premise plumbing. Water was completely changed using a relatively gentle "dump-and-fill" protocol three times per week for the first month. Jars were moderately inverted three to four times before dumping each sample into its corresponding collection bottle to avoid detachment by the sampling protocol. Each solder bead was visually monitored daily to detect cracking or detachment. All water was collected from each reactor and analyzed weekly according to Standard Method 3005A with 2% HNO_3 digestion for at least 24 h prior to total metals analysis via Inductively Coupled Plasma Mass Spectroscopy.

The experiment continued without a water change for another month. At the end of that time the jar was physically disturbed, to simulate the natural occurrence of water hammer or turbulent flow scouring that naturally occurs in pipes. Jars were disturbed by manually swirling the coupons lightly against the glass jar walls for three complete rotations and inverting the jar five times. The number of beads that detached at each point of the experiment and the cumulative solder release was then documented.

Lead weight loss was calculated via a mass balance approach following the application of a strong physical disturbance. Residual total lead concentration in the digested waters was multiplied by the volume of water in each jar to get the total mass of solder detached or released to water. For a 50:50 lead tin solder, this mass was divided by two producing the total mass of lead in solder released to water.

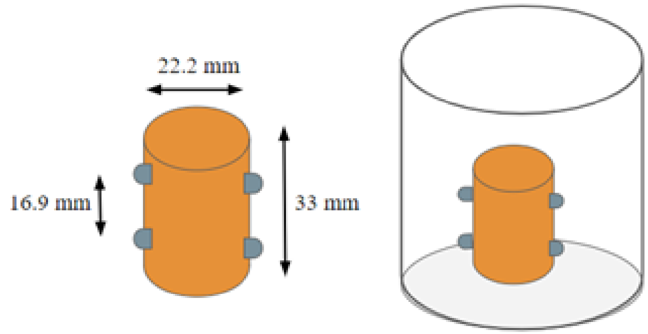


Figure 1. Schematic of Lead-tin Solder beads on copper coupling placed in a 125 mL glass jar

At the utility that had the solder spallation, pipes (cold and hot lines) from 6 homes in the community were extracted in Spring of 2022 and provided by the utility for surface analysis. The soldered joints were exposed to groundwater with elevated sulfate and undetectable nitrate (Table 1) for about 40 years. The water was then switched to surface water that tended to have relatively low nitrate from late Spring to early Fall, and very high nitrate during runoff events from early Fall to late Spring. Historical measurement of lead release suggested that the groundwater was very non-corrosive to solder, whereas the surface water with high nitrate runoff was extremely corrosive. Similar conditions were explored in this bench-scale study (Table 1).

Table 1. Water conditions for bench-scale study. Low alkalinity (46 mg/L as $CaCO_3$) and low sulfate water (28.8 mg/L SO4) is referred to as "K Synthetic."

Water Chemistry Condition	**Chloride (mg/L Cl^-)**	**Sulfate (mg/L SO_4^{-3})**	**CSMR**	**Nitrate (mg/L NO_3^--N)**	**Phosphate* (mg/L PO4-P)**	**Orthophosphate (mg/L PO_4-P)**	**pH**
UP Well Water + SO_4	7	47	0.15	0	0	0	7.2
K Synthetic (will have ~ 0.8 mg/L NO_3^--N)	35	74.5	0.47	~0.6	0	0	7.4
K Synthetic + Polyphosphate	35	74.5	0.47	~0.6	0.8	0	7.4
K Synthetic + high NO_3^-	35	74.5	0.47	10	0	0	7.4
K Synthetic + high NO_3^- + Zn-Orthophosphate	35	74.5	0.47	10	0	0.8	7.4

K Synthetic + high NO_3^- + Polyphosphate	35	74.5	0.47	10	0.8	0	7.4

*Seaquest was used for polyphosphate.

Gamry Electrochemical Cell Study. Direct current (DC) potentiostatic corrosion tests were performed in electrochemical cells using a GAMRY ECM8 Electrochemical Multiplexer. Cells consisted of a 1 L beaker with 2 cm tin wire as the working electrode (anode), and a 25 cm^2 304-stainless steel counter electrode (cathode) located 1 cm apart (Appendix Figure B1). The pure tin wire was polarized +1 V between the anode and stainless-steel cathode using the general approach of (Nguyen et al., 2010) and galvanic currents were automatically recorded. Initial and final pure tin wire mass were noted and subtracted when calculating percent weight loss of pure tin wire.

After 5 days, the weight loss of the working electrodes was determined. The tin wire was scrubbed lightly 5 times with a 3M scouring pad to remove loose debris. This cleaning protocol did not cause significant weight loss when tested on new metallic wire.

Gamry Electrochemical Tests with NO_3^- and Cl^- versus SO_4^{-2}. All testing was conducted in water with 10 mg/L NO_3^--N and no alkalinity. To evaluate the effects of sulfate on nitrate-induced spallation, a range of sulfate levels from 0-961 mg/L SO_4^{-2} via Na_2SO_4 was added to water (Table B1). Beakers were pH adjusted to 7.5 ± 0.05 prior to the start of the test and ranged from 5.96-9.24 by the end. Most of the above experiments were repeated with 27.2 mg/L Cl^- was tested instead of 10 mg/L NO_3^--N (equimolar concentrations). As per specific experiments, alkalinity was added as $NaHCO_3$, orthophosphate as NaH_2PO_4, polyphosphate as Seaquest, and chloride as NaCl.

Faraday's law was used to calculate predicted weight loss according to current data produced in electrochemical studies. Actual weight loss measured in the lab was divided by this predicted weight loss to derive Actual/ Predicted values.

Statistical Analysis. Statistical analysis used Student's t-test to compare inhibitory chemical weight loss to the nitrate control for the electrochemical GAMRY studies. Statistical significance was determined in R (version 4.3.2) using an alpha (α) value of 0.05.

Results and Discussion.

After reproducing the essence of spallation corrosion that caused the Pb/Sn solder contamination of potable water, the impacts of various ions on anodic corrosion of tin were explored.

Lead-tin Solder Bead Bench-Scale Study.

Trends in Bead Detachment. The copper exposed to the ground water had visible green corrosion products by the end of the study, but all the Pb/Sn solder beads remained firmly attached to the pipe (Figure 2d & 3). In contrast, in all the other water conditions with detectable nitrate of 0.6 or 10 mg/L, some beads of solder sometimes detached fully from the pipe into the water (Figure 2d & 3). Before falling off completely, a chunk of metal often fell from the very tip of the solder furthest from the copper, creating a "divot" of missing metal (Appendix Figure B2).

Quantitatively, in the surface water with relatively low nitrate of 0.6 mg/L NO_3^--N, one of the 12 beads detached. Two of the 12 beads detached in this water amended with polyphosphate (Figure 2e). In the surface water with very high nitrate during runoff events, all twelve (100%) of the solder beads detached. In this high nitrate water with polyphosphate or zinc orthophosphate, only 5 and 6.5 beads detached (42% & 54%).

Trends in Lead Release. When the Pb/Sn solder beaded copper coupons were placed in the non-corrosive groundwater with high sulfate and undetectable nitrate, lead release to water was very low (average 30 ppb, high of 72 ppb) over the duration of the 1-month study (Figure 4). The somewhat more corrosive surface water, K-Synthetic with seasonally low nitrate of 0.6 mg/L NO_3^--N had average lead of 1442 ppb (range 418-2260 ppb). In contrast, the surface water, K-Synthetic with high nitrate of 10 mg/L NO_3^--N had average lead release of 4014 ppb (range 3436-4554 ppb).

Cumulative lead weight loss trends. The cumulative mass of lead released to water was compared to the measured initial mass of lead in the solder beads, to calculate the percentage of lead weight loss for each coupon to the water during the experiment. The average synthetic high nitrate lead weight loss was highest at 79%. The same water with zinc orthophosphate or polyphosphate averaged 39-42% lead weight loss (Figure 2f). In contrast, the well water with high sulfate, K-synthetic and K-synthetic with polyphosphate only lost an average of 1.1% of the initial lead.

Visual differences in jar bulk waters. The total lead analysis was mostly consistent with visual observations of jar cloudiness. The K-Synthetic with high nitrate, high nitrate and zinc orthophosphate as well as high nitrate and polyphosphate produced the most intense snowy white color of lead and tin corrosion products (Figure 2a). The remaining conditions produced mostly clear waters with much less release of corrosion by-products.

Overall, the ranking of the waters in terms of lowest to highest spallation corrosion in terms of bead detachment, lead weight loss and visual observations was consistent as follows: groundwater < surface water low nitrate < surface water with low nitrate and polyphosphate < surface water with high nitrate and phosphate inhibitors < surface water with high nitrate. The essence of the problem was recreated in this 4-week test, since this ranking was consistent with field measurement trends of lead release (Lopez et al., 2022).

Electrochemical Cell Study.

Spallation corrosion in the presence of nitrate alone. In the presence of nitrate, the pure tin anode disintegrated with weight loss of 9% and production of 0.6 mg/L NH_3-N after just 5-days of exposure to 10 mg/L NO_3^--N. A total of 14.7% of the nitrate disappeared from the reactor, indicating that the conversion of 6% of the total nitrate into ammonia was only about half of the nitrate reaction products. Reaction products such as NO or N_2 gas were not measured.

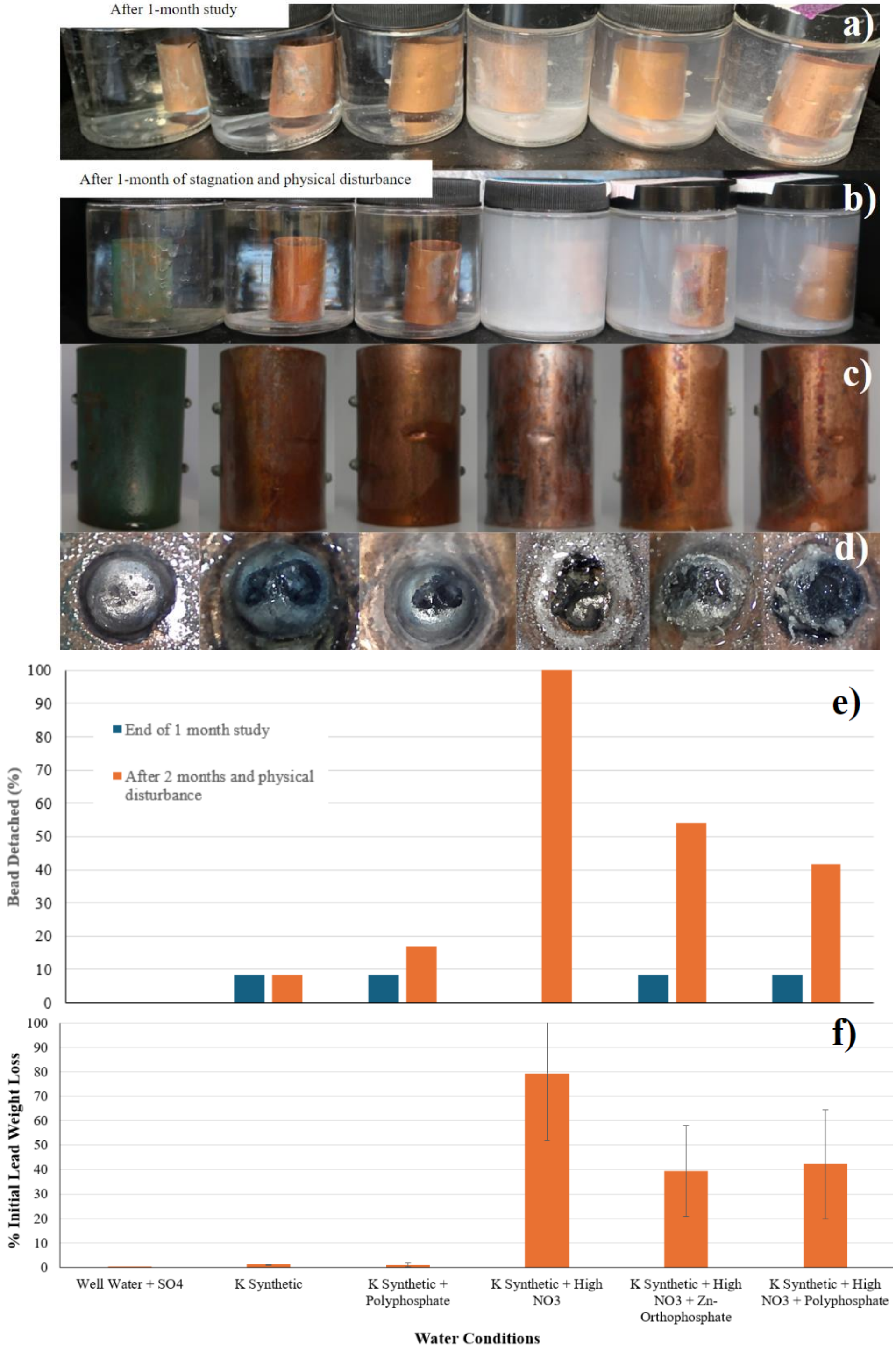


Figure 2. Jar water appearance after 1 month study (a), and after a month of stagnation and application of a physical disturbance (b). Photo of coupon beads at end of 2-month study (c). Condition of representative solder beads for condition at end of study for condition (d). Percent of lead-solder beads detached at each point of the study (e). Percent of lead weight loss after 4 months of study (f).

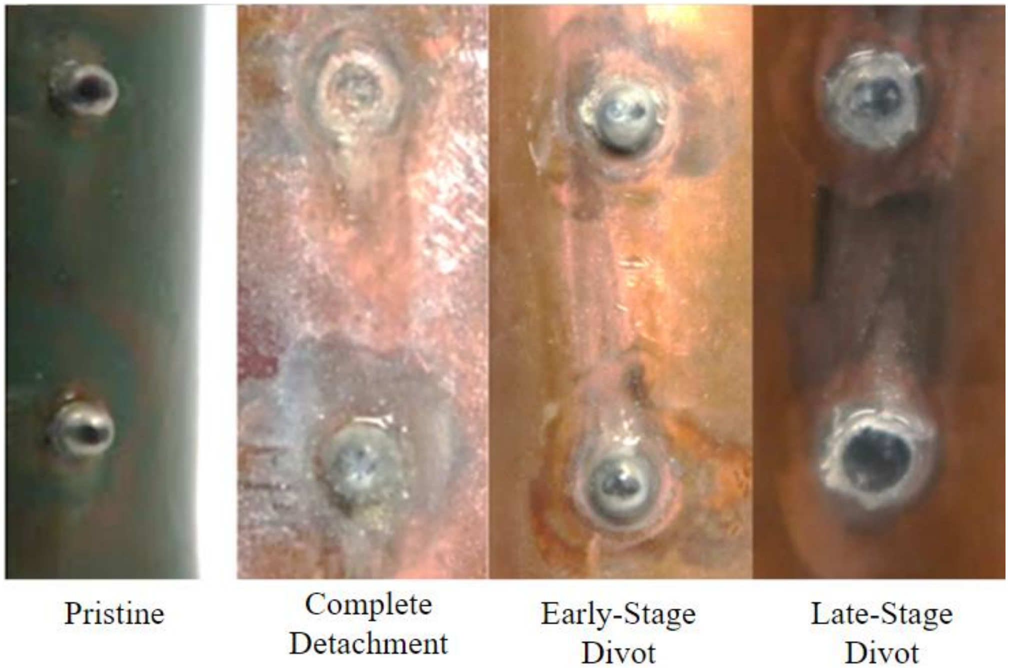


Figure 3. Close up of solder beads from left to right.

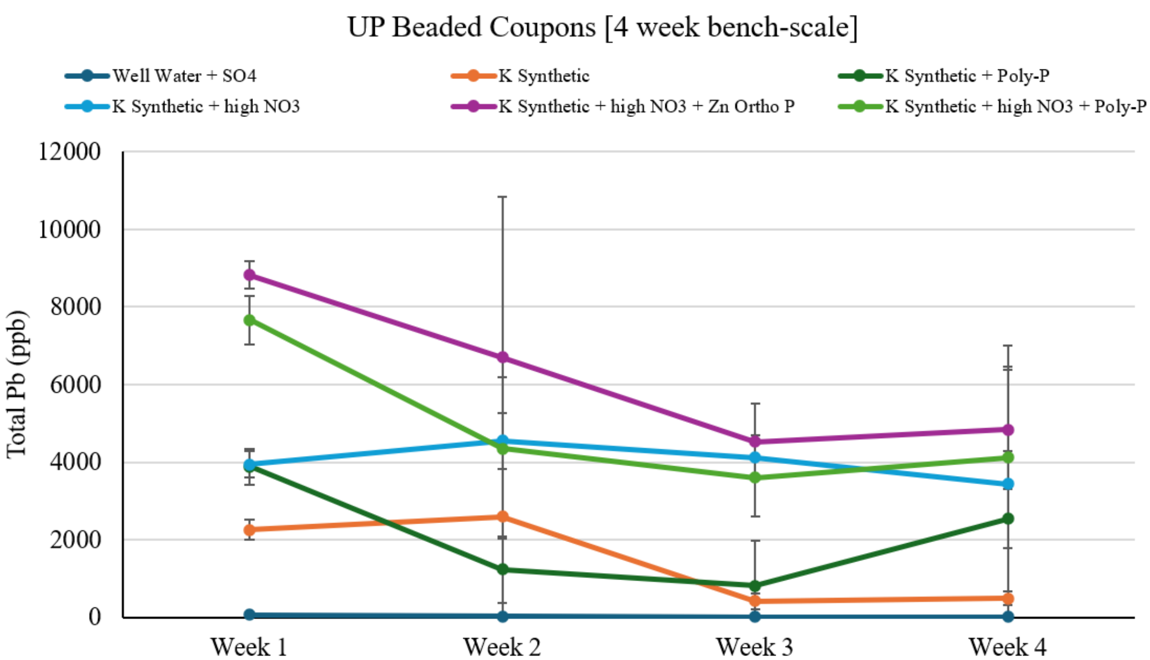


Figure 4. Lead release for weekly composite samples

Mitigating Effects of Other Ions. A broad range of conditions were evaluated to identify possible factors that could mitigate nitrate attack on tin (Appendix Table B1). This included zinc, orthophosphate, zinc orthophosphate, polyphosphate, sulfate, and combinations of these chemicals with bicarbonate (Figure 5 & 6). Zinc addition had little effect on anodic current or percent weight loss (11.1% vs 10.5%) (p-value >0.05, Student's t-test, n=3). Addition of polyphosphate along with nitrate produced significantly greater weight loss of 18.7% (p-value >0.05, Student's t-test, n=3) than the control. In contrast, orthophosphate, zinc combined with orthophosphate, sulfate, and the combination of all three tested chemicals all provided a degree of inhibition. For instance, addition of 10 mM of sulfate lowered the anodic current by 76.3% and weight loss by 93.3% relative to the control (p-value <0.05, Student's t-test, n=3).

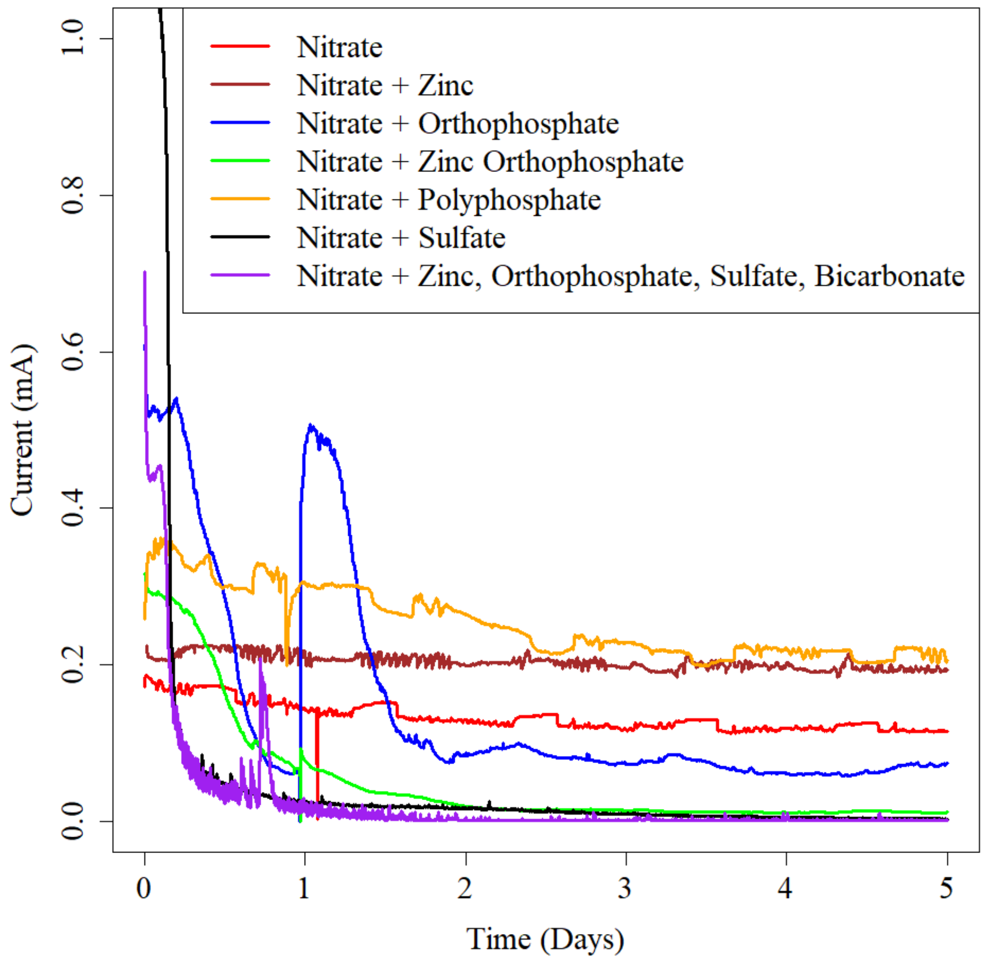
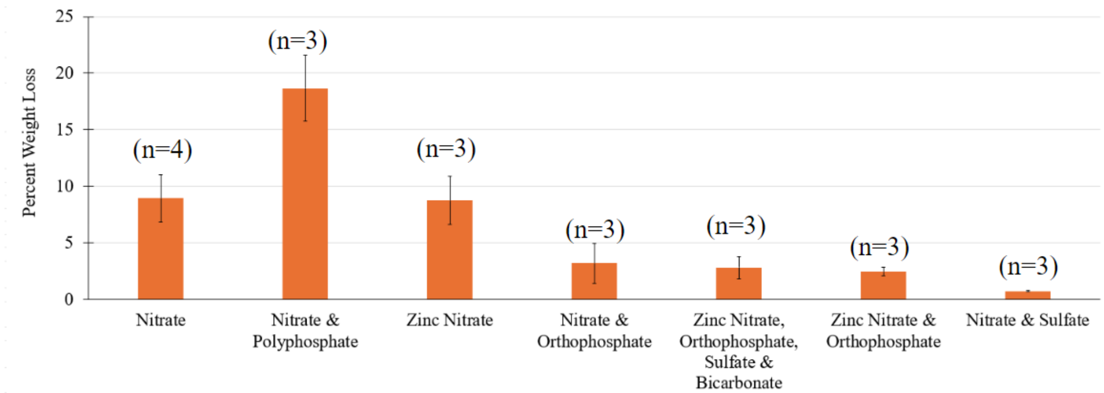


Figure 5. Effect of inhibitory chemicals in preliminary study on galvanic current between pure tin wire and stainless-steel electrode in the presence of high nitrate. The pure tin anode was +1 V anodic to the stainless-steel cathode in all conditions.



