

Lead and Copper Contamination in Potable Water: Impacts of Redox Gradients, Water Age, Water Main Pipe Materials and Temperature

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ABSTRACT

Potable water can become contaminated with lead and copper due to the corrosion of pipes, faucets, and fixtures. The US Environmental Protection Agency Lead and Copper Rule (LCR) is intended to target sampling at high-risk sites to help protect public health by minimizing lead and copper levels in drinking water. The LCR is currently under revision with a goal of better crafting sampling protocols to protect public health. This study examined an array of factors that determine the location and timing of “high-risk” in the context of sampling site selection and consumer health risks. This was done using field studies and well-controlled laboratory experiments.

A pilot-scale simulated distribution system (SDS) was used to examine the complex relationship between disinfectant type (free chlorine and chloramine), water age (0-10.2 days), and pipe main material (PVC, cement, and iron). Redox gradients developed in the distribution system as controlled by water age and pipe material, which affected the microbiology and chemistry of the water delivered to consumer homes. Free chlorine disinfectant was the most stable in the presence of PVC while chloramine was most stable in the presence of cement. At shorter water ages where disinfectant residuals were present, chlorine tended to cause as much as 4 times more iron corrosion when compared to chloramine. However, the worst localized attack on iron materials occurred at high water age in the system with chloramine. It was hypothesized that this was due to denitrification-a phenomenon relatively unexplored in drinking water distribution systems and documented in this study.

Cumulative chemical and biological changes, such as those documented in the study described above, can create “high-risk” hotspots for elevated lead and copper, with associated concerns for consumer exposure and regulatory monitoring. In both laboratory and field studies, trends in lead and copper release were site-specific and ultimately determined by the plumbing material, microbiology and chemistry. In many cases, elevated levels of lead and copper did not co-occur suggesting that, in a revised LCR, these contaminants will have to be sampled separately in order to identify worst case conditions.

Temperature was also examined as a potentially important factor in lead and copper corrosion. Several studies have attributed higher incidence of childhood lead poisoning during the summer to increased soil and dust exposure; however, drinking water may also be a significant contributing factor. In large-scale pipe rigs, total and dissolved lead release was 3-5 times higher during the summer compared to the winter. However, in bench scale studies, higher temperature could increase, decrease, or have no effect on lead release dependent on material and water chemistry. Similarly, in a distribution system served by a centralized treatment plant, lead release from pure lead service lines increased with temperature in some homes but had no correlation in other homes. It is possible that changes throughout the distribution system such as disinfectant residual, iron, or other factors can create scales on pipes at individual homes, which determines the temperature dependency of lead release.

Consumer exposure to lead can also be adversely influenced by the presence of particulate iron. In the case of Providence, RI, a well-intentioned decrease in the finished water pH from 10.3 to 9.7, resulted in an epidemic of red water complaints due to the corrosion of iron mains and a concomitant increase in water lead levels. Complementary bench scale and field studies demonstrated that higher iron in water is sometimes linked to higher lead in water, due to sorption of lead onto the iron particulates.

Finally, one of the most significant emerging challenges associated with evaluating corrosion control and consumer exposure, is the variability in lead and copper during sampling due to semi-random detachment of lead particles to water, which can pose an acute health concern. Well-controlled test rigs were used to characterize the variability in lead and copper release and compared to consumer sampling during the LCR. The variability due to semi-random particulate detachment, is equal to the typical variability observed in LCR sampling, suggesting that this inherent variability is much more important than other common sources including customer error, customer failure to follow sampling instructions or long stagnation times. While instructing consumers to collect samples at low flow rates reduces variability, it will fail to detect elevated lead from many hazardous taps. Moreover, collecting a single sample to characterize health risks from a given tap, are not adequately protective to consumers in homes with lead plumbing, in an era when corrosion control has reduced the presence of soluble lead in water. Future EPA monitoring and public education should be changed to address this concern.

AUTHOR'S PREFACE

The five chapters in this dissertation are arranged as individual manuscripts according to Virginia Tech's specifications and are formatted based on the journal to which it was published or submitted. Each manuscript was produced in collaboration with the student's adviser and other researchers, with intellectual contributions appropriately indicated by authorship or co-authorship.

Chapter 1 examines the interplay between disinfectant type, water age, and pipe material in creating redox gradients that can impact the microbial and chemical water quality that consumers receive. Not only does this work shed light on this interplay, but it also broadens the current understanding of the implications of denitrifying bacteria on aesthetics and corrosion in plumbing systems. This chapter has been published in *Water Research: Masters*, S., H. Wang, A. Pruden, and M. Edwards (2015). Redox Gradients in Distribution Systems Influence Water Quality, Corrosion, and Microbial Ecology. *Water Research*, 68 (1), 140-149.