NO3-N	0.71	0.71	0.71	0.71	0.71	0.71	0.71
Zn	0	0	0.36	0	0.36	0.36	0
PO4-P	0	0.1	0	1	1	1	0
HCO3	0	0	0	0	10	0	0
SO4	0	0	0	0	1	0	10

Figure 6. Percent weight loss of tin wire anode in electrochemical cells at 10 mg/L NO_3^--N and other varying chemistries in mM. Error bars indicate 95% confidence intervals.

Effects of Polyphosphate and Orthophosphate. At the same molar concentration (3 mg/L PO4-P), Polyphosphate increased the galvanic current above the control while the orthophosphate exhibited inhibitory behavior (Figure 7). Polyphosphate produced a very thick and unusual white precipitate around the tin anode which was absent in the presence of orthophosphate. This gel like deposit may have created concentration cell effects that worsened corrosion (Appendix Figure B3).

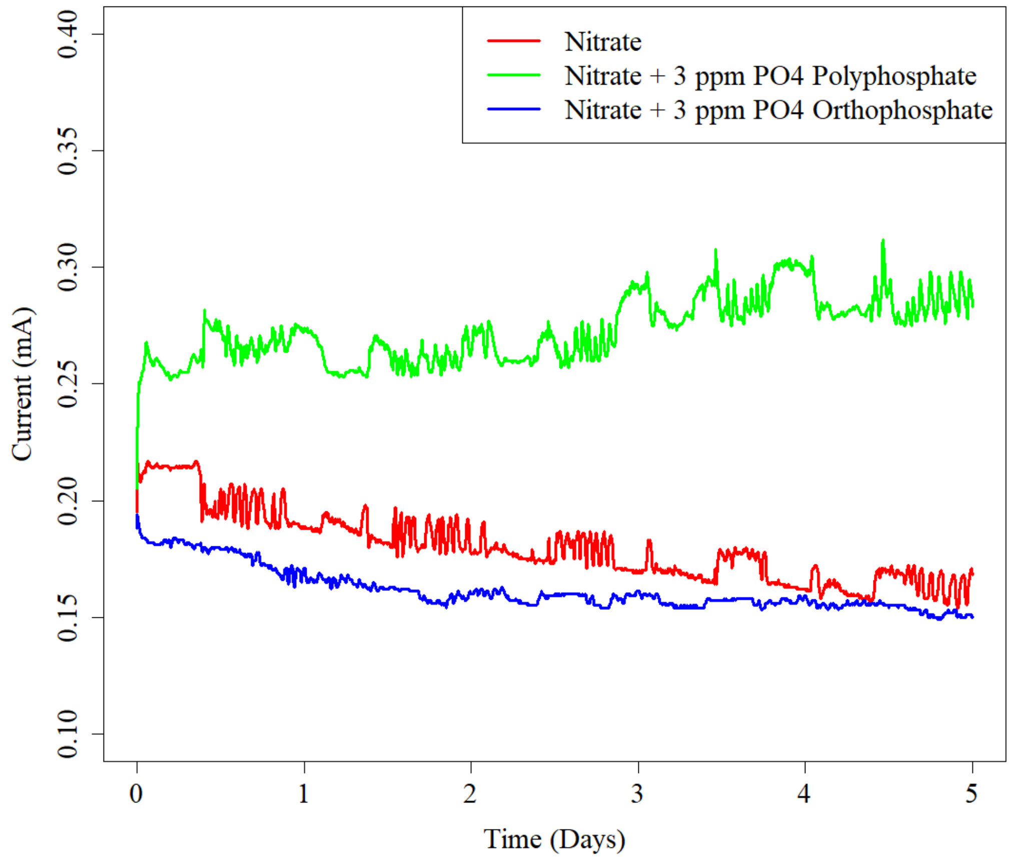


Figure 7. Effect of polyphosphate and orthophosphate at the same molar concentration on galvanic current between pure tin wire and stainless-steel electrode. The pure tin electrode was anodic to the stainless-steel electrode in all conditions.

Nitrate versus Chloride. At the same molar concentration, chloride initially displayed high currents above those of nitrate, but they decreased while nitrate remained fairly stable throughout the 5 days. Chloride caused a slightly higher anodic current than nitrate (1.16 x), but it caused only 50.7% of the weight loss (Figure 8 & 9a). This is attributed to spallation corrosion from the nitrate, which causes weight loss beyond that predicted by the anodic current and Faradays law. Anodic tin attacked by nitrate had severe cracks, whereas tin attacked by chloride was relatively smooth and coated with a uniform gray layer (Figure 10). Despite both beakers having milky white particles, black chunks of tin up to 1 mm in diameter were found at the bottom of the nitrate control beaker, consistent with a chunk corrosion mechanism while beakers exposed to chloride did not have chunks of tin at the bottom consistent with a dissolution mechanism (photo not shown).

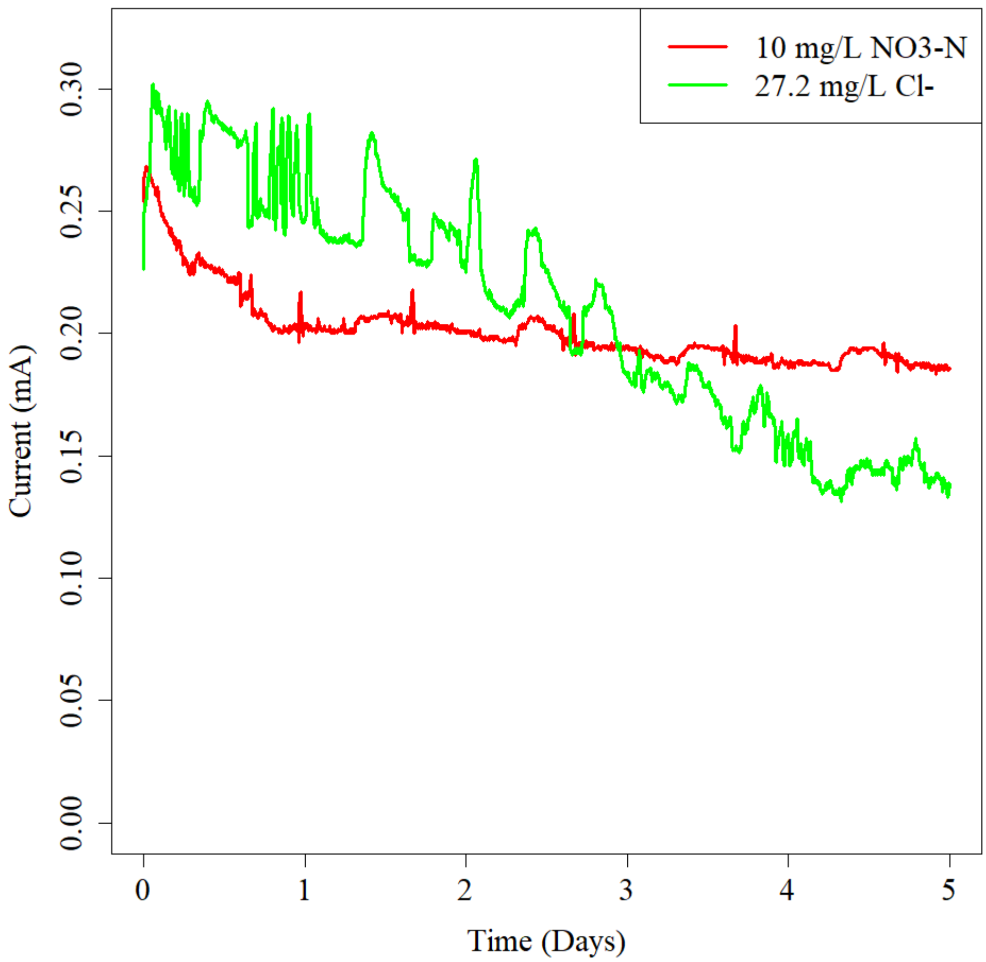


Figure 8. Effect of equimolar nitrate (10 mg/L NO_3^- as N) and chloride (27.2 mg/L Cl^-) on galvanic current between pure tin anode and stainless-steel cathode.

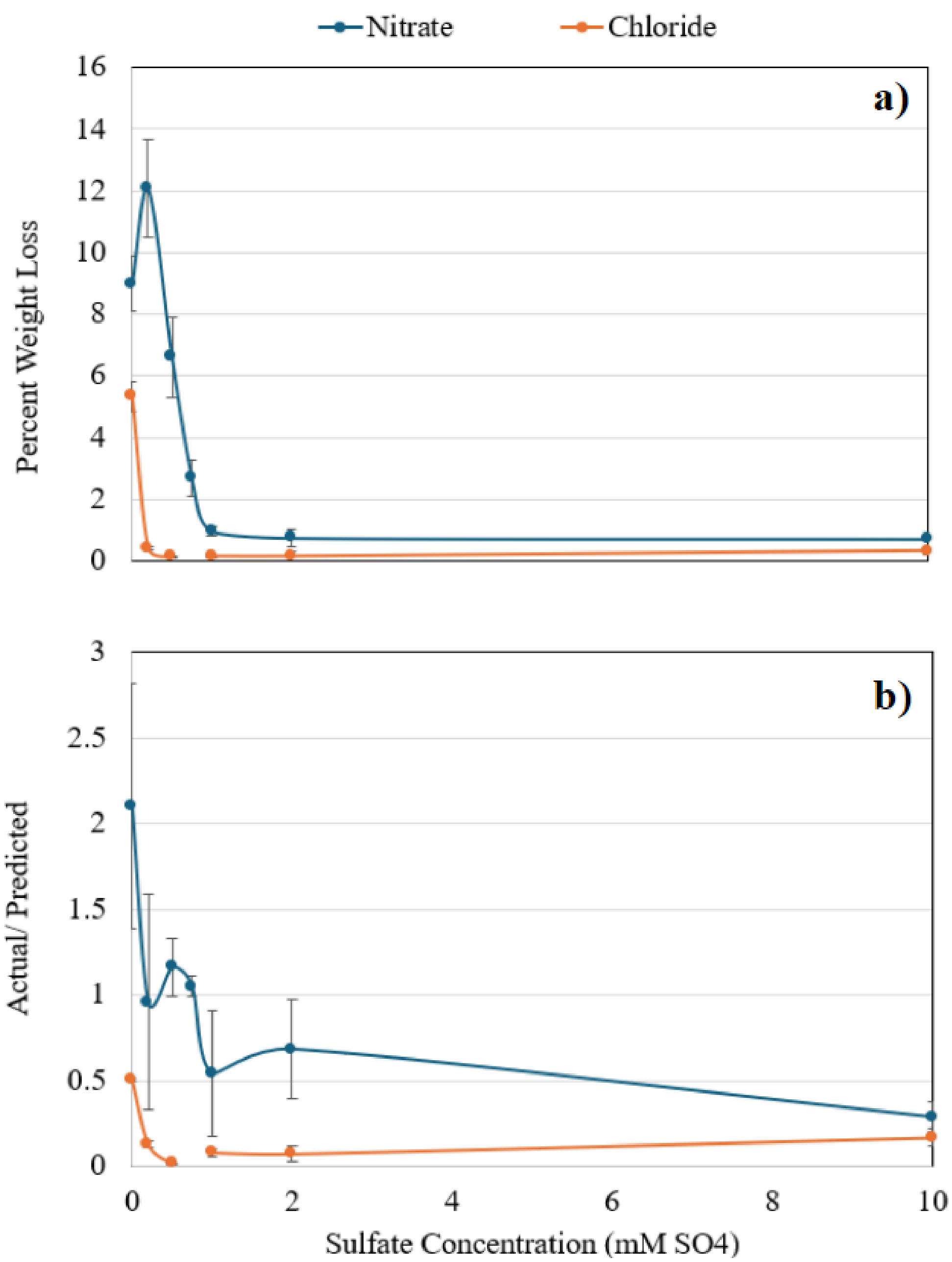


Figure 9. a) Percent weight loss of tin wire anode in electrochemical cells at 10 mg/L NO_3^--N and 25.3 mg/L Cl^- exposed to 0-10 mM of sulfate (n=3), but (n=12) for the condition with zero sulfate and high nitrate. b) Fraction of actual versus predicted weight loss for tin wire in nitrate and chloride solutions in the presence of sulfate (n=3). Error bars represent 95% confidence intervals.

Actual weight loss decreased with increasing sulfate concentration in the presence of moderate nitrate. Since sulfate addition was found to inhibit galvanic current in a preliminary study, a series of electrochemical tests were performed at varying sulfate concentrations for pure tin anodes. Sulfate concentrations of 0.2-10 mM were assessed to identify an optimal sulfate concentration that effectively inhibits spallation of tin wire anode when exposed to moderate levels of nitrate. Percent weight loss generally decreased with sulfate addition, despite a slight increase for 0.2 mM SO_4^{-2} compared to zero sulfate (Figure 9a). A similar trend exists for chloride corrosion at higher sulfate (Figure 9a). Sulfate addition exceeding 0.2 mM SO_4^{-2} for chloride and 0.5 mM SO_4^{-2} for nitrate sufficiently inhibited galvanic corrosion leading to significantly lower weight loss. Physical and visible markers of spallation, were reduced if not eliminated with addition of sulfate in the presence of both chloride and nitrate (Figure 10).

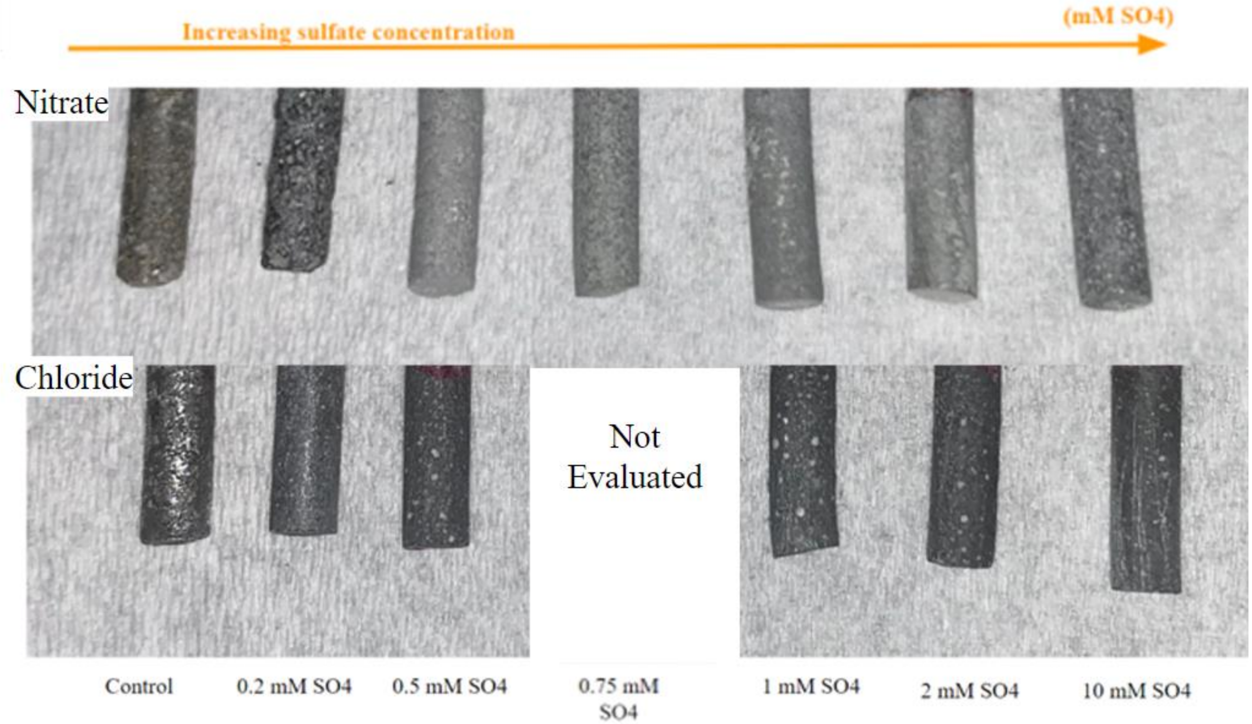


Figure 10. (Top) Tin wire exposed to moderate levels of nitrate in increasing sulfate concentration order from left to right. Less visible spallation from left to right. (Bottom) Tin wire exposed to chloride in increasing sulfate concentration order from left to right. White specs over solid passivating layer visible.

Sulfate inhibits nitrate-accelerated galvanic current. The anodic current between the corroding pure tin wire and the stainless-steel cathode was 0.18 mA for suspensions with 10 mg/L NO_3^--N (Figure 11). The galvanic current was 1.17 times higher for the same molar concentration of chloride before decreasing with time. Galvanic currents for both nitrate and chloride generally decreased upon addition of sulfate within the first 14 hours (Figure 11), although 0.2 mM SO_4^{-2} did not decrease galvanic current. Galvanic current in the presence of moderate levels of nitrate decreased by 76.2% upon addition of sulfate at concentrations of 0.75 mM SO_4^{-2}, whereas the same percentage reduction in current in the presence of chloride occurred with sulfate 0.5 mM SO_4^{-2}. Thus, it appears less sulfate is required to inhibit the anode in the presence of chloride versus the same molar concentration of nitrate.

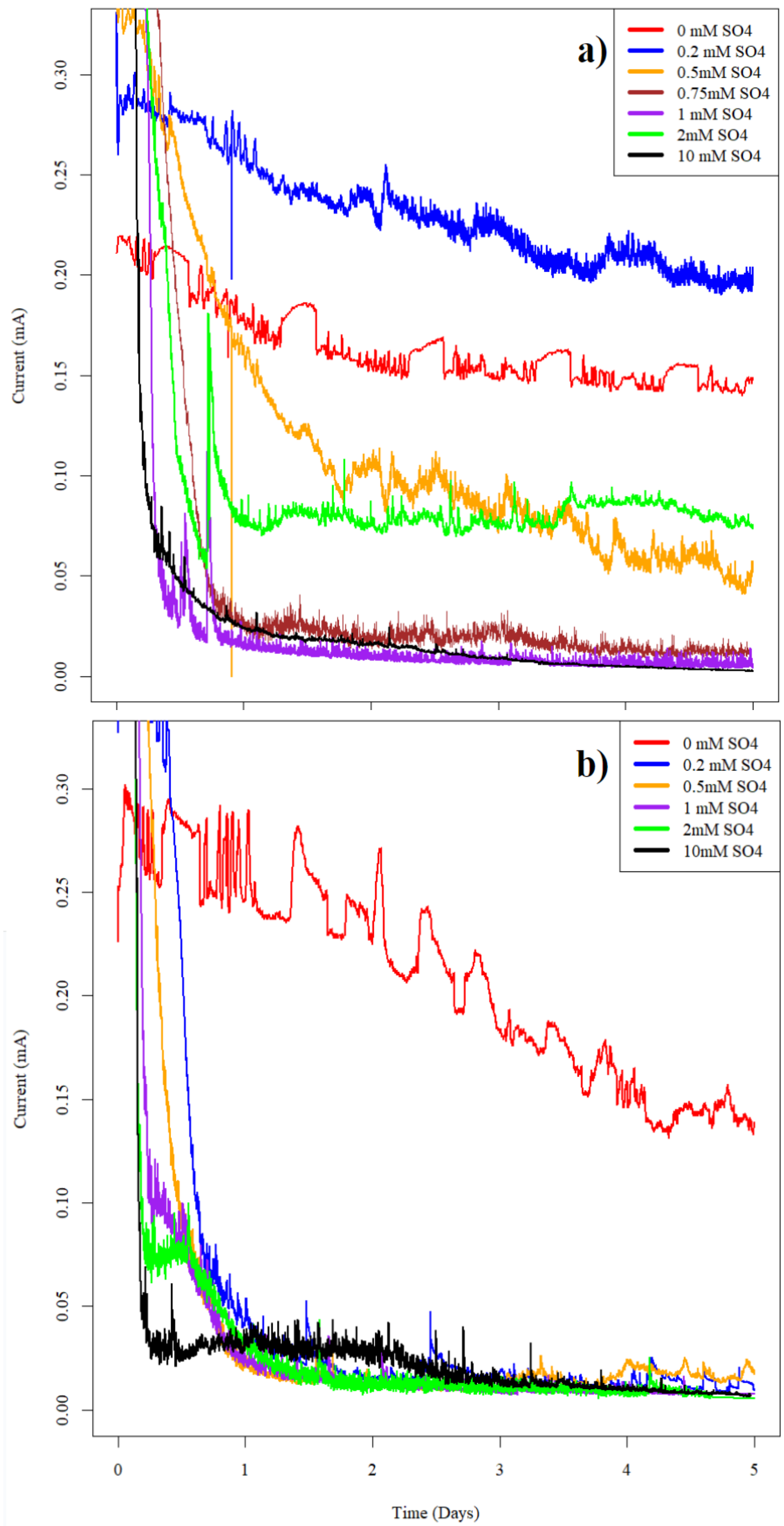


Figure 11. a) Effect of nitrate (10 mg/L NO_3^- as N) and sulfate (0-2 mM SO_4^{-2}) on representative galvanic current between pure tin wire and stainless-steel electrode. b) Effect of chloride (25.2 mg/L Cl^-) and sulfate (0-10 mM SO_4^{-2}) on galvanic current between pure tin wire

and stainless-steel electrode. The pure tin electrode was anodic to the stainless-steel electrode in all conditions.

Weight loss from wires exposed to nitrate at lower sulfate concentrations exceed Faraday's law. A predicted weight loss was calculated by integrating the currents and applying Faraday's law assuming a 2-electron transfer. Given that some corrosion by-products remain attached to the anode, it is normally the case that the weight loss is below predictions of Faraday's law, but never above the prediction. The actual weight loss values for nitrate at no sulfate exceeded predicted Faradaic values (p-value <0.05, Student's t-test, n=12), consistent with the "chunk effect" due to disintegration of metallic tin that has not been oxidized (Marsh & Schaschl, 1960; Rumpel et al., 1964). Wire exposed to nitrate and sulfate above 0.5 mM SO_4^{-2} resulted in the routinely observed case that actual weight loss is below predicted values. Likewise, predictions in the presence of chloride, were also below predicted values, indicating a conventional corrosion mechanism without spallation mechanism (Figure 9b). These studies validated that Faraday's law is ineffective at predicting weight loss from current for chunk corrosion.

Conclusions.

The essence of spallation corrosion was recreated in simple beaker tests, with sections of copper pipe and lead:solder beads. In a water with low nitrate and high sulfate, no beads detached in 4 months, but in a water with high nitrate and low sulfate all the beads fell into the water after 2 months.

In tests with a separated tin anode and stainless-steel cathode, higher levels of sulfate eliminated spallation corrosion from nitrate. Despite conventional inhibitors not reducing spallation corrosion under the studied conditions, sulfate at concentrations as low as 0.75 mM effectively inhibited the accelerated nitrate induced spallation on the tin wire and its subsequent weight loss.

Additional research on this important form of corrosion and water contamination is needed. Future electrochemical studies should explore the mechanism by which sulfate inhibits nitrate induced spallation via surface analyses. Additional work should add nitrate corrosivity to the list of factors that should be considered before switching source waters and evaluate the feasibility of measures to inhibit nitrate corrosion. Cost-benefit analysis can be employed in these studies to gauge the most effective and affordable method for protecting soldered joints and legacy solder present in drinking water systems.

Acknowledgements.

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CHAPTER 4:

Household Point-of-Use Water Faucet Filters for Lead Removal: Field Performance and User Experiences

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Abstract.

Lead certified point of use (POU) filters were field tested in occupied homes during normal use and under extreme conditions in two unoccupied homes. In an unoccupied home with a 28 m long lead service line with average lead of 17 ppb in flushed water, treatment by POU filters generally produced water with < 5 μg/L Pb even when tested to 200% of rated capacity. Another unoccupied home with a disturbed lead service line (LSL) had erratic influent particulate lead of 9-3000 μg/L particulate lead, and the POUs could not consistently produce water with <10 μg/L Pb despite very high percentage removals. The same model of POUs were tested in 21 occupied homes known to have lead over 5 ppb. Eight of the homes were in New Orleans which does not normally have elevated iron or manganese, while thirteen were in Enterprise, LA which does. The POUs always reduced lead to <1 μg/L. In Enterprise, the filters also removed iron and manganese, but they tended to clog before reaching half of their rated capacity. Laboratory experiments demonstrated varying susceptibility to iron clogging even amongst duplicate filters of the same brand.

Introduction.

In recent years, point-of-use filters (POU) have been used to reduce lead exposure during water crises, in schools and day care facilities, and after lead service line (LSL) replacement.[1–10] Filters are often considered more environmentally friendly and less expensive than bottled water.[10-12] Some small water systems will soon be allowed to use POU filters as a means of complying with the Lead and Copper Rule (LCR) in place of corrosion control.[13]

A recent literature review highlighted prior research evaluating filter performance.[14] Over a decade ago it was demonstrated that POU filters removed soluble lead effectively, but they occasionally had problems removing particulate lead.[1] Follow up work indicated POU filters were generally very effective at reducing lead levels below <5 μg/L in field studies both in Flint (100%, n=242) homes, and in Newark, NJ (97.5%, n=198).[7,15] There were a few exceptional cases in Newark, NJ (2.5%, n=198) in which filtered water lead levels were as high as 112 μg/L.[14] Subsequent lab work revealed difficulties removing nanoparticles, large particles and manufacturing defects could contribute to these problems.[16-18] Nonetheless, POUs were generally effective at reducing elevated lead levels even when operated beyond their rated capacity despite exceptional cases of relatively poor performance.[1,7,8]

As utilities and consumers increasingly rely on POUs to protect public health from lead exposure, there is a need to better manage consumer expectations and understand factors that limit their performance in the field. Premature clogging of filters due to iron and other sediment is an important emerging concern. [9,11,19] Rouillier et al. (2021) recently reported a correlation between the influent iron concentration and the length of time before clogging,[11] and further demonstrated that above certain iron thresholds bottled water is more cost effective than filters. Other factors that limit consumer adoption of POU filters are deserving of increased attention.[20]

Here, we evaluate various aspects of faucet mount POU filter performance in longitudinal field studies. Specific goals were to (1) sample water without filtration to characterize lead levels as a function of water flushing (control condition), (2) monitor POU filter performance under extreme scenarios in two unoccupied homes for 200% of each filters rated capacity, and (3) monitor performance in occupied homes in a situation with low iron or high iron, and (4) document participant experiences with POU faucet-mount filters.

Methods.

Study Area and Sampling Efforts. This study was conducted in New Orleans (NOLA) and Enterprise, LA (ELA) homes identified with water lead concerns. NOLA represents a diverse urban community with a high proportion of low-income residents.[21] In NOLA, the municipal drinking water supply meets regulatory requirements for lead, but about 5% of homes still exceed the first draw action level. [22] We previously illustrated that NOLA samples collected after about 1 minute of flushing often have higher lead than first draw. Elevated lead after partial replacement of LSLs is also an important concern.

In ELA, our prior sampling revealed that 41% of homes sampled had lead above the 15 ppb action level, 71% exceeded the aesthetic standard for iron, and 94% exceeded the aesthetic standard for manganese [23]. There are no lead service lines and the community cannot afford centralized removal of iron and manganese from the water. This is a very rural community with only about 250 residents[24]. ELA is representative of some small system which might try to use POU filters for LCR compliance.

We evaluated POU performance using two distinct sampling efforts. The first was in two unoccupied homes that were challenged by running filters to 200% of capacity using waters with serious water lead hazards. The second sampling effort was in occupied NOLA and ELA homes to measure lead removal rates, flow rates, and user perceptions under routine use.

Unoccupied Home Study. We sampled in NOLA homes that were unoccupied during testing, in order to evaluate two practically important and high water lead risk scenarios, without endangering consumers when filters were beyond manufacturers recommendations. A co-author of this paper (Katner) owned one of these homes and knew the owner of another. Home A was estimated to have a 28 m long LSL with documented sustained water lead release (average 17 μg/L) problems.[23] Home B was used to test a 6-ft long LSL that was extracted from service and severely disturbed.

Rig design and Flow Sequence. We designed a semi-automated sampling rig to determine the effectiveness of filtration through POU filters (Appendix Figures C1 and C2). An NSF-ANSI 53 certified lead filter was tested in duplicate in each home. The POU selected used carbon-block technology and had a 100-gallon capacity. Our prior testing documented that this brand consistently reduced lead to less than 15 μg/L for up to 200% capacity in a laboratory setting.[16] Flow was controlled using solenoids, valves, and timers that were powered by a DC rechargeable 12 Volt 35 Amp hour battery. The flow sequence through each pipe was a 7.5-hour stagnation event, followed by 0.5 hours flow, repeated three times daily. Flow was for 20-30 min at 0.3-0.5 gallons per minute to achieve a target of 10-gallons per event (i.e, 10% of treatment capacity). To prevent water damage to property the entire apparatus was placed within a secondary container and equipped with an emergency shut-off valve triggered by leak sensors. We installed the rig in Home A by connecting it directly to the kitchen tap, and in Home B by connecting the home water supply at a sink to the disturbed partial LSL. The rigs were operated in both homes for 20 days to achieve 200% of the POU rated capacity.

Stagnation sampling. Every drop of water passing through each LSL for 20 days was collected and sampled. The first flow event through the LSL each day was directed though one of the POU filters and into a dedicated reservoir. The second flow event each day did the same for the second POU filter. The third flow event went directly into a reservoir with no filtration (control). Prior to each sampling event, the sampling reservoirs were dosed with 50 g of Alpha Chemicals food-grade citric acid. QA/QC demonstrated that this safely reduced pH to <3.0 and prevented soluble lead sorption to the walls of containers. After rigorously mixing the acidified reservoir to homogenously suspend any undissolved lead particulates, we collected an aliquot from the reservoir in a 250 mL container.

Profile Sampling. A special profile sampling of water flowing from the tap was collected from Home A on days 0, 10, and 20 and Home B on days 0, 8, 14, and 20. These samples were also collected after stagnation. Instead of having water flow into the sampling reservoirs, 15 one liter samples were manually filled in sequence, followed by 250 mL grab samples after a 5, 7, and 9 gallons had been flushed (Figure 1). All water not collected in a bottle was directed into the sampling reservoirs. After stirring the acidified samples as before, a 250 mL composite sample from the reservoir was collected. To determine the fraction of particulate lead, 10 mL aliquots were collected from samples 1, 3, 5, 7, 11, 15, and 17 and passed through a 0.45 μm pore size filter. After returning to the lab, all samples were acidified with 2% nitric acid and digested for a minimum of 16 hours prior to analysis on a Thermo Electron iCAP RQ Inductively Coupled Plasma Mass Spectrometer (ICP-MS) per standard method 200.7 and 200.88[25] If iron was present, samples underwent addition digestion prior to analysis of 2% hydroxylamine hydrochloride and a heated digestion (50°C) for 24 hours.

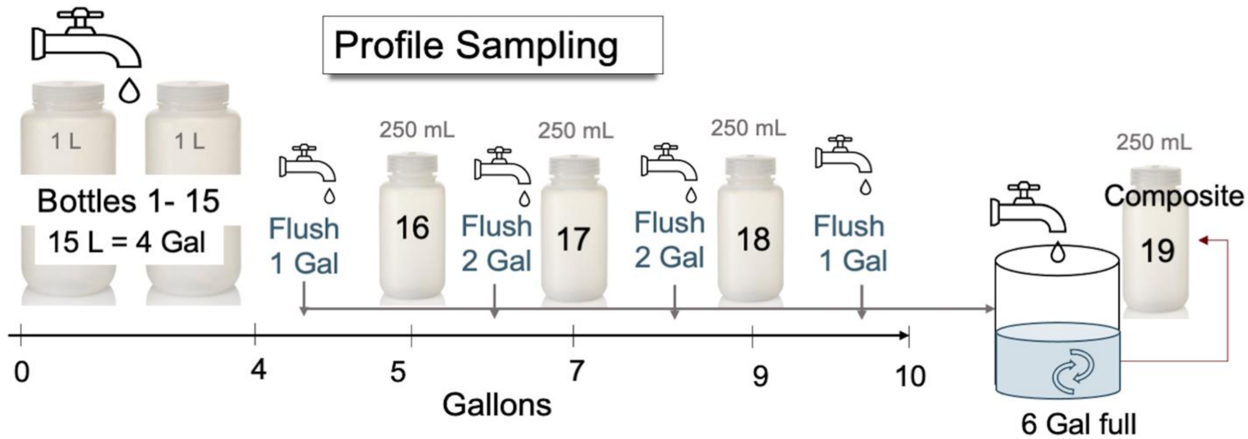

Figure 1. Profile sampling of water after stagnation.

Consumer Testing in Normal Field Use. We provided POUs to residents in NOLA and ELA with known lead in water problems to monitor long-term performance of POUs and user behaviors.

Recruitment. We had previously sampled drinking water from 376 homes in NOLA[22] and 17 homes[23] in ELA. All participants with > 5 µg/L lead in first draw or flushed samples were invited to participate in this study. Our previous experience suggested that filters in ELA water with high iron and manganese might have problems with clogging.

The research team visited interested participants to install the POU filters and train participants in their proper use (e.g., not filtering hot water, how to change cartridge). Only homes with a kitchen tap design suitable for use of a POU were considered (e.g., removable aerators). One home was excluded on this basis. In addition, participants were given a sampling kit that contained sampling bottles, instructions, reminder cards, a stopwatch, a permanent marker, and pre-paid return postage.

This human subject experiment was reviewed and approved by the Virginia Tech IRB board (17-541). The study protocol, informed consent procedures and data collection instruments were reviewed and approved by the Louisiana State University- Health Institutional Review Board (IRB # 887 and 10069).

Temporal sampling. Participants were asked to use the POU as per their normal daily routine and to collect a weekly first draw sample for 12 weeks unless (1) the POU reached its capacity before 12 weeks as indicated by its built-in indicator light turning yellow/red or (2) the participant felt that the POU was clogged (i.e., filtering water was taking too long). It is important to note that NSF/ANSI 42 and 53 defines POU clogging as the time at which the initial flowrate is reduced by 75%.[26,27] While the POU had a design flowrate of 1.9 lpm at 60 psi, the initial flow rate will fluctuate with varying water pressures in homes.
The night before sampling, participants were instructed to let the water remain stagnant overnight for at least 6 hours. Thereafter, participants collected a 250 mL unfiltered first draw sample. For comparison, the next night, this process was repeated but participants collected a

250 mL filtered first draw sample from the POU. In addition, participants were asked to measure the time required to fill the bottle. If participants felt their filter was clogged, they were asked to repeat the filtered first draw sampling one additional time. As before samples were acidified and digested with 2% nitric acid and 2% hydroxylamine hydrochloride (as needed) prior to analysis on the ICP-MS.

User behavior surveys. Participant and household information were collected via interviews and observations during a home visit to install the filters, at which time study consent forms were signed and collected. Participants were asked to complete a survey when the research team visited to install the POU and at the end of the study.

Once the lifetime of the filter had been reached or the resident discontinued use of the filter, residents were surveyed to assess their use of the filter, perceptions of the quality of their filtered water, ongoing support or information needs, problems encountered during POU filter testing, knowledge of filter maintenance, their likelihood of continuing POU use, and reasons for discontinuing use.

Iron Flow Reduction Laboratory Study. To validate clogging observations in ELA, we conducted a laboratory experiment. We selected four brands of faucet POUs for analysis and tested performance in duplicate. We exposed POUs to the standard National Sanitation Foundation test water but with increasing iron concentrations: 0, 150, 300, 600, 1000, 2000, 4000, and 5000 μg/L Fe added as $FeCl_3$.

We used the automated faucet rig described in Purchase et al. (2020), which was powered by a booster pump and had a water pressure range between 35-45 psi.[16] Each filter was conditioned by flushing iron free water for 5 minutes prior to testing. During testing, we filtered 3 gallons of each test water through the POU followed by 3 gallons of deionized water. We measured the length of time required to fill a 250 mL bottle during the deionized water flush. We continued to expose the POU to this test water and repeated this process until the filtration time doubled.

Results and Discussion.

Controlled Testing in Unoccupied Homes.

Home A With Long LSL and Sustained Lead. The unoccupied home with sustained high-water lead had average influent lead (10-gallon composite) of 10-24 μg/L (Figure 2B) during the 20-day study. When characterizing the 10-gallon flushed profiles taken on Day 0, 10, and 20 the influent lead fluctuated between 5.6-31.3 μg/L and the average percentage particulate lead was 15-21% of the total lead (Figure 2A).

As water flowed from the tap after stagnation events, the lead concentrations peaked after flushing in bottles 15-17, which is consistent with expectations of sampling water that sat stagnant in the lead service line. Except for the first 6 L of the Day 0 profile, lead levels were all >10 μg/L even after flushing >8 min (10-gallons). Clearly, the NOLA public health recommendations to flush the tap 30 sec – 2 minutes, to reduce lead exposure in water used for cooking or drinking, would not have been effective in this home.[22] As the study continued the lead in the control samples increased slightly from Day 0 up to Day 20. This rising level of lead might reflect the relatively low water use of 30 gallons per day during this study, compared to thetypical 120 gallons per day[28] when the home was occupied.

Filter Performance. The faucet filters consistently produced water with less than 5 µg/L lead, with 3 exceptional samples which had >10 µg/L (Figure 2B). Filter duplicate 1 had lead levels below 2 µg/L and removal efficiencies between 85.2-99.6%, except for Day 8 and 9 (composites of gallons 80-100) which had effluent lead of 12 µg/L that occurred before reaching the filter's 100-gal capacity. The filtered lead concentrations when tested beyond the rated capacity were always <2 µg/L. Duplicate 2 always had effluent lead levels below 5 µg/L and removals of 73.8%-99.9%, except for one sample with 15 µg/L on Day 11 at a point just 10% beyond the rated capacity.

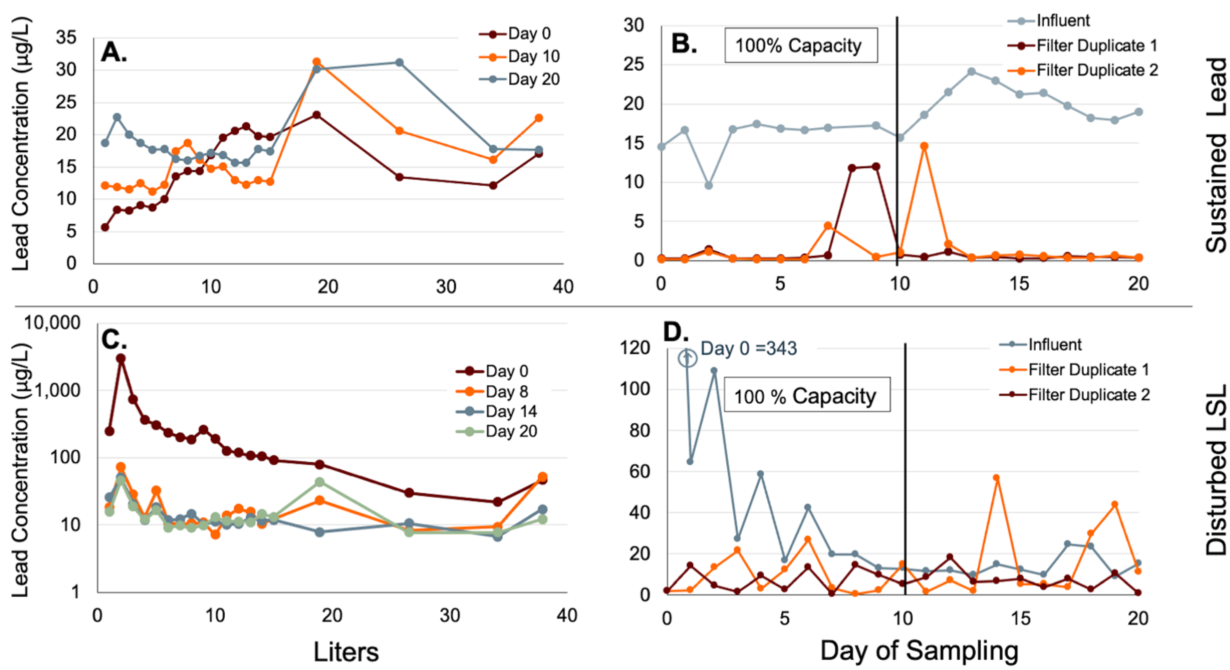

Figure 2. Unoccupied Home profile sampling and filter performance over time. (A) The lead profiles of the Home with Sustained Lead. (B) The duplicate POU filtered lead concentrations for the Home with Sustained Lead. (C) The lead profiles of the Home with Disturbed LSL. (B) The duplicate POU filtered lead concentrations for the Home with Disturbed LSL.

Home B with Disturbed LSL. The unoccupied home with a disturbed LSL had average influent (10-gallon composite) lead levels between 9 and 344 µg/L throughout the 20-day study (Figure 2D). LSLs often release these high levels of lead immediately after a disturbance, with levels declining slowly over weeks, months or years depending on circumstance.
The four 38 L (10-gallon) profiles had the highest lead concentrations in the first 4L, after which the concentrations steadily declined. The lead levels in the profiles always peaked in bottle 2 (2L), which corresponds with the water sitting stagnant in the rig's disturbed LSL (6 ft long and 1 in diameter). Day 0 had the highest lead levels with the 2 L sample at 3,053 µg/L lead and an average particulate lead of 89% (Figure 2C, Appendix Figure C4). The lead decreased to range between 100-250 µg/L with additional flushing and eventually decreased to 50 µg/L at bottle 19.

The other three profiles Days 8, 14, and 20 were similar with average particulate lead at 36-41% of the total lead, which fluctuated between 7-55 μg/L.

Filter Performance. The very high lead in the water of home B proved challenging for the POUs, as they could not consistently treat the water to levels <10 μg/L. Duplicate filter 1 produced 5 grab samples with effluent lead levels >10 μg/L before reaching the rated capacity of 100 gallons. These high levels of lead occurred on Days 2, 3, 5, 6, and 10 and ranged from 12-27 μg/L (Figure 2C). The estimated POU removal efficiencies ranged from 21.1-99.4%, based on the best available estimate comparing the unfiltered control condition to the filtered condition which was collected 8 hours apart. Duplicate filter 2 had lead levels >10 μg/L in 3 samples with effluent lead of 14-15 μg/L on Days 1, 6, and 8 with removal efficiencies of 25-99.4%.

Home A with sustained lead levels never had filtered water lead concentrations greater than the comparison to the control. However, home B with the Disturbed LSL had filtered lead exceed the corresponding influent lead on 4 different days between Day 10 and 20. This is not attributed to poor filter performance, but rather, to the difficulties of characterizing performance when lead particulate release is semi-random (i.e., the influent sample to the filter during one flow event might be wildly higher or lower than during another flow event on the same day). For instance, the Day 14 samples of untreated water had influent lead of 15 μg/L, whereas the corresponding sample for filtered water lead later was 57 μg/L when collected 8 hours later. Due to the erratic nature of the lead release, it is possible that the actual influent to the filter when this water was treated was much higher than when the corresponding unfiltered water sample was collected. It is also possible that previously removed lead particulates were being released from within the filter at semi-random intervals as documented previously by Deshommes et al (2010).[1]

These findings reinforce problems of calculating removal efficiencies when there is semi-random release of discrete particles of lead. Capturing and analyzing every drop of water minimizes errors but does not eliminate them. It is hypothetically possible that the POU lead removal efficiencies were always greater than 90%.

Consumer Field Testing POU Performance.

Quality of Unfiltered Water. Water quality from NOLA and ELA illustrated significant differences (Appendix Table C1 & C2; Figure 3). Specifically, the 8 NOLA homes had unfiltered water with relatively low levels of lead (Pb), iron (Fe), and manganese (Mn). Unfiltered lead levels were all less than 5 μg/L, except for one sample with 22 μg/L lead. Over 75% of iron concentrations in NOLA were below 10 μg/L with a maximum of 57.3 μg/L, whereas manganese levels were all <1.3 μg/L. None of the NOLA samples exceeded the EPA Secondary Maximum Contaminant Level (SMCL) for Fe (300 μg/L) and Mn (50 μg/L).

In contrast, 4 out of 13 ELA homes had samples that exceeded the EPA Action Level for lead at some point in the study with a maximum value of 86 μg/L. However, the median unfiltered Pb concentration for all ELA homes was only 1 μg/L (Appendix Table C2). ELA also had several untreated tap samples that exceeded the EPA SMCL for both Fe and Mn. The unfiltered median Fe concentration was 383 μg/L with a maximum of 19,700 μg/L, and the median unfiltered Mn concentration was 106 μg/L with a maximum of 917 μg/L (Appendix Table C1).

Filter performance. All filtered lead samples for ELA and NOLA were <0.8 μg/L, iron <171 μg/L, and manganese <180 μg/L. The filters performed well in reducing lead and iron levels in all homes throughout the duration of the study (Figure 2, Appendix Table C1 & C2). However, 10% (n=88) of all filtered samples in 4 ELA homes exceeded the manganese SMCL of 50 μg/L (Appendix Table C1, C2). The average POU removal efficiencies were 94.8% for Pb, 98% for Fe, and 79% for Mn for the ELA homes, Overall, the filters effectively removed Pb and Fe throughout the test, but the performance in removing Mn was less consistent. NOLA homes always had relatively low Fe and Mn in the influent and filter effluent.

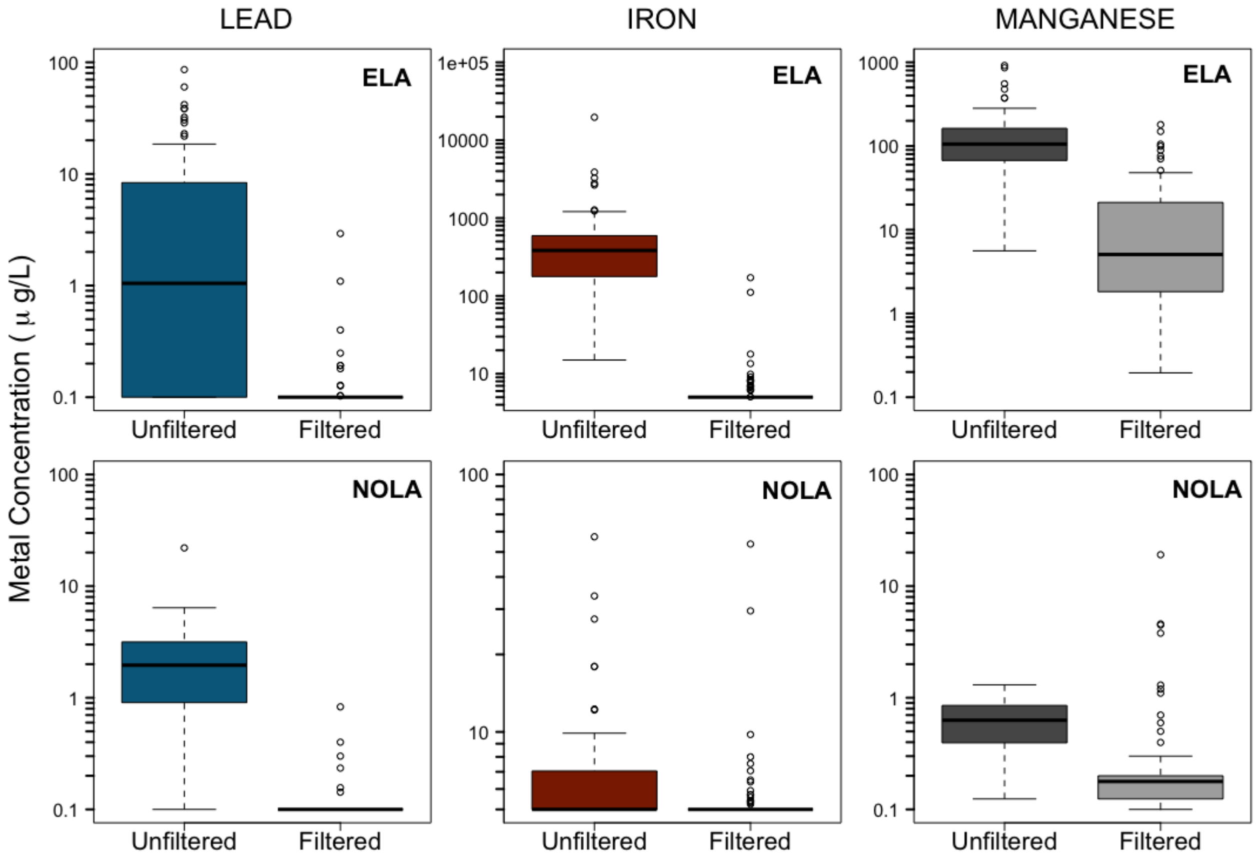

Figure 3. Influent and Effluent Metal Concentrations

Consumer Experiences with Clogging.

Comparing Flowrates in NOLA and ELA. Our field study confirmed a serious problem with filter clogging when high iron was present. Third party certification testing under guidelines of NSF/ANSI 53 for lead and 42 for Nominal Particulates defines the point of filter clogging as the time at which the initial flowrate is reduced by 75%.[26,27] The POU filter used in this study has a design flowrate of 1.9 lpm at 60 psi, but the initial flow rate fluctuates with varying ambient water pressures in homes. The initial flowrate in this study ranged from about 0.9 to 2.5 lpm (Figure 2).

Residents decided when the filter was clogged based on their own judgment. For instance, one resident decided the filter was clogged after it took 30 secs to filter 250 mL (≈1 cup of water). At another extreme, one resident did not yet judge a filter clogged even if they had to wait >3 min to filter 250 mL of water. The average final flowrates for ELA homes, at the point consumers replaced the cartridges or abandoned the study, was 0.55 lpm.

In the few homes where residents replaced cartridges in NOLA the final flowrate was 1.28 lpm (Figure 4).

Examining these results from the perspective of percentage reduction in flow, residents in NOLA only saw flow reductions of 16% on average before the end of the study. In ELA, at the point where a resident declaring the filter clogged, its average flow was 62% of its initial value. This lower, but in the range, of the 75% flow reduction clogging criterion in the NSF testing protocol.

The POU filter had a rated capacity of 100 gallons or 12 weeks. By this standard none of the filters in ELA reached the filter's capacity. Most were replaced before 50% of the rated capacity. As a result, these residents would likely need to replace the filter cartridges 2-4 times more frequently than expected based on the rated capacity, making POU use much more expensive than anticipated.

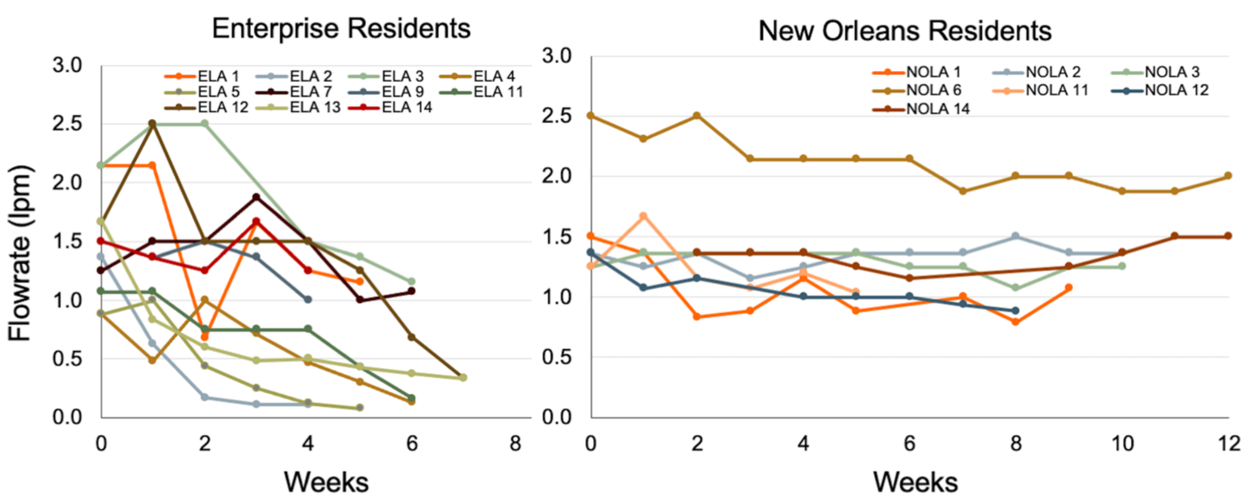

Figure 4. Filter Flowrate in NOLA and ELA over time. The POU's manufactured rated flowrate at 60 psi is 1.9 lpm.

Quantifying the Impact of Iron on Filter Life.

In the present study, there was only a weak correlation between average iron concentration in the ELA homes and filter life based on the weeks of use (Figure 4A). The weak correlation is not surprising given the small number of homes (n=13), and variations in water use by consumers and the consumers judgment of clogging.

We conducted a controlled laboratory experiment that sought to estimate the amount of iron that would need to be removed to clog the filters (Figure 4B). When testing the POU used in this study (Brand E), duplicate filter F1 required 23 mg of Fe to reduce the initial flowrate of 1.3±0.3 lpm by 50% whereas duplicate F2 removed 46 mg iron before achieving the same reduction in flow (Figure 5). On this basis it seems clear that even duplicate filters have highly variable susceptibility to clogging. The testing of faucet filter Brands D, F, and K (Appendix Figure C5) showed less variability between duplicates in terms of the iron removed at the point of a 50% reduction in initial flow. Brand D clogged at 77-92 mg of total iron accumulation, Brand F clogged at 32-47 mg of Fe removal, and Brand K clogged at 62-92 mg of Fe removal.

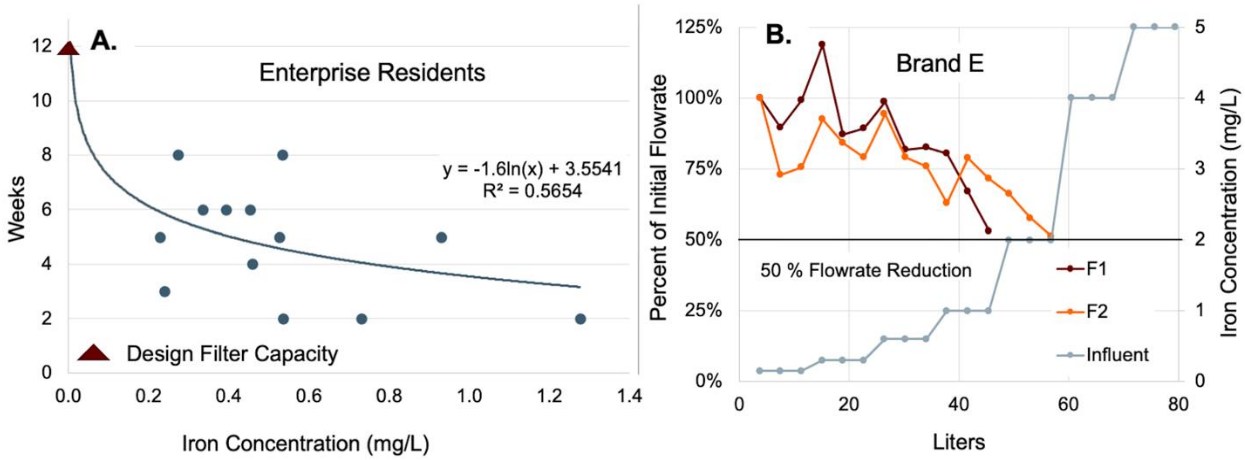

Figure 5. Iron Concentration and filter life

Consumer Experiences.

There were some notable differences in responses by ELA and NOLA respondents with regards to water quality, perceptions and behaviors prior to POU filter installation and testing (Table 1). All ELA respondents reported that their water has an unpleasant odor (primarily a sulfur/rotten egg smell), while no NOLA respondents reported unpleasant odors. The majority of ELA respondents reported having particulates in their water; or equivalently having a red, muddy, brown or yellow tint to their water, whereas a minority of NOLA respondents reporting particulates. Over half of ELA respondents were either “extremely” or “very” concerned about the quality of their unfiltered water (69%, n=13) compared to only two NOLA respondents (22%, n=9). The majority of ELA respondents did not drink unfiltered tap water (77%), while the majority of NOLA residents did so (67%). Of the individuals who did drink their unfiltered tap water, all participants from ELA (100%, n=3) and only one from NOLA (11%, n=2) said their unfiltered drinking water had an unpleasant taste.

During the testing phase, one participant from ELA stopped using their filter due to early clogging and inconvenience (n=13); while another participant from NOLA stopped using their filter due to technical incompatibility between a newer model faucet fixture and the filter which resulted in leakage and subsequent connection failure (n=9).

A total of 47% of our residents in ELA and NOLA self-reported that hot water ran through the filters, even though they were instructed not to do so per manufacturers recommendations.[20] It seems clear that some incidental use of warm water will occur, and because there is no data showing that doing so creates a problem, it is possible that the manufacturers warning is creating unnecessary angst amongst consumers.

After the field test was completed, participants were asked to characterize their experience with the POU filter during testing (n=18). Seventy-eight percent of ELA residents reported clogging or slow water flow (n=9); while only 22% of NOLA residents reported slow flow (n=9). Eighty-eight percent of NOLA residents said they would continue to use the filters, while only 22% of ELA residents reported being likely to continue filter use. One ELA resident asserted *"We will not be using the filter anymore,"* confirming the impracticality of using POUs under conditions with high particulates and rapid clogging. But under normal water quality conditions POUs can usually protect public health while satisfying consumers. One NOLA resident reported: *"I like this filter and will certainly continue using it. I would prefer a whole house filter system but I have been hesitant to spend the money on a system like that…. The water tasted better."*

Table 1. Differences in pre-POU testing water quality, user perceptions and behaviors reported by participants from ELA (n=13) and NOLA (n=9)

	Enterprise %	New Orleans %
Water Quality		
Particulates	92	33
Colored tint	100	22
Stains	100	11
Perceptions		
"Extremely" or "very" concerned about water	69	22
Do not believe/know if unfiltered water is safe to consume	92	100
Unpleasant taste	100	11
Unpleasant odor	100	0
Behaviors		
Never had a filter	31	11
Do not drink tap water	77	33
Unfiltered tap water primary drinking water source	0	22
Bottled water primary drinking water source	92	22

Discussion.

Effects of Flushing to Reduce Lead Levels. The control testing in unoccupied homes, confirmed prior research that the effectiveness of flushing according to available public health guidelines (for 30 secs – 2 minutes prior to filter use) is dependent on the situation. In a study conducted by Katner et al. (2018) using flushing samples from NOLA homes (Feb 2015-Nov 2016), there was no reduction in lead after 3 minutes of flushing in 81% (n=372) of homes. Lead was reduced with flushing in 13% of homes but increased in 6% of homes.[22] Here we profiled the lead concentrations for up to 10 gallons (>8min flushing) in the home with the long LSL multiple times throughout the 20-day study. Out of the 3 profiles (19 bottles each) collected in the home with sustained lead, the max lead concentration was 31.3 μg/L. The lowest flushed sample occurred in the first sample 5.6 μg/L and 91% (n = 57) of flushed samples were >10 μg/L. In the home with the disturbed LSL (4 profiles), the lowest flushed concentration was 6.7 μg/L, and

86% (n=76) of flushed samples were > 10 μg/L. There was always detectable lead in all the samples even with extended flushing.

Filter Performance for Lead Reduction. All the filtered samples collected by residents in the occupied home testing in NOLA and ELA homes had lead levels below 1 μg/L. In the ELA homes, the filters removed iron well below the SMCL. However, the POU removal of manganese was inconsistent (27-100%), even though most filtered samples (75%, n=88) had < 25 μg/L Mn (Appendix Table C1). The relatively poor removal of manganese was consistent with reports of Carriere et al.[28] The occasional low removal of Mn did not correlate with the removal of Pb or Fe, consistent with prior work on pitcher filters with high removal efficiencies with co-occurring Fe/Pb waters.[11] Likewise in Flint, MI, 19% of homes had unfiltered iron above the SMCL of 0.3 mg/L, but this did not affect the removal of lead by the POU.[6]

The POUs in the home with sustained lead performed well in reducing lead levels up to 200% capacity as treated water in the composite samples was <5 μg/L, with only 3 samples >10 μg/L among both filters (400-gallons filtered). In contrast, POUs in the Home with the Disturbed LSL had inconsistent lead removals of 22-99% that decreased over time. Duplicate POUs had 8 out of 20 samples >10 μg/L prior to 100% filter capacity. The poor removal by the POUs in the Home with the Disturbed LSL (treated water >10 μg/L) is consistent with other laboratory and field studies with difficult to treat lead particulates.[7,16–18]

These results reinforce the need for remedial flushing, filter distribution, and managing expectations of consumers after partial pipe replacements.[11,29–32] There is a high risk of elevated particulate lead after disturbing lead pipes and the use of POU filters always markedly reduced lead exposure, but not always to below 1, 5 or 10 ppb.

Filter Performance from a Consumer's Perspective. The faucet filter used in these field studies was selected because it had adapters that allowed it to fit most faucets, a by-pass valve to test the unfiltered water, and easy installation and removal by residents. Some consumers felt the filter was too big (blocking the sink) for their household sinks, though the filter was about the same size as other commercially available filters. There was only one instance where the filter was incompatible with the existing faucet.[20]

Some residents reported the filter flow rate was too slow. When installed in NOLA and ELA homes the initial flow rate ranged for this POU from 0.68 – 2.5 lpm with an average of 1.35 lpm. Out of 7 filter brands tested in a prior study the clean filter flow was 1.21± 0.23 lpm at 35-45 psi. The POU brand selected for use in this study was the 2nd slowest filter with an average of 1.05 lpm and it did clog quickly in ELA.[16]

Greater Impact of Clogging. A significant factor that emerged in this study is that clogging can be a major problem for consumers. POU filters might not be suitable in higher turbidity or discolored waters, and their cost-effectiveness relative to bottled water is markedly reduced by rapid clogging. We recently demonstrated that in waters with high iron or high particulates, the use of POUs can be more costly than purchasing store-brand bottled water.[11] It is hypothetically possible that flushing the water before it is applied to filters or using a whole house filter to reduce the burden of particulates, could be used to increase the time before clogging of the POU filter such situations, but evaluation of this possibility would require additional research.[20,33]

Conclusions.

Water lead levels can be reduced by many different strategies. All remediation strategies including (1) distribution of bottled water, (2) remedial flushing to reduce lead levels, (3) installation of lead-certified point-of-use filters, and (4) replacement of leaded plumbing have strengths and limitations.

Our studies in unoccupied high-risk homes showed that flushing did not satisfactorily reduce lead levels even after >8 minutes. The presence of high particulate lead after disturbing an LSL, created a severe challenge to POU faucet performance, as the lead levels frequently exceeded 10 μg/L in this home despite removal efficiencies above 94.8%.

In a home with a very long LSL tested to 200% capacity, the duplicate POUs always reduced water lead levels <5 μg/L except for 3 (n=40) samples. Under regular use by consumers in the NOLA and ELA residential homes, the POUs always reduced lead below 1 μg/L.

In waters with relatively high iron the filters clogged quickly which frustrated consumers similar to (Patton et al., 2024) who found that flow reduction from clogged filters discouraged consumers from continuing filter use despite its contaminant reduction abilities. The reduction in the practical filter capacity can significantly increase the treatment costs of POUs, and even make bottled water more cost-effective and less burdensome for lead remediation in some circumstances (high iron or particulates). Clogging was not a significant problem in NOLA where iron was relatively low (median <5 μg/L, max <60 μg/L) but became a major concern in ELA where the median iron level concentration was 380 μg/L and maximum iron was up to 19,700 μg/L.

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CHAPTER 5:

Mechanisms of Lead Phosphate Particle Removal by Ion-Exchange Media Depend on Particle Size and Lability

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Mechanisms of Lead Phosphate Particle Removal by Ion-Exchange Media Depend on Particle Size and Lability

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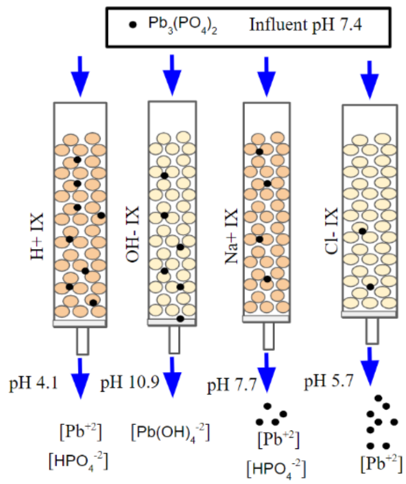


Abstract.

We examined removal mechanisms for different types of lead phosphate particles by ion-exchange media. Fresh lead phosphate nanoparticles were rapidly dissolved by resin at acidic pHs of H^+ form resin, dissolved slowly after removal of phosphate at basic pHs by OH^- form resin, the dissolved lead was readily removed by these resins. Aged and larger lead phosphate particles remained relatively insoluble at acidic or basic pHs and were more difficult to remove. Na^+ and Cl^- form resins with water at circa neutral pHs, did not readily dissolve lead phosphates. Some of these chemical changes that occur during long stagnation, may cause release of previously removed lead back into the water. Removal of lead phosphate particles did not follow expectations based on electrostatic repulsion or attraction to the resin filter media. These results demonstrate why the best filter might depend on the type of particulate lead present in the treated water.

Introduction.

Point-of-use (POU) filters are used to protect consumers from lead exposure during water contamination events (e.g., Washington, DC, Flint, MI, Newark, NJ, Benton Harbor, MI) and for routine removal of taste, odor and iron. POUs have also been distributed following partial or full LSL replacements and during system upsets (abc, 2018; Bosscher et al., 2020). Revisions to the Lead and Copper Rule (LCRR) may soon require POU filter use to mitigate lead risks in schools and childcare facilities, during LSL replacements or disturbances, and allow their use in place of CCT for small systems (EPA, 2021).

It is now understood that significant concentrations of particulate lead can sometimes elude capture by POU filters during water lead contamination events (Deshommes et al., 2010; Lytle et al., 2021; Giammar et al., 2022; Min et al., 2023; Abc News, 2019; Federal register, 2021). Some of these problems were observed at utilities using phosphate corrosion control treatment, which can create nanosized lead phosphates with a strongly negative surface charge (Lytle et al., 2021; Giammar et al., 2021). Proposed mechanisms for these poor removal efficiencies an inability to sieve nanosized particles (Giammar et al., 2021 & Lytle et al., 2021), repulsion of negatively charged lead phosphate particles by filter media (Giammar et al., 2021), presence of (~1 µm) particles that are too big for effective removal by sedimentation and too small for effective removal by Brownian motion (Purchase et al., 2020) and filter media manufacturing defects (Purchase et al., 2020). All previously published work documenting lead particle removal problems were understandably conducted using off-the-shelf filters for which more than one proprietary media is present (Min et. al., 2023), making it difficult to unambiguously identify mechanistic causes for the observed removal difficulties.

Here, we examine mechanisms of POU removal for representative lead phosphate particles of different sizes and lability, using batch or packed-column testing of commercially available cation (H^+ or Na^+) or anion (OH^- or Cl^-) form ion-exchange resins. Results were then applied to interpret the performance of proprietary POU pitcher media.

Methods.

Ion-Exchange Media. Commercially available Resin Tech ion-exchange media (297-1190 µm in diameter) in Na^+, Cl^-, OH^- form were purchased for these studies. An H^+ form resin was created from the Na^+-IX resin by charging it with 1M HCl. All resins were thoroughly rinsed with deionized water prior to use. The zeta potential of the resin beads and particles in the study were determined using a Zeta-Meter 4.0. Ion-exchange resins had zeta potentials of -37 mV for H^+ form resin, 31 mV for OH^-, -32 mV for Na^+ and 36 mV for Cl^- form resin (Appendix Table D3).

Challenge Water and Representative Lead Phosphate Particles. Three types of challenge waters with lead phosphate particles of various size distributions (Appendix Figure D1) were operationally characterized by filtration through 0.1, 0.2, 1.2 and 5 µm pore size membrane filters. These challenge suspensions had pH of 7.4-7.5 and alkalinity 0-30 mg/L (Appendix Table D2) and highly negative particle zeta potentials < -30 mV (Appendix Table D3). Soluble lead was operationally defined as the fraction of lead passing through a 0.1 µm pore size syringe filters. The fresh lead phosphate nanoparticle solutions (i.e., Lytle water) were prepared daily following the recipe of Formal et al. (2021) and Lytle et al. (2020). Older, larger chloropyromorphite lead phosphate suspensions were made according to the recipe of Ryan et al. (2002). Another solution with water borne lead particles was shipped from a New York City (NYC) pipe rig that used harvested lead pipes exposed to phosphate corrosion control water in a pipe rig for over 6 years (Sapienza, 2020).

Testing of Resins and Filters. Phase 1 of this filter challenge study evaluated lead-particle removal mechanisms and performance using commercially available ion-exchange media in beaker batch testing. Phase 2 tested lead removal in columns with the same media. Phase 3 tested proprietary pitcher filters certified for lead and particulate (Class I) using NSF/ANSI-53 and NSF/ANSI-42 (Appendix Table D1).

Phase 1: Batch Testing. Lead phosphate particle removal kinetics were evaluated in simple batch beaker tests. The experiment began after adding six grams/L of ion-exchange media to the suspension of Lytle particles, while stirring with a 5.8 cm teflon stir bar at 150 rpm. Suspensions were then regularly sampled for pH, total and soluble lead, total and soluble phosphate.

Phase 2: Column Testing With Ion-Exchange Resins. Lead phosphate particle removal efficacy was determined using commercially available ion-exchange resin in H^+, Na^+, OH^-, or Cl^- form packed 6.35 cm deep in 17.8 mm I.D. columns. One hundred and fifty mLs of lead phosphate particle water was passed through the resin in about 6 minutes, resulting in an empty bed contact time of about 37 seconds. This water was then collected, analyzed, and then re-poured through the resin. This process was repeated a total of 10 times, and samples were collected after the 1st, 5th and 10th pass through the resin which was sampled in triplicate for effluent pH and total metals analysis.

In one test, old ion-exchange columns that had previously filtered all the challenge suspensions at least once, and which sat for 8 months, were rinsed once with 100 mL of deionized water at pH 5.65 and the water was discarded. Thereafter, flushed 95 mLs of NYC Tap Water with no lead was adjusted to pH 7.5 and passed through the column. This water was captured, an aliquot was collected, and the process was repeated 10 times. Samples and pH measurements were taken after the 1st, 5th and 10th pass. Cation exchange resins were tapped, to simulate a physical disturbance, such as that occurring when a pitcher is jarred by placement on a table after it is removed from the refrigerator.

Phase 3: POU Filter Testing. An NSF-ANSI 53 lead-certified filter was purchased that has a coarse filter screen, a foam distributor, a layer of activated carbon, H^+ and OH^- form resin and a filter membrane (Appendix Table D1). Of the two NSF-ANSI 53 lead certified filters tested, one was partially converted to a Na^+ and Cl^- form resin, by repeatedly 1 M NaCl salt solution through it, and then partially neutralizing its tendency to produce acidic solution by passing a 10 mM sodium bicarbonate solution once prior to use.

The POU was conditioned and operated according to manufacturer guidelines. The filter was also rinsed three times with deionized water. The 2 L of challenge water was adjusted to pH 7.5 ± 0.1 all at once. Water samples were collected from the pitcher filters at three time points: 1) at the beginning of the experiment after passing the first 100 mLs through the filter, 2) after half of the challenge water volume had been filtered (1 L), after the last batch of 100 mLs passed through the filter and analyzed in triplicate.

Water Quality Analysis. Total metals were analyzed by Inductively Coupled Plasma Mass Spectrometry using EPA method 200.7 after acidification in 2% nitric acid for at least 16 hours.

pH was adjusted using 0.6 N HCl and NaOH. pH was measured using a Fisherbrand acumen AP 115 Portable pH meter with a AE series double junction gel pH electrode.

Results.

Phase 1: Beaker Tests with Ion-Exchange Media.

The conventional wisdom is that soluble lead in drinking water is a cation (e.g., Pb^{+2}, $Pb(OH)^{+1}$) that is quickly and completely removed by H^{+} or Na^{+} form resins, but which is not removed by anion exchange resin. In preliminary experiments we confirmed that is generally true for dissolved lead at pH 5-8. In contrast, the removal of insoluble lead phosphate particles by POU filters, is interpreted almost exclusively as a phenomenon of physical particle removal by filtration.

Each of the lead phosphate particulate suspensions tested in this work had a characteristic particle size distribution (Appendix Figure D1). Lytle water had more than 83% lead particles passing through a 0.2 μm pore size filter and only 19% removed by a 5 μm filter, consistent with the reported small characteristic particle diameter size of about 40 nm (Lytle et al., 2020). More than 99% of the recalcitrant lead phosphate particles were removed by a 5 μm pore size filter and some were visibly up to a mm in size. The NYC water passed 31% of the lead through a 0.2 um pore size filter, but 62% was removed by a 5 μm filter and there was very few particles in between these extremes. In other words, the rough characteristic particle size ranges were nanometer for Lytle water, micrometer for NYC water, and nearly mm size for recalcitrant particles.

The dissolution (lability) of these particles varied dramatically as a function of pH. When exposed to water at pH 4, all the fresh lead phosphate nanoparticles dissolved before the first sample was collected, but at pH 5.3 only a small fraction dissolved even after 10 minutes (Figure 1). In contrast, the older and larger lead phosphate particles remained mostly particulate under neutral or slightly acidic conditions. For instance, about 80% of the NYC water was particulate even after 10 minutes at pH 4, as was more than 90% of the RP. At pH 3.4, about half of the NYC particles dissolved in 10 minutes whereas only about 14% of the RP did so. Thus, the rate to significant dissolution at pH 4 was on the order of seconds to a minute for the nanoparticles, minutes to hours for the NYC water, and probably days to months for the recalcitrant particles. This slow dissolution rate is consistent with prior work describing the slow dissolution kinetics and stability of chloropyromorphite under most environmental conditions (Ryan et al., 2002).

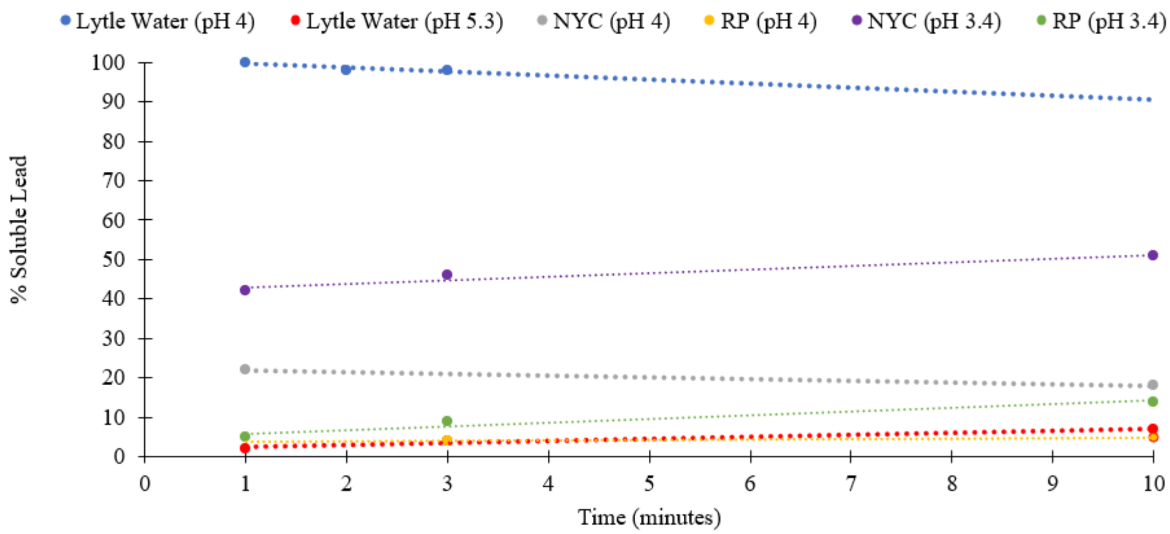


Figure 1. Soluble Lead for fresh nanoparticle challenge water, NYC and RP particles at pH 3.4, 4 and 5

Lytle Particles with Ion-Exchange Media in Batch. The Lytle water particles behaved as expected based on results of Figure 1. In the presence of H^+ resin the water quickly dropped to pH 4.1 and completely dissolving the Lytle particles within 1 minute. The resulting cationic soluble lead was nearly completely removed from the water by this cation exchange resin in 14 hours in the batch beaker test with very low ion exchange bead surface area per unit volume of water (Figure 2b). Other tests indicated this is consistent with the removal rate of Pb^{+2} soluble ions.

The Na^+ form resin at ambient pH about 7 did not dissolve the nanosized lead phosphate particles (Figure 2a). The ratio of soluble to total lead remained roughly constant at about 0.49 throughout the experiment (Figure 2b). The rate of lead removal at this higher pH in the presence of Na^+ resin was at least 42 times lower than that observed for the H^+ resin. For example, the time to drop lead to 0.83 mg/L Pb increased from 1 hour for H^+ to 42 hours for Na^+ (see Figure 2b). Thus, the ability of the H^+ resin to make the pH more acidic, dissolving the lead phosphate particles, resulted in a dramatic improvement in lead removal rates (Appendix Table D3). As expected, neither of these cation exchange resins significantly removed anionic phosphate (Figure 2c).

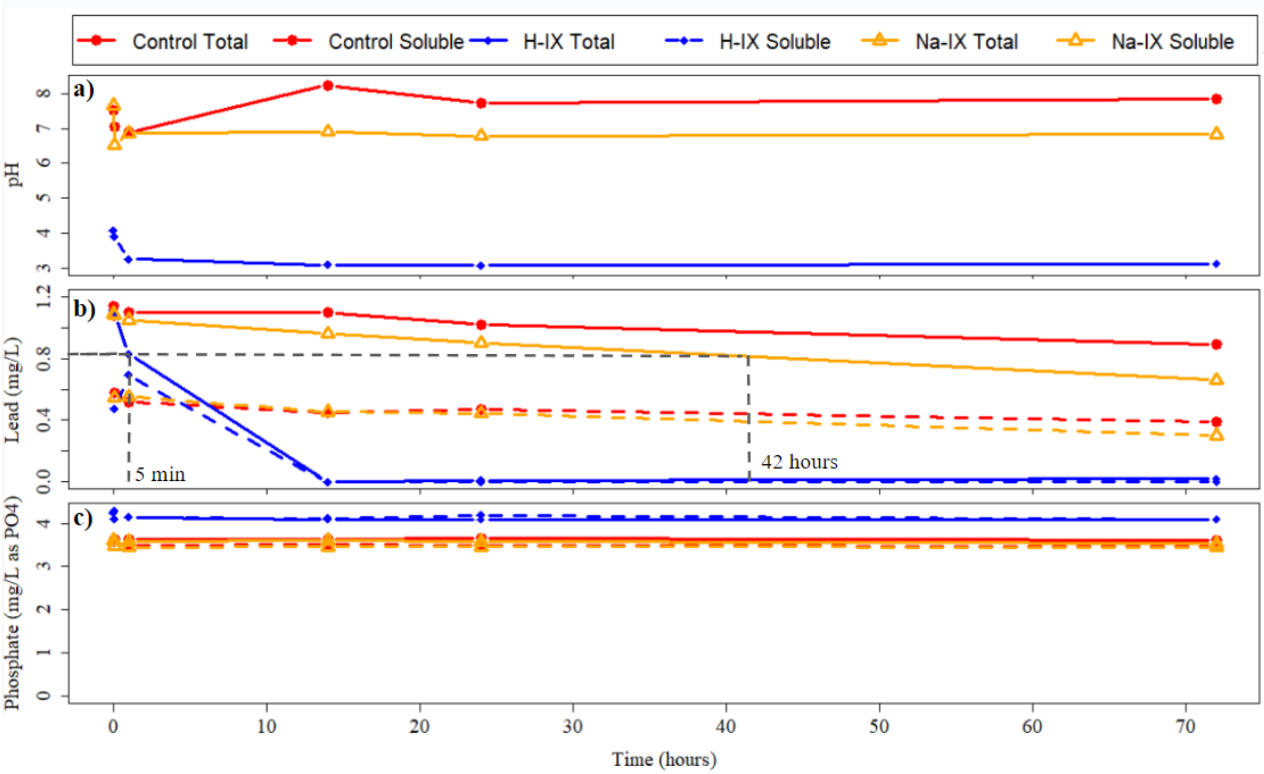


Figure 2. Fresh lead phosphate nanoparticle suspension a) Batch reactor pH b) Total and soluble lead c) Total and soluble phosphate by cation exchange resins as a function of time.

When the same sort of batch experiment was conducted using the anion exchange resins, the OH^- form resin immediately raised pH to about 11 and removed all the phosphate from the water before 15 hours (Appendix Table D4). As the phosphate was removed, lead also decreased, until such time as all the lead was dissolved and further removal of lead stopped. We tested the Cl^- form resin at pH of 3, which dissolved all of the lead by 1 hour, and then removed about 3/4 of the PO_4^{-3} within 15 hours, but no phosphate was removed beyond this time and very little of the cationic Pb^{+2} was removed at this low pH (Figure 3b).

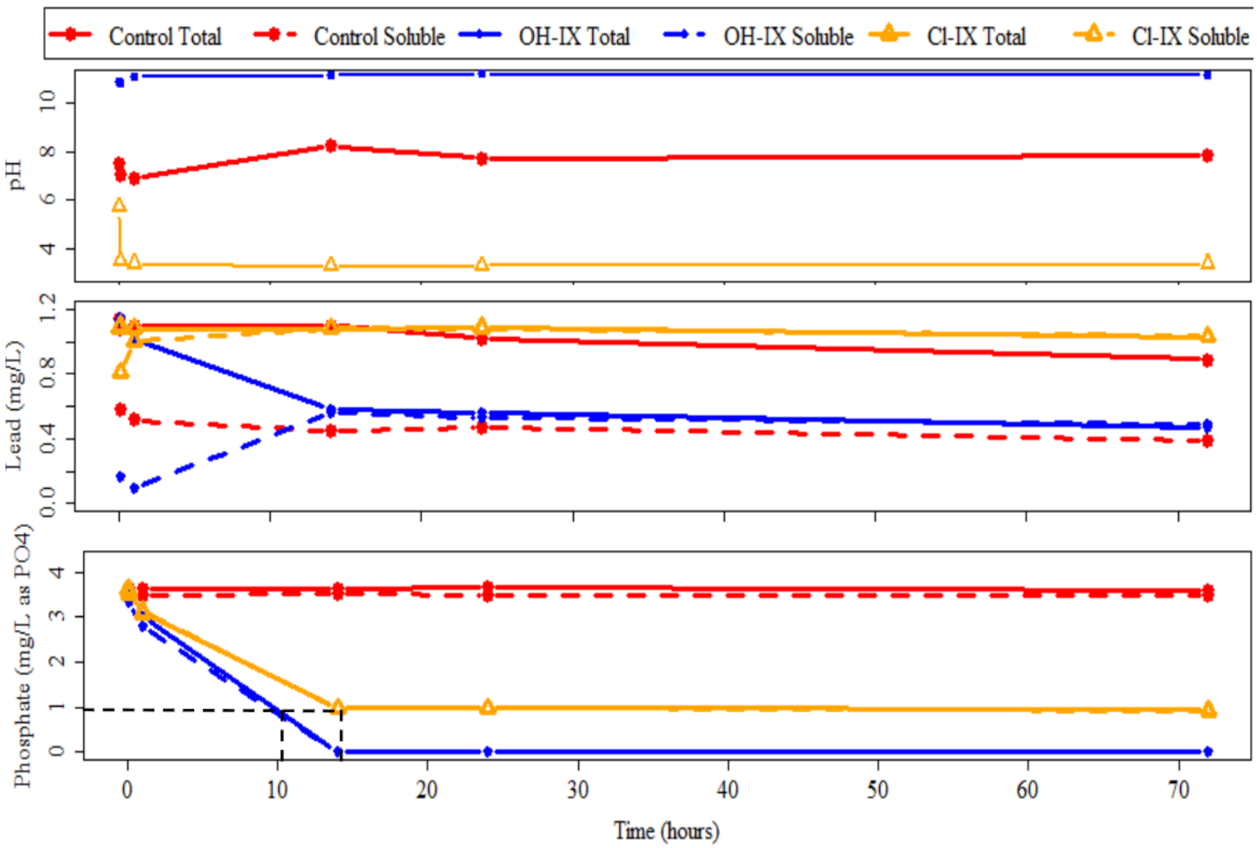


Figure 3. Fresh lead phosphate nanoparticle suspension a) Batch reactor pH b) Total and soluble lead c) Total and soluble phosphate by anion exchange resins as a function of time.

These trends for lead removal rates are all consistent with predictions based on LeChatlier's principle, the ambient pH, and the type of resin present. At low pH lead dissolution is rapid, forming soluble lead (Pb^{+2}) that is rapidly removed by the cation exchange resin, which in turn maintains a high driving force for lead dissolution (Reaction 1).

At pH 3-5 in the presence of Cl^- form resin, much of the soluble phosphate is removed, and the lead dissolves rapidly (Reaction 1), but the cationic lead is not removed by the anion exchange resin.

$$Pb_3(PO_4)_2(s) + 4H^+ \rightarrow\ 2H_2PO_4^{-1}\ + 3Pb^{+2}\ [Low\ pH] \quad \text{Reaction 1}$$

At circa neutral pH, the levels of Pb^{+2} are much lower, causing much slower rate of solid dissolution, Pb^{+2} formation, and slower removal of Pb^{+2} by the Na^+ form resin.

At very high pH with OH^- form resin, the pH rises and the anionic phosphate is removed, which increases the driving force for the forward solid dissolution (Reaction 2). The dominant soluble form of lead at pHs above about 9 is expected to be anionic $Pb(OH)_3^{-1}$ or $Pb(CO_3)_2^{-2}$, which allows for some lead removal by anion exchange resin.

$$2H_2O +\ 7OH^- + Pb_3(PO_4)_2(s)\ \rightarrow\ 2HPO_4^{-2}\ + 3Pb(OH)_3^{-1}\ [High\ pH] \quad \text{Reaction 2}$$

In contrast, the RP particles had much slower rates of lead dissolution, and slower removal of lead by the resin, in all situations (data not shown). The beaker data is not presented or discussed, because these large recalcitrant particles were so large, they often settled to the bottom of the container, and could not be reasonably sampled homogenously in suspension (Appendix Figure D2 & D3, Table D4).

Phase 2: Column Treatment by Ion-Exchange Resins.

When passing the target waters through columns of ion-exchange resin, the removal of the lead phosphate particles can occur by some combination of filtration onto the media, by ion-exchange of the soluble cationic or anionic species in the original suspension, or by ion-exchange of ionic lead species newly formed by dissolution. By passing the same batch of water through the column multiple times the progression of reactions can be tracked mechanistically.

Fresh lead phosphate nanoparticles. Filtration through H^+ form resin columns lowered pH from the initial value of 7.4 down to 4.1 after the first pass through the column (Figure 4). Effluent Pb after 1 pass decreased from an initial 135 ppb to 96 ppb for H^+ resin, 98 ppb for OH^-, 127 ppb for Na^+ form resin and 118 for Cl^- form resin. The OH^- form resin columns raised suspension pH to 10.9 upon the first pass (Figure 2), but the Na^+ effluent was pH 7.7 and the Cl^- form resin was pH 5.7 after 10 passes. Both anion form resins quickly removed 99% of the soluble phosphate whereas cation exchange resins removed very little.

When fresh lead phosphate nanoparticle suspensions were filtered through ion-exchange columns for 6 consecutive passes, the cumulative H^+ form resin removal increased to 95% (Figure 4). The H^+ form resin only removed 59% of the lead in the first pass, decreasing the lead from about 121 ppb in the influent down to 50.3 ppb (Figure 4). On the second pass the effluent lead was dropped to 1.2 ppb, indicating the removal percentage *increased* to 98% for that pass from only 59% in the first pass. We hypothesize that this is because the lead was only partly dissolved while contacting media during the first pass, since the water was present in the column for only about 12 seconds based on an empty bed contact time of 37 seconds and an assumed void space of 33%. But after the pH dropped before the second pass the lead would have been almost all dissolved Pb^{+2}, causing higher percentage removals on the second pass than for the nanoparticles present on the first pass.

The strong OH^- base resin showed a similar effect. During the first pass the percentage removal was only 28%, but on the second pass the removal percentage increased to 74% of what went into the column from the first pass achieving a cumulative removal of 82%. We again note, that the OH^- form resin removed the soluble phosphate and raised the pH on the first pass, which probably had little effect on the nanosized lead phosphate during the 12 seconds the water was in the column. But during the second pass much more of the lead would have been dissolved and would have been in an anionic form, which increased the percentage lead removal by about 2.5 times during the second pass. OH^- base resin achieved a cumulative lead removal of 97% by the sixth pass.

The Cl^- form resin never markedly changed the pH of the water to a point where the lead was quickly dissolved or that the soluble lead was anionic. In this case the lead removal percentage with each pass was approximately constant at about 2.83% for each pass with a cumulative removal of 23% by the sixth pass. These trends are more consistent with expectations of particle removal by filtration with a constant particle capture efficiency factor.

The Na^+ resin did not remove phosphate and it removed slightly more Pb during pass 1 than did the Cl^- form resin, as expected if traces of lead were present in the form of soluble Pb^{+2} in the original Lytle particle solution. But the pH remained relatively high and there was no additional removal on pass 2 and 3, and removal only gradually increased on passes 4 through 6. The Na^+ and Cl^- form resins achieved the same low cumulative lead removal of about 23% (Figure 5).

Comparatively, cumulative lead removal for 10 passes decreased in the order H^+ (95%) ≈ OH^- (94%) > Cl^- (34%) > Na^+ (26%) (Appendix Figure D4).

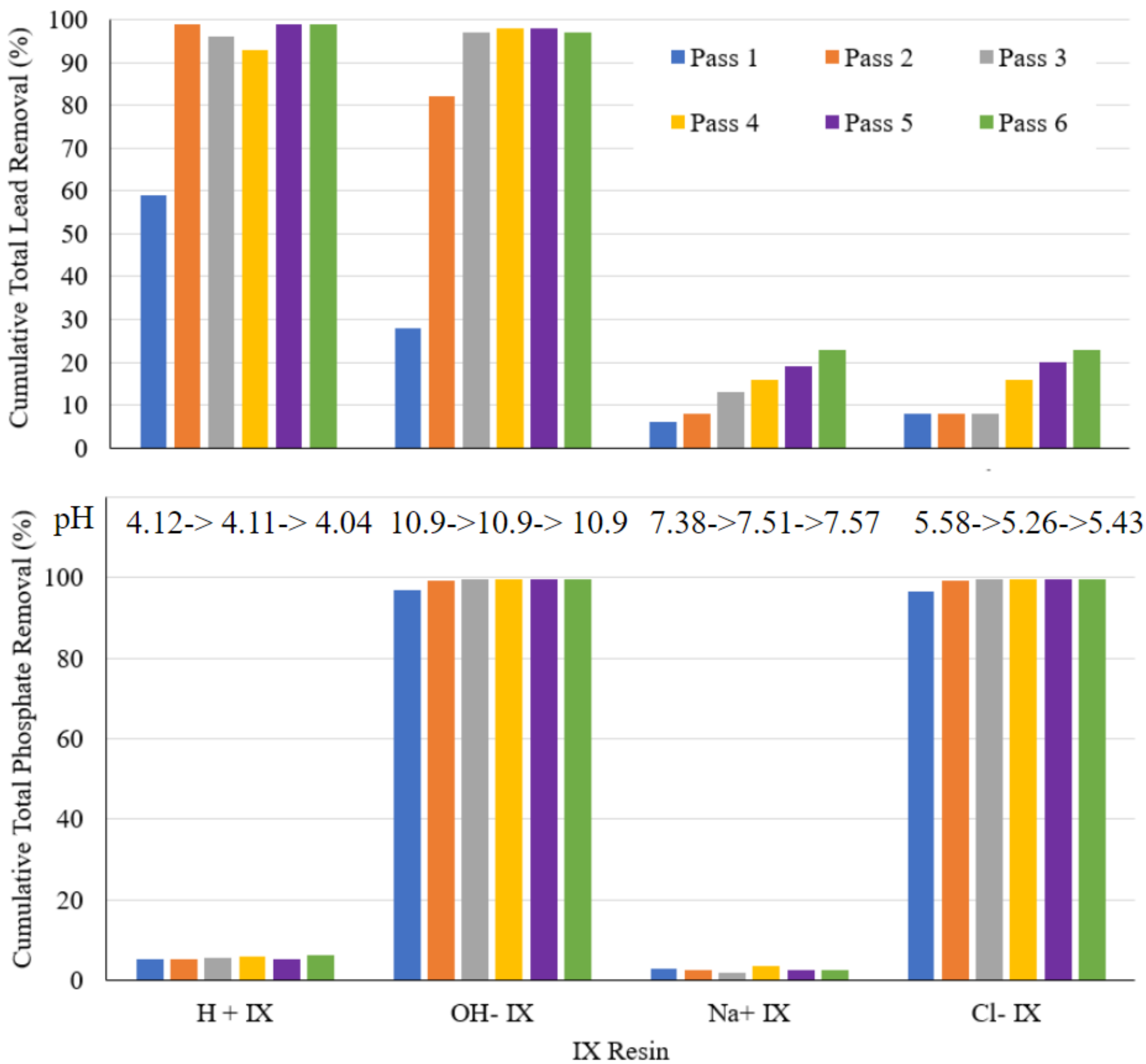


Figure 4. Cumulative percent lead removal of fresh lead phosphate nanoparticles by resin passes 1-6. The pH of the first, second and last pass of water through the resin pH is indicated above the bars for phosphate removal.

Well-aged lead phosphate particles. These column tests were repeated using the NYC water and RP water lead phosphates (Figure 5 and Appendix Figure D4). When NYC water was filtered through ion-exchange columns for 10 consecutive passes, the H^+ form resin removal after the first pass was only 7.8% (Figure 5). Passes 2-5 produced a cumulative lead removal of only 44% and a total lead removal at pass 5 of 52%. Passes 6-10 removed an additional 34% of lead with a total lead removal of 85% at pass 10. This is consistent with slower dissolving lead particles in NYC water.

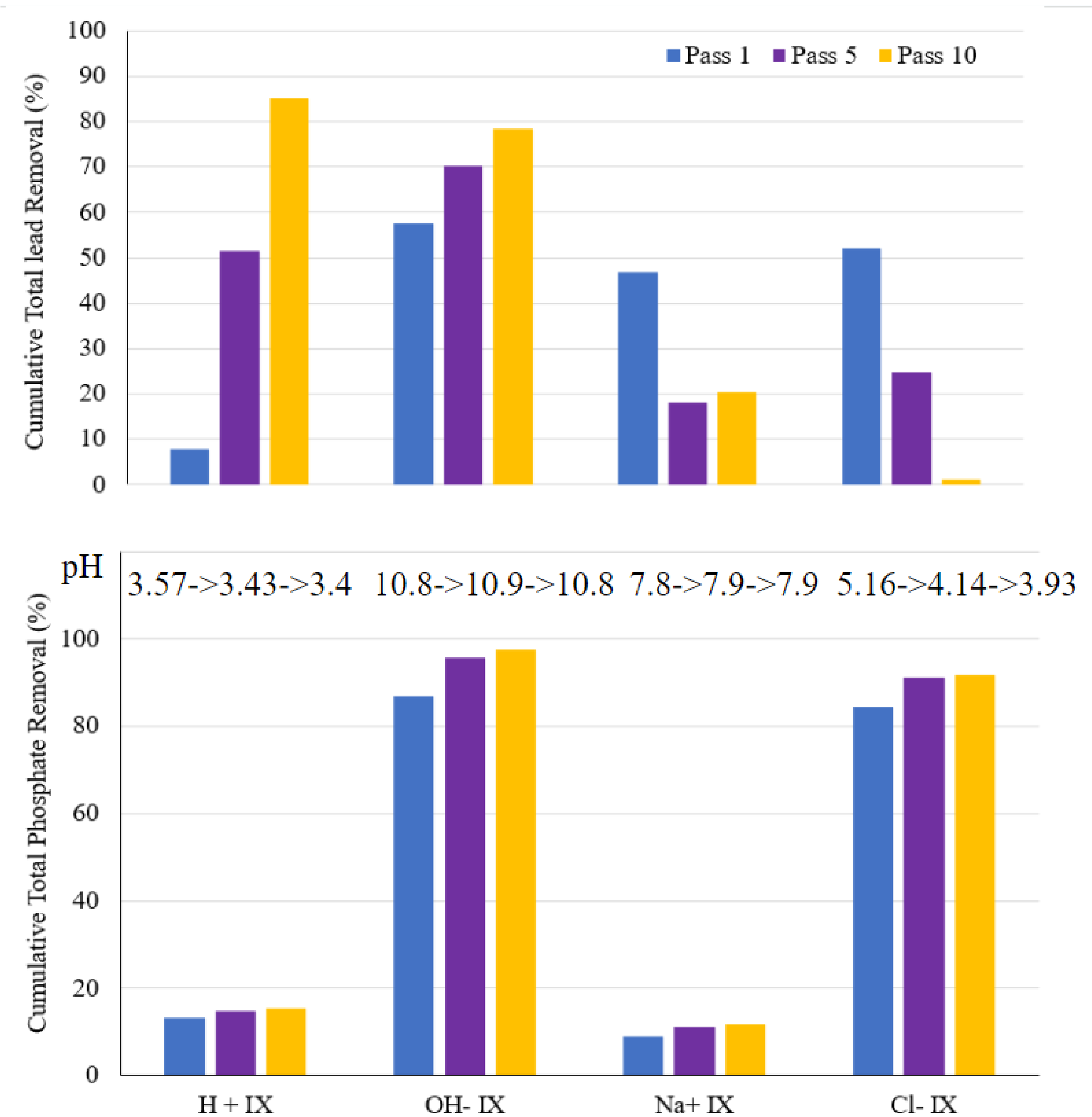


Figure 5. Cumulative percent lead removal of NYC by resin passes 1, 5 and 10. The measured pH for each of the indicated passes is above the resin type.

The OH^- form resin removed a much greater percentage of lead in the first pass than the H^+ form resin. This may be due to a higher filtration efficiency, which is expected, since the OH^- form resin has a positive zeta potential whereas the NYC particles had a highly negative zeta potential creating attraction for filter removal (Appendix Table D3). In contrast, the H^+ form resin had a negatively charged zeta potential that created repulsion which is expected to decrease particle removal by filtration. But by pass 10 with the poorly buffered water at pH 3 using the H^+ resin, the NYC particles are expected to dissolve, creating lead cations that are easily removed. Consequently, by pass 10 the cumulative percentage removal for H^+ resin exceeded that for the OH^- form resin (Appendix Figure D4).

Unlike the situation with Lytle water, the lead removal for the lower alkalinity NYC water (10 mg/L as $CaCO_3$) *decreased* with each pass by the Na^+ and Cl^- form resins. This can be explained by the changes in pH. On the first pass, we suspect removal was due to capture of some particulate lead, with the resin acting as a filter. The first pass effluent pH of 5.16 was not low enough to rapidly dissolve the lead (Figure 1). But by pass 10 the effluent pH of the poorly buffered NYC water (initial alkalinity 17.6 mg/L $CaCO_3$) dropped down to pH 3.93. That pH was low enough to dissolve the lead phosphates previously removed by the column (see Figure 1), which caused previously removed lead to dissolve and be released, causing cumulative removal by the anion exchange media to be insignificant at this low pH (see Figure 3).

Older particle suspensions (NYC and RP) particles did not readily dissolve even at pH 4, although they did dissolve somewhat at pH 3.4 (see Figure 1). Based on zeta potential of the media and particles (Table 2), it would be predicted that the very highly positive charge on the OH^- and Cl^- media, would have produced the best filtration removal of the negatively charged particles (Figure 5).

But the lead removal efficiency for the largest RP particles increased in the order: OH^- (5.5%) < H^+ (43%) < Cl^- (68%) < Na^+ (86%). The lead removal efficiency of the moderate sized NYC particles increased in the order: Cl^- (1%) < Na^+ (20%) < OH^- (78%) < H^+ (85%). Thus, removal of RP and NYC particles did not follow expectations based on classic concepts of electrostatic repulsion or attraction between the particles and the filter media. For very large lead particles, passage through the media might involve semi-random "channeling," as documented for large lead solder particles by Deshommes et al. 2010 and described by EPA in 2006.

Columns with prior lead release and prolonged stagnation. The ability of some columns to release previously removed lead was concerning (i.e., Cl^- exchange resins in Figure 5). To examine if changes are occurring during stagnation that could create problems with release, we took old ion-exchange columns that had previously filtered all three of the challenge water suspensions and rinsed them once with 100 mL of deionized water at pH 5.65 and discarded the water. Thereafter, NYC Tap Water with low lead (<1 ppb), was adjusted to a pH of 7.5, and passed through the media for a total of 10 passes. Samples and pH measurements were taken at the 1st, 5th and 10th pass. The cation exchange resins were also tapped, to simulate a physical disturbance, such as that occurring when a pitcher is jarred by placement on a table after it is removed from the refrigerator.

After the first pass, the effluents from all the resins released previously removed lead at levels well above the 15 ppb action level (Figure 6). Orthophosphate removal and pH changes were consistent with prior results (Appendix Table D5). With additional passes, the H^+ resin, removed nearly all of the lead it released, as pH of the water dropped. The OH^- form resin, likewise, decreased the lead removal from about 392 down to 266 ppb with additional passes, even though it ended up with the highest overall lead release. But the Na^+ and Cl^- resins released more lead with additional passes through the resin indicating weakening lead removal with stagnation. On pass 10 most of the lead released from the OH^- form resin was particulate, whereas for the sodium and chloride form resin it was mostly soluble (Figure 6).

This study confirms a prior report, that stagnant filters might sometimes produce lead levels exceeding 5 ppb and provides additional insights about the types of chemical changes that occur in these columns that create a range of effects on lead release (Clark, 2020).

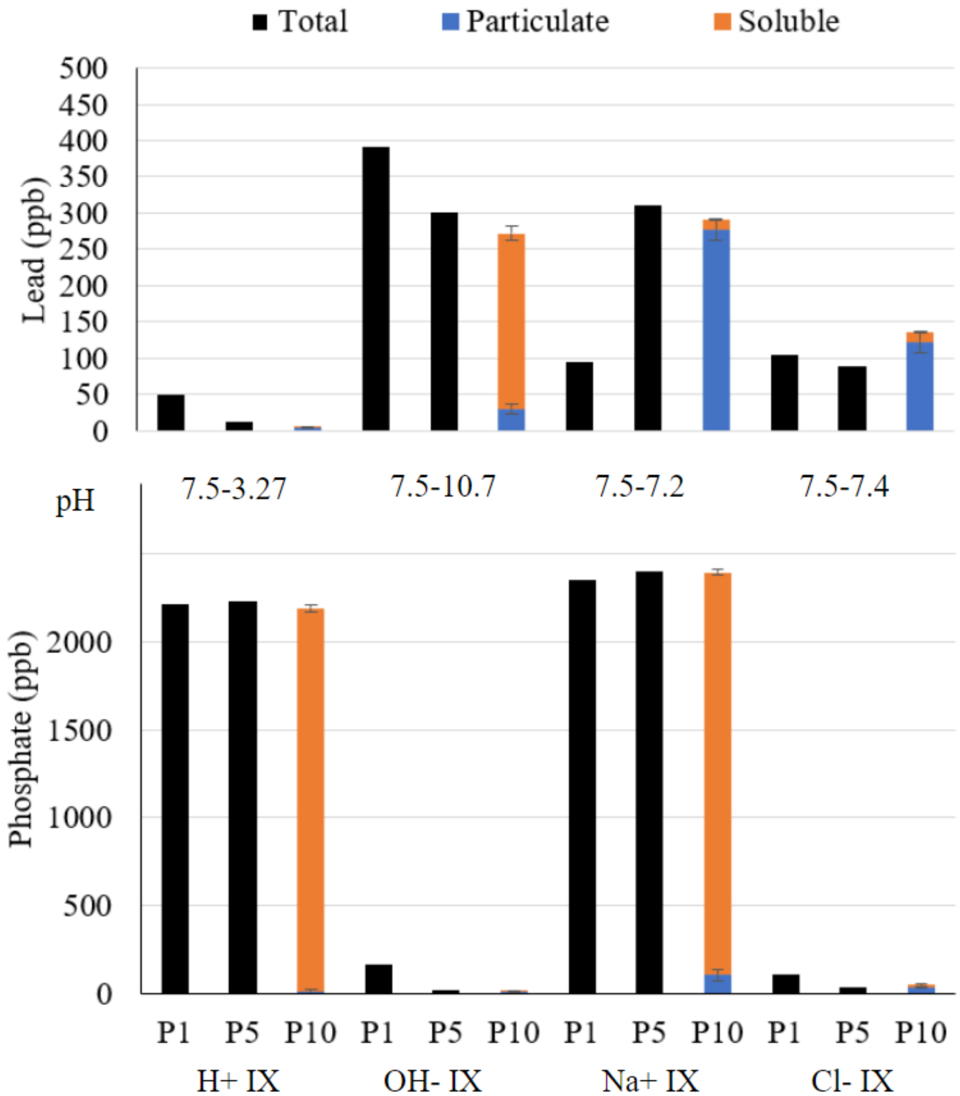
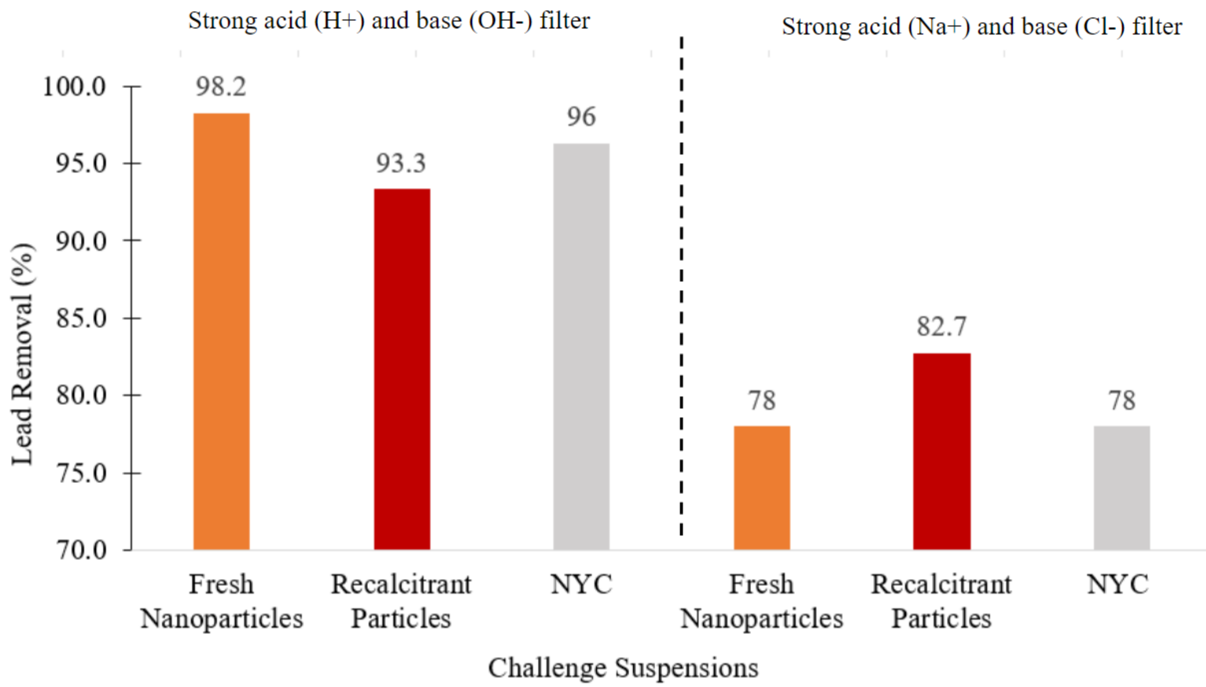


Figure 6. Lead release from 8-month-old ion-exchange resins previously exposed to mixtures of Lytle, NYC and RP particles. Total effluent lead denoted at the top of bars (n=3). Error bars represent 95% confidence intervals. Cation (H^+ and Na^+) columns were tapped during filtration. Soluble lead was operationally defined by filtration through an 0.1 μm pore size filter.

Phase 3: Impact of particle size and lability on Proprietary POU pitcher filter removal.

It was hypothesized that the H^+ and OH^- form resins would have certain advantages in dissolving and removing particulate lead phosphate when used in combination, versus the Na^+ and Cl^- form resins. The off the shelf version of the pitcher filters had both H^+ and OH^- resin, and we converted some into Na^+ and Cl^- form for a performance comparison.

The Na^+ and Cl^- form resins only removed 78-83% of the lead from the three lead phosphate particle test waters, compared to greater than 93% removal for the H^+ and OH^- form resins (Figure 7). In most cases, effluent pH was close to the influent pH, even though near the surface of individual resin beads in the column, pH shifts were undoubtedly still occurring. The exception was NYC water in which the effluent pH dropped to 3.8.



Effluent pH	6	6	7.9	7.1	7.3	3.8
% Phosphate removal	99.8	100	99.3	99.5	100	94.6

Figure 7. Lead and phosphate removal by strong acid and base pitcher filter versus strong acid filter and effluent pH

Conclusions.

This study evaluated the lead removal mechanism of fresh and well-aged lead phosphate particles by pitcher filters in batch and packed column flow through testing. As opposed to prior work that interpreted results almost exclusively based on assumptions of filtering particles, this work demonstrates that complex dissolution pathways can occur, that can be fast or slow, if phosphate is removed and pH is very high or low. This mechanistic study demonstrated that fresh nanoparticle lead phosphate particles can dissolve quickly, which allows for enhanced lead removal by H^+ and even OH^- form resin, as observed in batch testing and column testing. Older particles are more difficult to dissolve and tend to have lower percentage removals. This explains why fresh lead particles in NYC water tended to have much better removal than the older lead particles obtained from scouring in a pipe loop (Sapienza et al., 2020).

Comparatively, Na^+ and Cl^- form resins achieved poorer removals due, in large part, to their inability to drastically alter suspension pH required to transform lead from particles to soluble species that could be better removed by each resin. Off the shelf pitcher filters with mixed H^+ and OH^- form resins had better removal than the same filters in Na^+ and Cl^- form.

Removal of well-aged, recalcitrant lead phosphate particles (>1 um or > 5 um) was complex. Results are not explained by simplistic filtration theory based on electrostatic attraction and repulsion.

The problematic release of previously removed lead particles in 8-month-old ion-exchange resin confirmed concerns from some field testing (Clark, 2020). Once again, the H+ form resin, had advantages in better holding the lead in the column, whereas Cl^- form resin seems to have problems retaining previously removed lead.

The LCRR will require POU distribution under certain conditions effective on Oct 16, 2024. POUs will be distributed for remediation efforts in schools and childcare facilities, during LSLR, after LSL disturbance and in the place of CCT. This study adds to a body of work (Master et al., 2023) that indicates a utilities specific water chemistry and the nature of particulate lead, can affect POU filter metal removal performance. The approaches developed in this study can be used to evaluate the lability of lead particles, and its possible effect on removal and release of previously removed lead from columns after stagnation.

Acknowledgements.

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CHAPTER 6: Engineering Significance/ Conclusions

The experimental results from Chapters 2-5 provide the following key contributions:

Chapter 2 elucidated the electrochemical mechanism of lead-tin solder spallation in high nitrate that was observed in a city that experienced a water lead contamination event. Alloys with higher tin content were particularly susceptible to cracking during corrosion as nitrate was reduced to ammonia. Initial indications were that the metal weight loss exceeded that predicted based on Faraday's law.

Chapter 3 recreated the essence of nitrate induced solder spallation in the presence of high nitrate at a bench-scale. Beads of solder attached to copper pipe, did not detach over a three-month experiment in a groundwater with high sulfate and low nitrate, but 100% did so in a surface water with high nitrate and low sulfate. Electrochemical testing revealed that addition of 0.75 mM SO4, inhibited spallation attack by high nitrate and pure tin metal. In contrast, under the conditions studied, traditional inhibitors such as bicarbonate, orthophosphate, polyphosphate and zinc orthophosphate did not strongly inhibit spallation corrosion. The methods developed herein can be used by utilities switching source waters, to anticipate problems with spallation corrosion that might cause water contamination events. Future work should study inhibition of nitrate attack on lead:tin solder alloys over longer time periods using the bead test.

Chapter 4 field tested point-of-use lead filters under a range of normal and extreme scenarios. Lead removals by filters were generally very good, but if very high concentrations of lead are present, even 98% removal is not adequate to always achieve lead below the 15 ppb action level in treated water. The results demonstrated that a better understanding of particulate lead removal by POU filters is needed. Notedly, clogging of filters was a major problem in waters that had high levels of iron and manganese in addition to lead.

Chapter 5 is the first study to mechanistically examine ion-exchange removal of lead phosphate particulates. Dissolution of lead phosphate particles within the filter media, at very low or high pH, was revealed to be a major factor enhancing removal of lead phosphate particles in some circumstances. Filtration efficiency of particles when dissolution did not occur, was not explained based on classic theory of electrostatics and particle capture. Differences in the size and lability (i.e., ease of dissolution) strongly impacted which ion-exchange media had good lead removal and which media had poor removal. The results suggest that filters may need to be tailored to the source water chemistry and type of lead contamination present. To better understand this issue, future work should examine and rank the lead removal performance of proprietary filters for a wide range of challenge waters.

Conclusions

1.The conversion of nitrate to ammonia and other nitrogenous products creates a corrosive microenvironment which allow for solder spallation to occur at the lead-tin solder surface. Lead-tin solder alloys consisting of more than 40% tin by weight are rapidly detinned and susceptible to severe cracking, spallation and potential complete detachment form pipe surface.

2. Bench-scale studies simulating prior lead contamination event illustrated the danger of the source water switch from non-corrosive, high sulfate groundwater to surface waters with high nitrate and low sulfate. Additional electrochemical studies with a separated anode and cathode revealed that nitrate induced tin spallation produced weight loss exceeding Faradaic predictions, contrastingly chloride was corrosive, but did not cause spallation.

3.Poor field POU lead removal performance was observed in homes with extremely high particulate lead. Despite good lead removal efficiency under circumstances with lower lead and high iron and manganese, filters frequently clogged and produced frustration among consumers.

4.Lead removal mechanism studies revealed complex dissolution pathways for lead phosphate particles that could enhance removal of phosphate at pH < 5 for H^+ form resin and at pH > 10 for OH^- form resin. The liability of lead phosphate particles was found to have a major influence on lead phosphate particle removal efficacy by conventional ion-exchange media. The problematic release of previously released lead particles after 8-months of stagnation was also observed.

APPENDIX A: CHAPTER 2- SUPPLEMENTARY INFORMATION

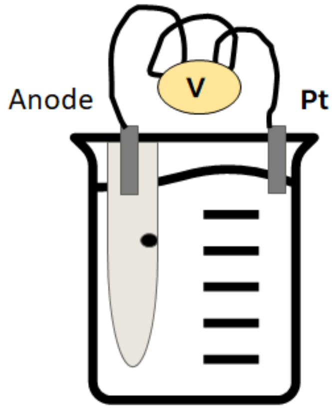


Figure A1. Electrochemical cell apparatus comprised of a 500-mL beaker containing a 25-mL occluded cell with a transport hole in its side. One cm of a pure tin or 50:50 lead-tin solder wire was placed in the cell (anode) and connected to a platinum cathode 2-in away. A constant supply of 3.4 volts was applied.

Figure A2. Additional pictures of the interior of the harvested pipes from the affected community: a) hot supply pipe with 0.5-cm solder bead, b) cold supply pipe with 1-cm solder bead, c) cold supply pipe with visible interior solder and crater, d) close-up of a crater from the cold supply pipe in (c), the source of one of the SEM detinning images.

Table A1. Ammonia production (mg/L total NH3-N) in the droplet jars over the course of the first month. Ammonia production decreased over time for pure lead and the alloys but remained elevated for pure tin.

Total Ammonia (mg/L NH_3-N)					
Day	Pure Lead	70/30 Lead-Tin Solder	60/40 Lead-Tin Solder	50/50 Lead-Tin Solder	Pure Tin
7	0	5.2	5.4	4.6	3.4
21	0.4	2	1.4	0.8	4.4
28	0	1.8	0.6	0.6	4.6

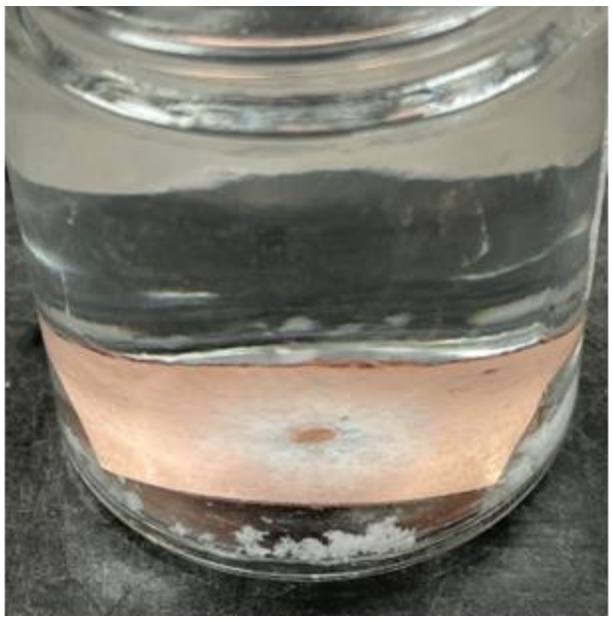
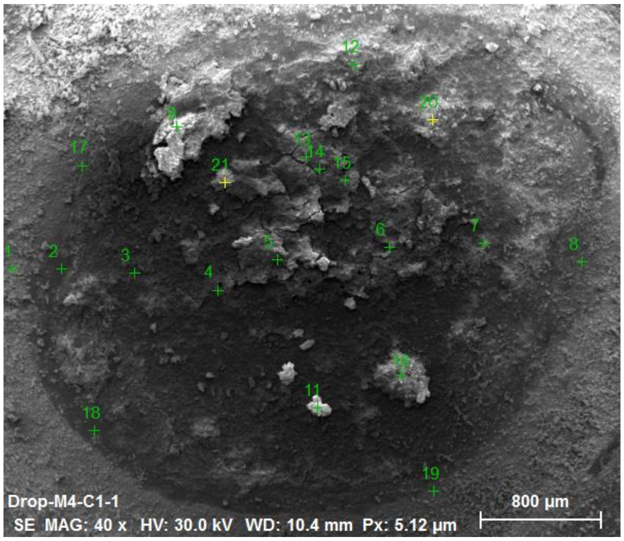


Figure A3. White powder that remained in jar after pure lead droplet uniformly dissolved.



Atomic percent (%)

Spectrum	C	N	O	Cu	Sn	Pb
3	20.35	0.00	52.13	7.23	19.65	0.64
1	21.94	0.00	50.90	5.16	21.99	0.01
2	18.78	16.84	13.18	46.75	4.44	0.01
4	13.84	0.00	62.44	0.67	22.53	0.52
5	15.98	0.00	62.73	0.20	21.01	0.09
6	12.27	0.00	53.66	0.45	33.02	0.60
7	18.57	0.00	56.42	0.83	23.91	0.26
8	25.28	7.28	38.83	19.13	9.46	0.03
9	17.22	0.00	64.72	0.18	17.57	0.31
11	12.83	1.33	53.43	1.07	30.39	0.96
12	11.74	0.00	68.00	0.22	19.93	0.12
13	16.50	0.00	60.98	0.18	21.77	0.56
14	15.87	0.00	64.14	0.16	19.48	0.35
15	16.25	0.00	61.78	0.52	21.25	0.21
16	19.34	0.00	57.49	0.37	22.44	0.37
17	20.16	0.00	58.50	1.71	19.60	0.03
18	20.30	14.94	19.70	39.42	5.62	0.02
19	22.84	0.00	48.83	10.33	17.86	0.14
20	16.62	0.00	64.26	0.58	18.20	0.35
21	13.42	0.00	61.77	0.28	24.34	0.20

Figure A4. SEM-EDS results for detachment site of 50/50 lead-tin solder droplet.

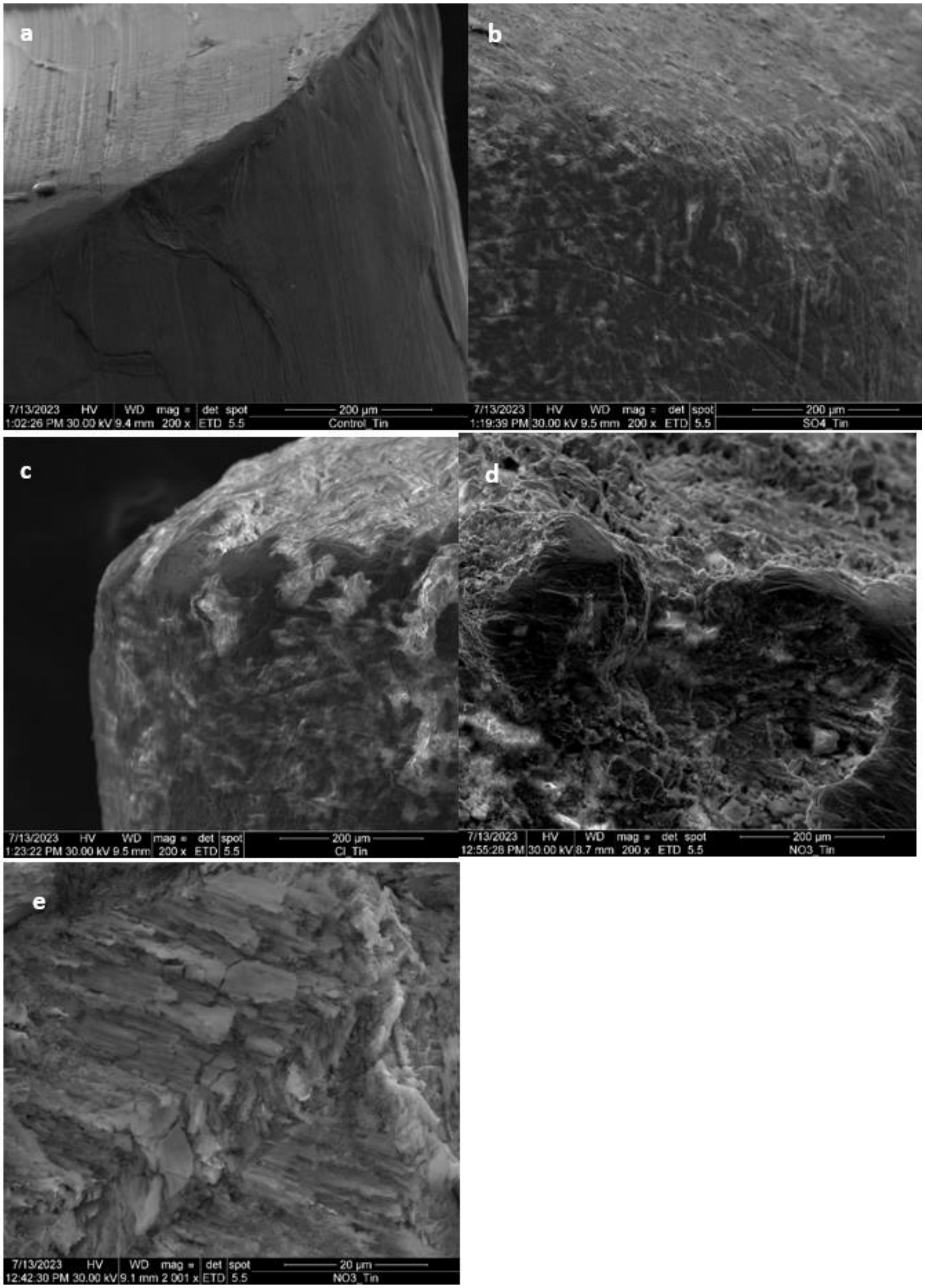


Figure A5. Select tin wires from the electrochemical cell study exposed to the a) control, b) sulfate, c) chloride, and d) nitrate. A higher resolution photograph of (d) is presented in (e) to show cracking within the crater.

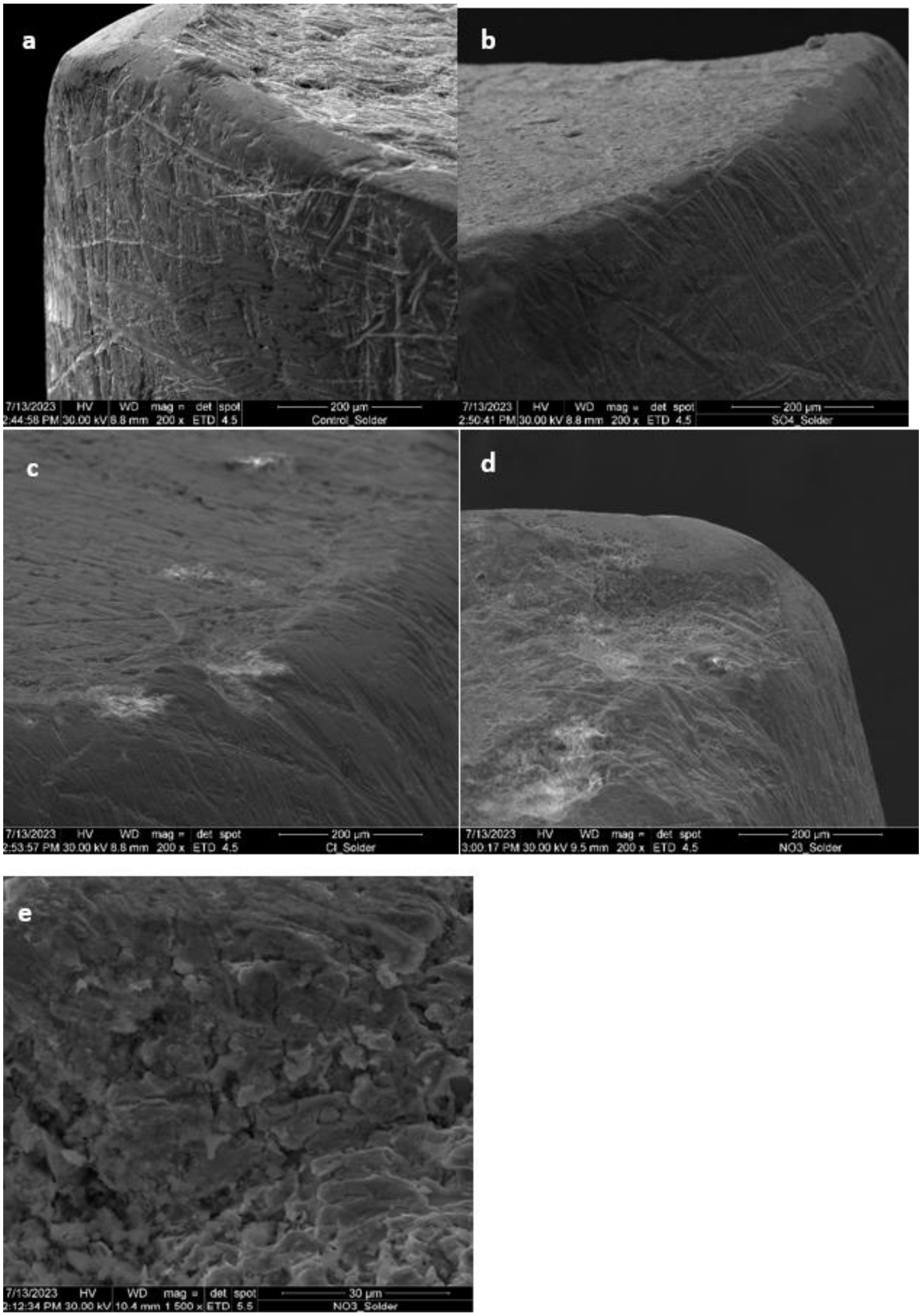


Figure A6. Select 50:50 lead-tin solder wires from the electrochemical cell study exposed to the a) control, b) sulfate, c) chloride, and d) nitrate. A higher resolution photograph of (d) is presented in (e) to show cracking within the crater.

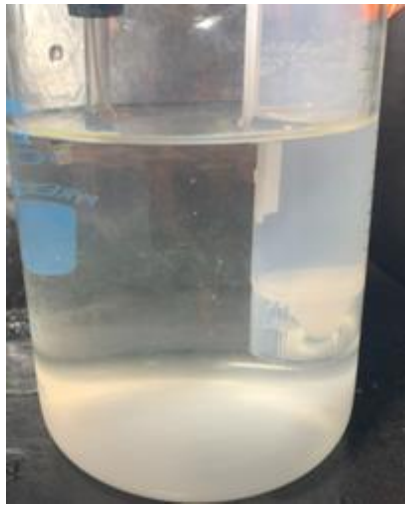


Figure A7. Dissolution of a pure lead wire exposed to nitrate solution in the electrochemical cell.

Table A2. Final cathode and anode pH values from the electrochemical cell study. Starting pH was 5.8 on average.

Metal	Condition	Final Cathode pH	Final Anode pH
Tin	Control	6.54	4.11
	Sulfate	6.06	3.40
	Chloride	7.31	2.87
	Nitrate	8.52	3.11
50/50 Lead-Tin Solder	Control	6.62	4.92
	Sulfate	6.17	3.28
	Chloride	7.92	3.53
	Nitrate	9.00	4.61
Lead	Nitrate	8.74	6.00

Table A3. Percentage of nitrate reduction products formed from tin, 50/50 lead-tin solder, and pure lead in the electrochemical cell study.

Metal	NO3 remaining (%)	NO2 formed (%)	NH3 formed (%)	Other (%)
Tin	81.9	0.00	0.98	17.2
Lead Solder	84.3	1.20	0.73	13.8
Pure Lead	77.6	1.69	0.90	19.8

APPENDIX B: CHAPTER 3 – SUPPLEMENTAL INFORMATION

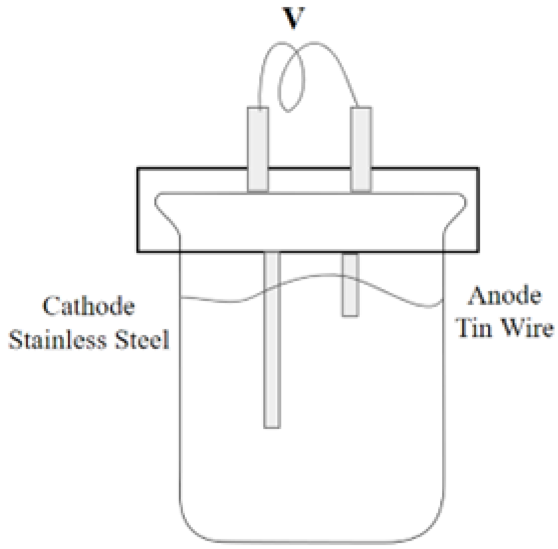


Figure B1. Electrochemical cell apparatus consisting of 1 L beaker containing a 0.84 in of pure tin wire which was submerged partially when placed in the cell (anode) and connected to a stainless steel cathode 1-in away. A constant supply of +1 V was applied

Figure B2. Picture of solder bead surface (left) cracking on copper coupling after spalling (right).

Table B1. Preliminary inhibitory study water chemistry

Condition Number	Water Chemistry Condition	Note
1	0.71 mM NO_3^--N	Nitrate-Control
2	0.36 mM $Zn(NO_3)_2$	Zinc
3	0.71 mM $NaNO_3$ + 1 mM Na_2HPO_4	Orthophosphate
4	0.36 mM $Zn(NO_3)_2$ + 1 mM Na_2HPO_4	Zinc & Orthophosphate
5	0.71 mM NO_3-N + 0.1 mM PO_4-P	Polyphosphate
6	0.71 mM NO_3-N + 10 mM SO_4	Sulfate
7	0.36 mM $Zn(NO_3)_2$ + 1mM Na_2HPO_4 + 1 mM SO_4 + 10 mM $NaHCO_3$	Zinc, Orthophosphate, Sulfate & Bicarbonate

Figure B3. Thick white precipitate forms around tin wire when reactor is dosed with polyphosphate.

APPENDIX C: CHAPTER 4 – SUPPLEMENTAL INFORMATION

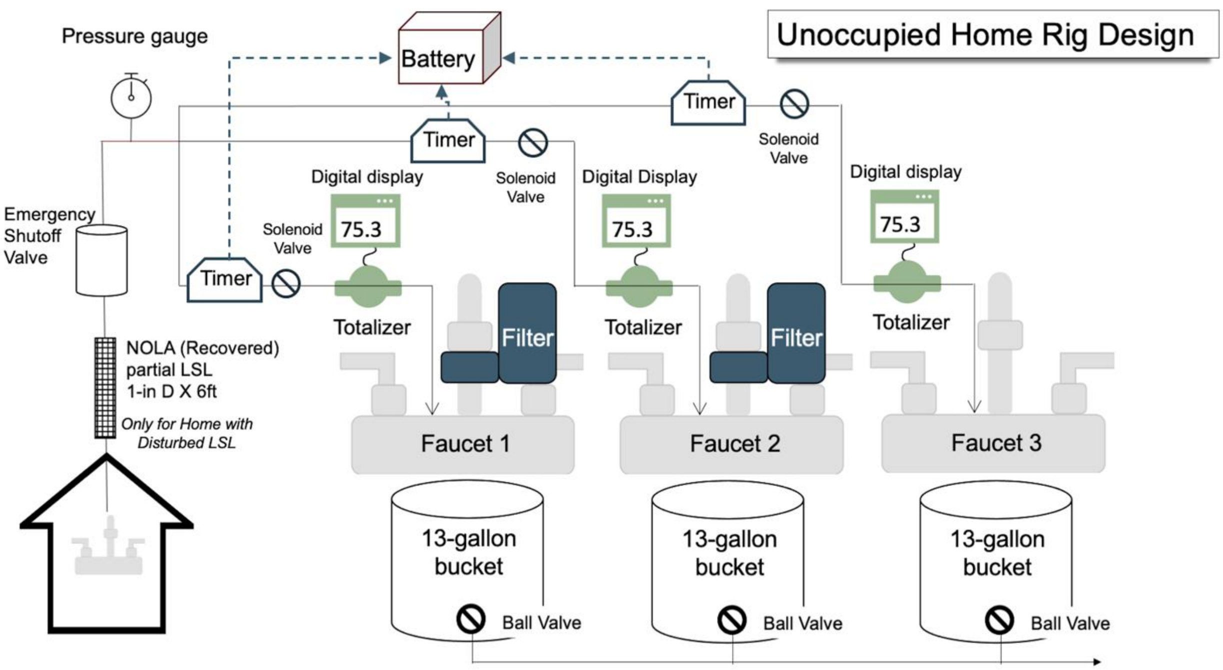


Figure C1. Unoccupied Home Rig Design

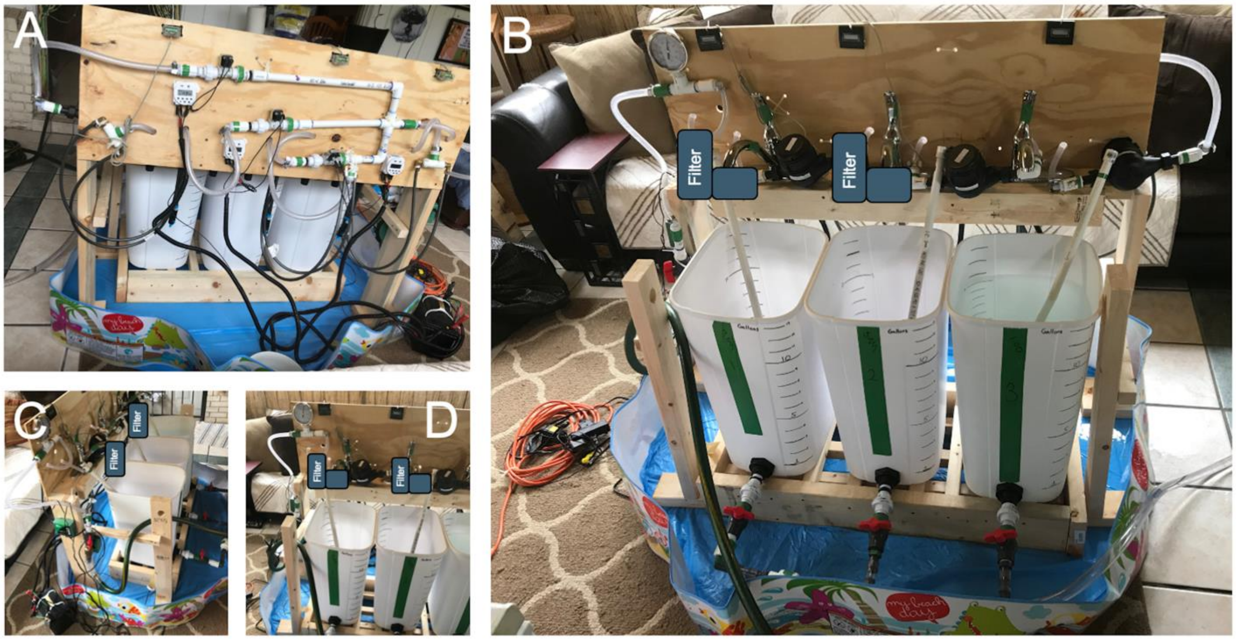


Figure C2. Unoccupied Home Rig Pictures

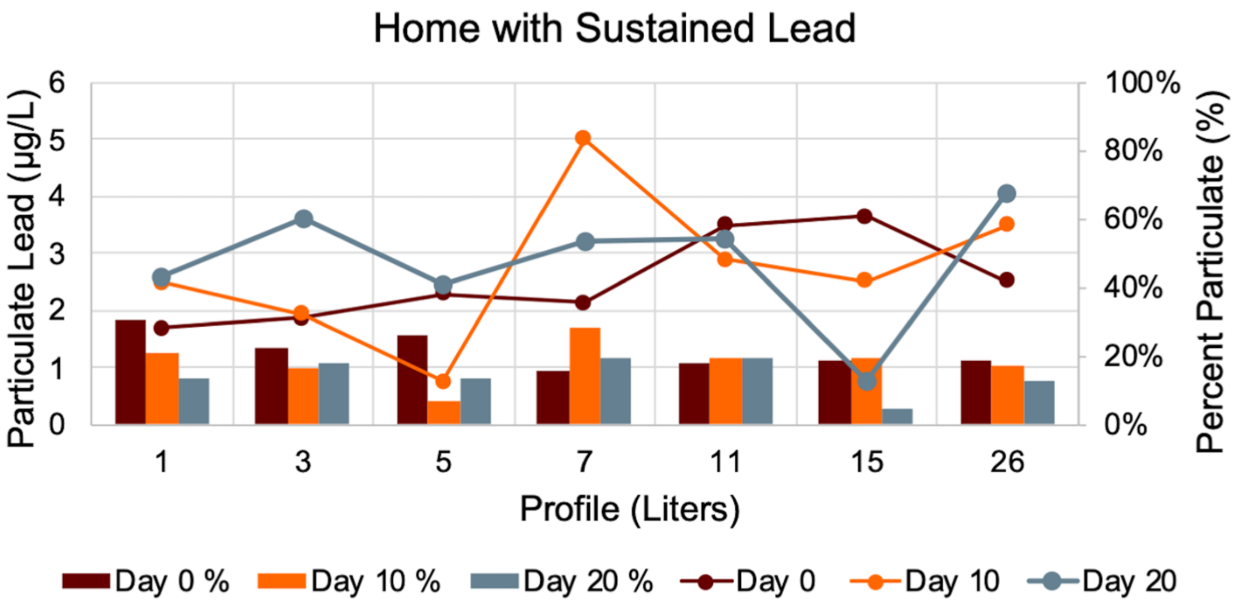


Figure C3. Home with Sustained Lead – Particulate Lead (concentration and percentage)

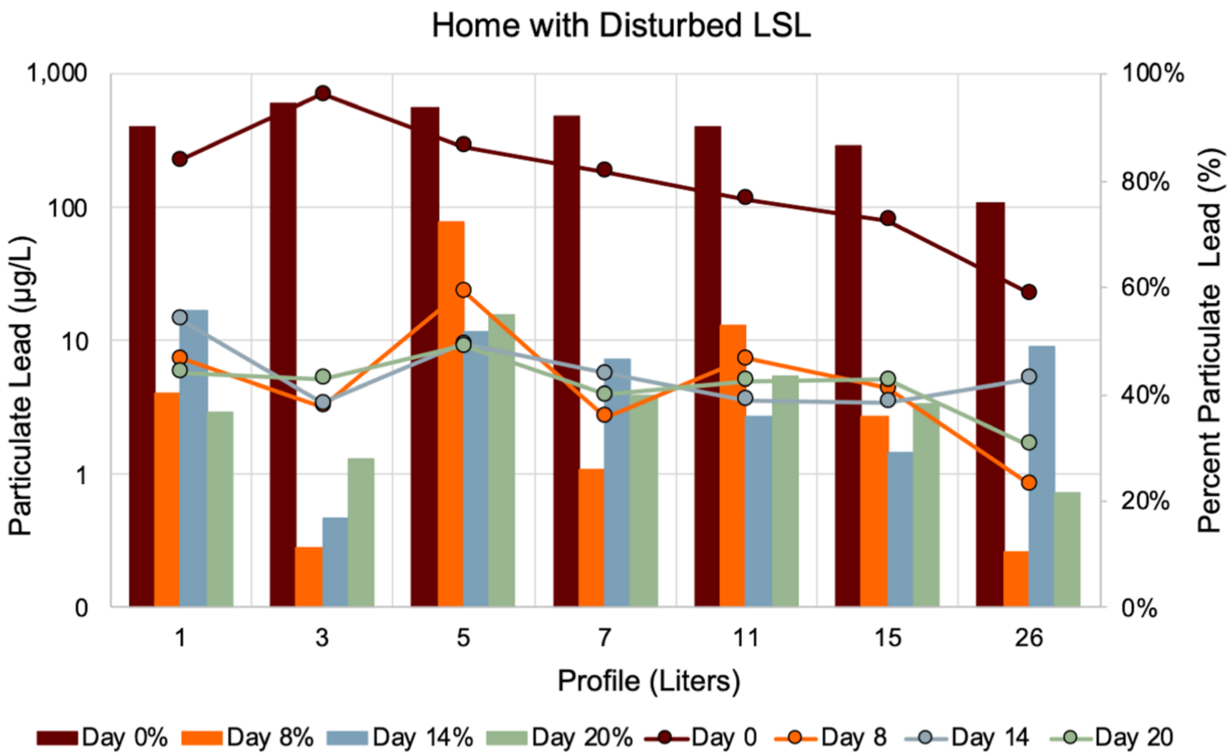


Figure C4. Home with Disturbed LSL– Particulate Lead (concentration and percentage)

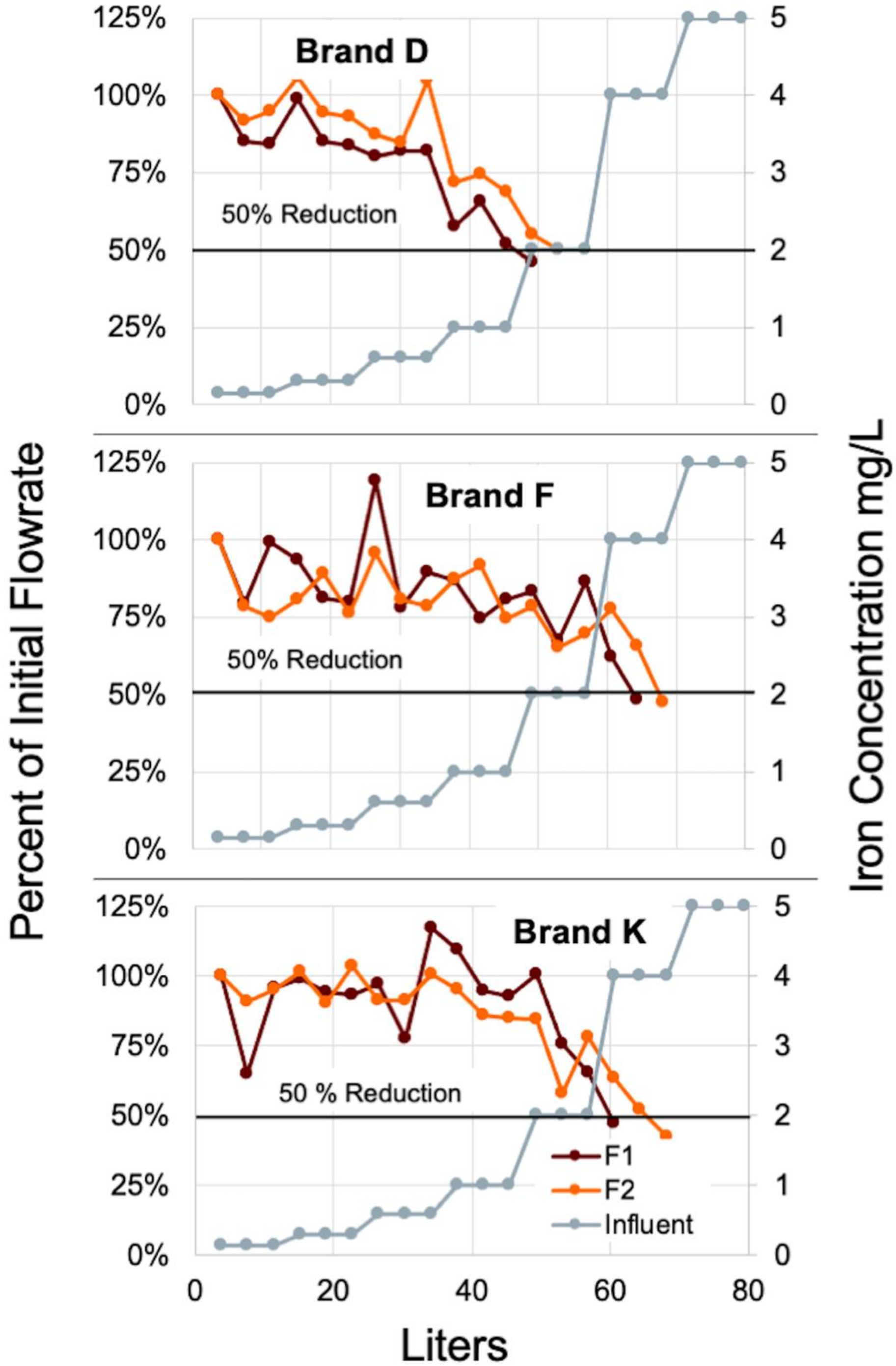


Figure C5. Filter Clogging for 3 faucet filter brands

Table C1. Residential Unfiltered and Filtered water data in Enterprise (ELA) and New Orleans (NOLA), LA

	Metal	Min (μg/L)	1st Qu. (μg/L)	Median (μg/L)	Mean (μg/L)	3rd Qu. (μg/L)	Max (μg/L)	n
ELA	Pb – UF	0.1	0.1	1.0	7.0	7.9	86.0	88
	Pb – F	0.1	0.1	0.1	0.2	0.1	2.9	88
	Fe – UF	15.0	179	383	762	587	19700	88
	Fe – F	5.0	5.0	5.0	8.8	5.0	171	88
	Mn – UF	5.6	67.2	106	142	162	917	87
	Mn – F	0.2	1.8	5.1	18.1	21.2	180	87
NOLA	Pb – UF	0.1	0.9	2.0	2.3	3.2	22.0	77
	Pb – F	0.1	0.1	0.1	0.1	0.1	0.8	77
	Fe – UF	5.0	5.0	5.0	7.6	7.1	57.3	77
	Fe – F	5.0	5.0	5.0	6.2	5.0	53.7	77
	Mn – UF	0.1	0.4	0.6	0.6	0.9	1.3	77
	Mn – F	0.1	0.1	0.2	0.6	0.2	19.1	77

Table C2. Residential Sampling filter performance by home in Enterprise (ELA) and New Orleans (NOLA), LA

Resident		Lead (Pb)			Iron (Fe)			Manganese (Mn)			Filter Life (Weeks)
		Unfiltered (µg/L)	Filtered (µg/L)	Avg Removal	Unfiltered (µg/L)	Filtered (µg/L)	Avg Removal	Unfiltered (µg/L)	Filtered (µg/L)	Avg Removal	
ELA	R1	<0.1 - 1.8	<0.1 - 0.2	90.9	33.9 - 1,150	<0.1 - 17.9	92	5.6 - 280	0.3 - 70.6	77.3	2,3
	R2	0.1 - 18.5	<0.1	99.3	42.0 - 384	<0.1 - 3.0	99.5	35.7 - 102	2.0 - 11.0	90.3	5
	R3	0.1 - 2.3	<0.1 - 0.2	79.7	62.3 - 1,230	0.5 - 6.7	98.6	25.1 - 376	1.6 - 11.3	82.3	6
	R4	<0.1 - 2.0	<0.1	100	15.0 - 2,650	<0.1 - 1.6	98.6	7.2 - 554	1.2 - 27.2	72.4	2,4,1
	R5	0.5 - 41.8	<0.1 - 0.1	98.3	89.4 - 1,210	<0.1 - 6.3	99.5	58.3 - 204	0.7 - 23.6	93.3	5,2
	R6	0.1 - 0.5	<0.1	100	377.0 - 3,270	3.9 - 8.1	98.7	83.1 - 860	2.8 - 43.7	77.4	5
	R7	10.6 - 38.6	<0.1 - 0.2	99.6	151.7 - 699	1.3 - 9.9	98.8	72.4 - 139	2.3 - 8. 0	93.8	6
	R8	0.2 - 86.0	<0.1 - 0.1	91.3	161 - 19,700	<0.1 - 171	99.2	28.7 - 917	0.2 - 25.2	96.2	1,3,2
	R9	<0.1 - 4.4	0.1 - 0.4	-	59.6 - 613	1.3 - 111. 1	91.9	136.0 - 260	99.4- 180.2	23.2	4
	R11	0.1- 10.3	<0.1 - 0.1	79.4	188 - 455	<0.1 - 6.9	98.8	42.9 - 146	2.2 - 89.1	44.7	6
	R12	0.1 - 1.8	<0.1	100	311- 836	<0.1 - 2.2	99.8	86.6 - 275	1.3 - 51.2	81.7	8
	R13	0.1 - 12.2	<0.1 - 0.2	99.7	159- 453	<0.1 - 6.9	99.5	45.1 - 202	1.5 - 5.7	96.2	8
	R14	<0.1 - 4.2	<0.1 - 0.1	99.7	155 - 632	<0.1 - 8.5	98.9	22.8 - 161	0.8 - 2.7	98.1	4
NOLA	R1	1.4 - 2.8	<0.1 - 0.4	97.4	<0.1 - 33.7	<0.1 - 53.7	-	0.6 - 1.3	0.1 - 1.1	54.3	9
	R2	<0.1 - 6.4	<0.1	100	<0.1 - 1.9	<0.1 - 29.5	-	0.2 - 0.8	0.1 - 0.4	74.9	10
	R3	3.3 - 22.0	<0.1 - 0.1	99.6	<0.1 - 1.7	<0.1 - 0.2	100	0.1	0.1 - 0.2	-	10
	R6	0.6 - 2.7	<0.1 - 0.3	97.5	<0.1 - 57.3	<0.1 - 2.5	96.2	0.3 - 0.7	0.2 - 0.5	55	12
	R11	0.9 - 1.0	<0.1 - 0.1	98.4	2.8 - 7.0	2.1 - 5.2	25.1	0.5 - 1.1	0.1 - 0.3	74.9	5
	R12	1.5- 3.2	<0.1 - 0.1	99.2	0.1 - 27.4	3.1 - 9.8	45.8	0.5 - 1.3	0.1 - 1.2	65.8	8
	R13	0.1 - 1.9	<0.1	94.2	6.6 - 56.4	4.7 - 5.7	28.6	0.4 - 2.3	0.2 - 0.7	45.5	5
	R14	2.7 - 6.1	<0.1 - 0.8	96.6	2.4 - 9.9	3.5 - 7.5	7.6	0.4 - 1.1	0.1 - 19.1	-	12

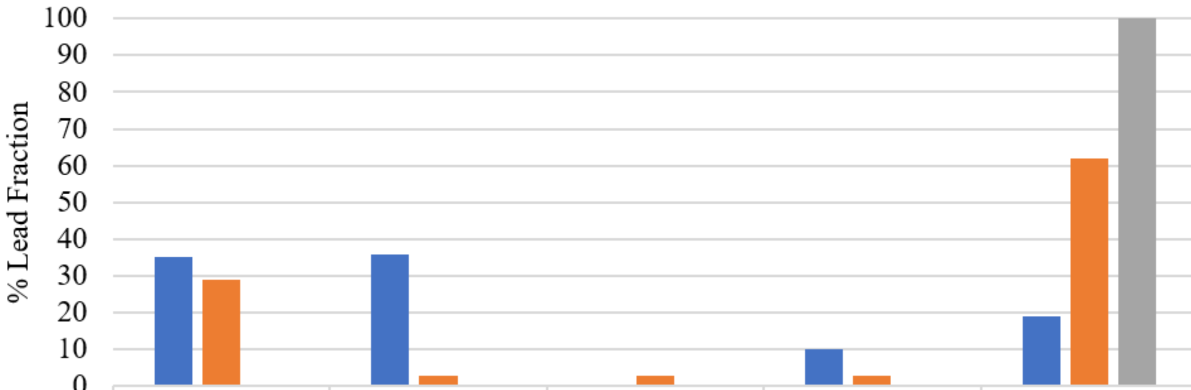
APPENDIX D: CHAPTER 5 – SUPPLEMENTAL INFORMATION

Table D1. Characteristics of the Pitcher Filter

					NSF/ANSI-53 Health Effects- % Reduction From 150 ppb	
Brand	Filter Media Type	Filter Conditioning Requirement	Filter Capacity (Gallons)	Filter Cartridge Bed Volume (mL)	pH 6.5	pH 8.5
A	Coarse filter screen, foam media distributor, activated carbon, oxidation reduction alloy, dual cation/anion exchange resin and non-woven membrane	None- filtered are rinsed before they are sealed	15	60	99.70%	99%

Table D2. Targeted water quality parameters for this study's challenge water relative to the NSF/ ANSI-53 test water

Water	Total Pb (μg/L)	pH	Alkalinity (mg CaCO3/L)	Total PO4 (mg PO4/ L)
Fresh Lead Phosphate Nanoparticle Water	100	7.5	28	3
NYC	44.3	7.38	17.6	2.4
RP	10,000	7.5	0	0



	Pb<0.1 um	0.1<Pb<0.2 um	0.2um<Pb<1.2	1.2<Pb<5 um	Pb> 5 um
LW	35	36	0	10	19
NYC	29	3	3	3	62
RP	0	0	0	0	100

Figure D1. Percent lead size fraction of challenge waters

Table D3. Zeta Potential of challenge suspensions and resins

Water	**Zeta Potential (mV)**
Lytle Water	-30.9 ± 0.04 (n=2)
NYC	-29.7 ± 23.9 (n=11)
RP	-36.1 ± 13.6 (n=12)
Resin Type	**Zeta Potential (mV)**
H+ IX	-36.6 ± 10.6 (n=16)
OH- IX	30.7 ± 5.94 (n=16)
Na+ IX	-31.7 ± 4.6 (n=50)
Cl- IX	35.7 ± 5.94 (n=16)

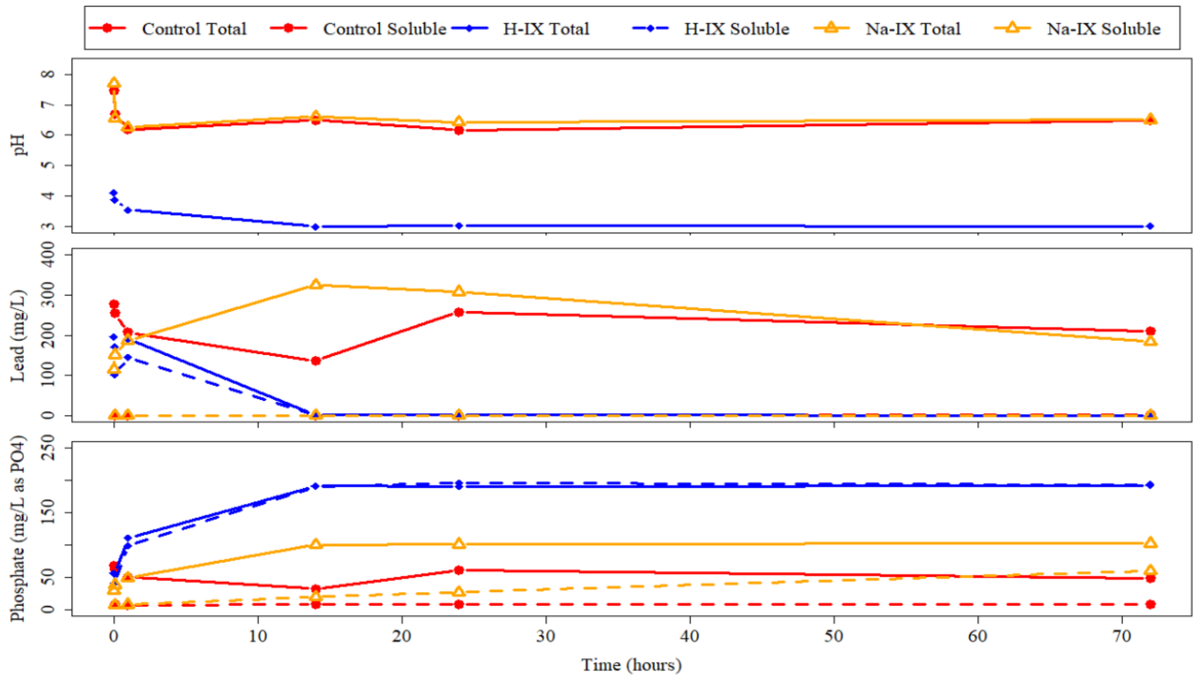


Figure D2. Total and soluble Pb as a function of time for RP suspensions.

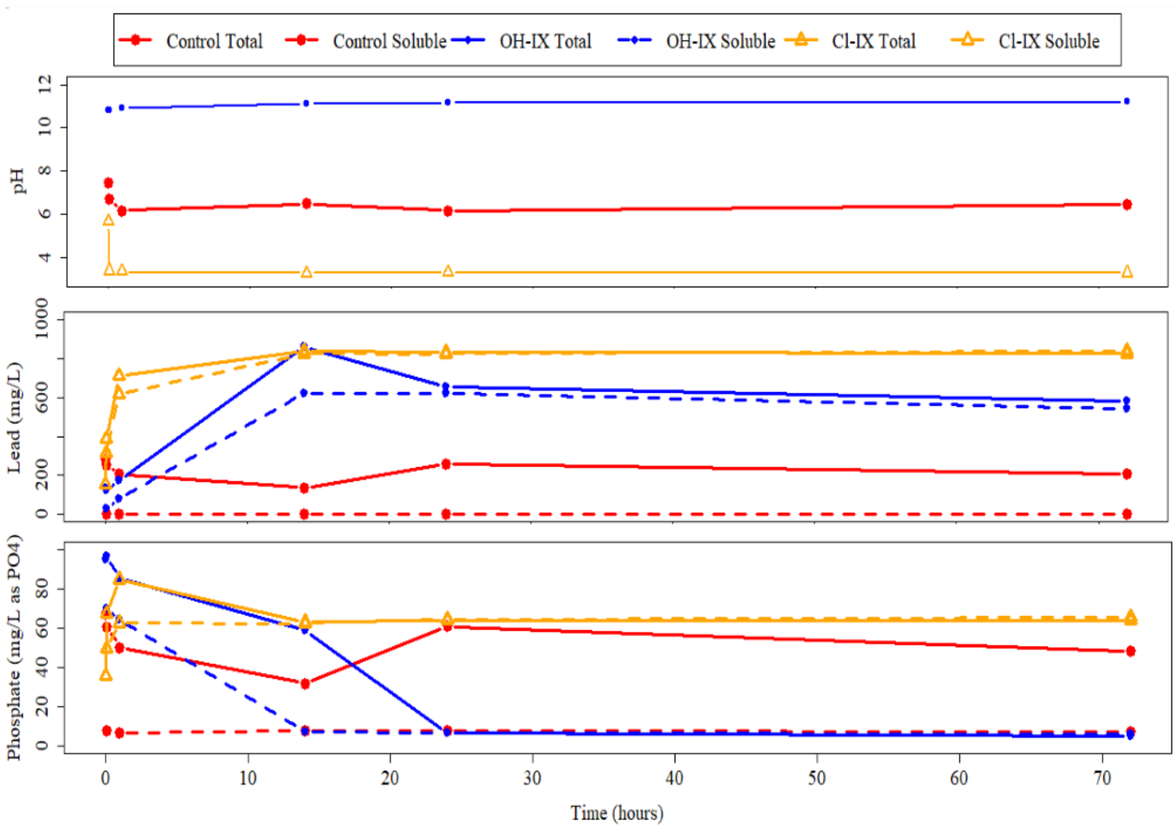


Figure D3. Total and soluble PO4 as a function of time for RP suspensions.

Table D4. Effluent pH for batch beaker tests

Suspension	t=0	t=5 min	t=1h	t=14 h	t=1 day	t=3 day
RP Control	7.46	6.7	6.18	6.49	6.17	6.48
RP H-IX	4.1	3.88	3.54	2.99	3.02	3.01
RP Na-IX	7.7	6.56	6.26	6.62	6.43	6.51
RP OH-IX	10.85	10.82	10.92	11.14	11.18	11.21
RP Cl-IX	5.68	3.39	3.37	3.27	3.3	3.29
LW Control	7.51	7.04	6.89	8.24	7.73	7.85
LW H-IX	4.07	3.9	3.26	3.09	3.07	3.12
LW Na-IX	7.66	6.52	6.89	6.91	6.78	6.83
LW OH-IX	10.85	10.79	11.05	11.18	11.21	11.14
LW Cl-IX	5.73	3.51	3.4	3.28	3.32	3.39

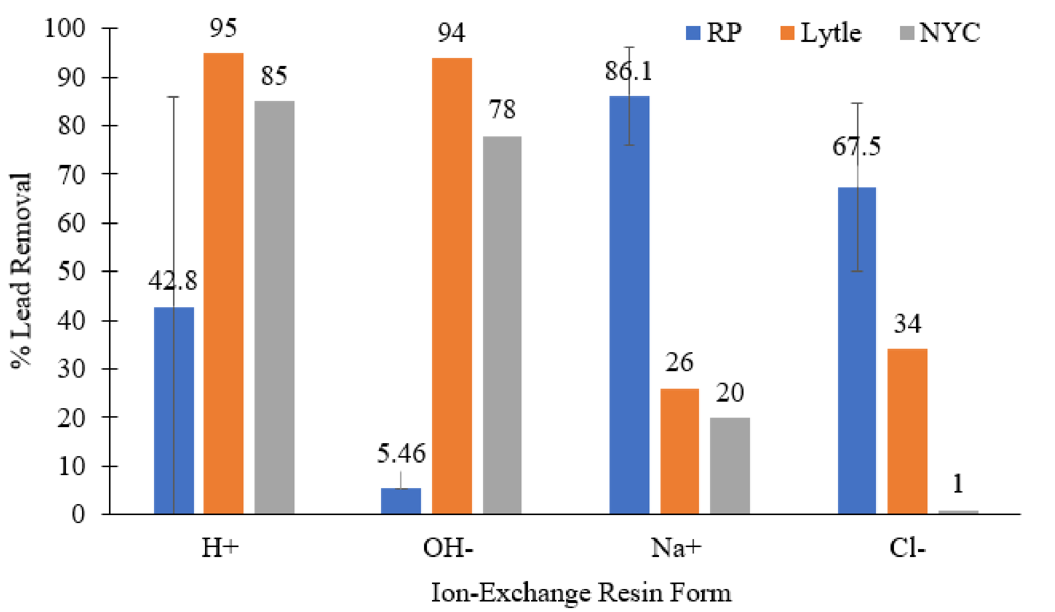


Figure D4. Lead particle removal achieved by each ion-exchange resin after 10 passes. Error bars represent 95% confidence intervals.

Table D5. Effluent pH for historic lead release NYC TW water used. Cation IX were whacked while filtering suspensions to release any loose particles stuck in resin

Ion-Exchange Resin	Initial pH	First Draw pH	Fifth Draw	Tenth Draw
H-IX	7.48	3.37	3.26	3.27
OH-IX	7.54	10.93	11.02	10.65
Na-IX	7.54	7.67	7.3	7.21
Cl-IX	7.53	7.4	7.36	7.36