Chapter 2 extends the results of Chapter 1 by examining how water with varying chemistry and biology throughout a distribution system, may affect corrosivity and regulatory compliance with lead and copper action levels. The results confirmed reasonable expectations that the risk of elevated lead and copper can vary dramatically throughout the distribution system. Future lead and copper sampling programs should consider this when identifying "worst case" homes for compliance sampling. This chapter has been submitted to *Environmental Monitoring and Assessment*.

Chapter 3 explores the case of increased lead corrosion and consumer red water complaints in Providence, RI after the finished water pH was decreased from ~10.3 to ~9.7. Bench scale tests were able to successfully predict that a decrease in the finished water pH would have resulted in an increase in lead release, and that the higher iron would increase problems with elevated lead in water. Complementary field studies also demonstrated that lead corrosion control is sometimes strongly linked to the corrosion of iron mains. This chapter has been published in *Environmental Engineering Science: Masters*, S., and M. Edwards (2015). Increased Lead in Water Associated with Iron Corrosion. *Environmental Engineering Science*, (In Press).

Chapter 4 investigated the effect of seasonal variations in temperature on lead release. This study adds to the growing body of work indicating that, in addition to soil and paint, drinking water may also be a significant contributing factor to incidence of childhood lead poisoning or elevated blood lead during the summer months. This chapter will be submitted to *Environmental Monitoring and Assessment*.

Finally, Chapter 5 characterizes the variability associated with lead and copper sampling and implications for hazard identification, risk assessment and monitoring of corrosion control. This chapter will be submitted for publication in *Environmental Monitoring and Assessment*.

In addition to the five chapters included in this dissertation, the overall body of the PhD research work includes several other manuscripts not included in this dissertation research as follows:

Published Manuscripts

- Clark, B., S. Masters, M. Edwards (2014). Profile Sampling to Characterizes Particulate Lead Risks in Potable Water. *Environmental Science and Technology*, 48(12), 6836-6843.
- Wang, H., S. Masters, M. Edwards, J. Falkinham III, and A. Pruden (2014). Controlling the Drinking Water Microbiome: Effect of Disinfectant, Water Age, and Pipe Materials. *Environmental Science and Technology*, 48(3), 1426-1435.
- Wang, H., S. Masters, Y. Hong, J. Stallings, J. Falkinham III, M. Edwards, and A. Pruden. (2012). Effect of Disinfectant, Water Age, and Pipe Material on Occurrence and Persistence of *Legionella*, *Mycobacteria*, *Pseudomonas aeruginosa*, and two amoebas. *Environmental Science and Technology*, 46(21), 11566-11574.

Manuscripts in Review

- Clark, B., S. Masters and M. Edwards. Lead Release to Drinking Water from Galvanized Steel Pipe Coating. *Environmental Engineering Science*, (In Review).
- Wang, H., S. Masters, J. Falkinham III, M. Edwards, and A. Pruden. Spatial and temporal variations in simulated distribution system water quality affect regrowth potential of opportunistic pathogens in premise plumbing. *Environmental Science and Technology*, (In Review).

Manuscripts in Preparation

- Martin, A., S. Masters, H. Wang, A. Pruden and M. Edwards. Assimilable Organic Carbon Generation in Premise and Main Plumbing. *Environmental Engineering Science*, (In Preparation).

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LIST OF CONTENTS

Chapter 1. REDOX GRADIENTS IN DISTRIBUTION SYSTEMS INFLUENCE WATER QUALITY, CORROSION, AND MICROBIAL ECOLOGY.....	1
ABSTRACT.....	1
INTRODUCTION	2
MATERIALS AND METHODS.....	3
<i>Simulated Drinking Water Distribution Systems (SDSs)</i>	3
<i>Water Quality Parameters</i>	4
<i>Microbial Analyses</i>	5
<i>Statistical Analyses</i>	5
RESULTS AND DISCUSSION	5
<i>Chemistry and Redox Gradients</i>	5
<i>Drinking Water Infrastructure</i>	10
DISCUSSION.....	13
<i>Water Chemistry and Microbial Growth</i>	13
<i>Impact of Redox Gradients on Drinking Water Infrastructure</i>	14
CONCLUSIONS.....	16
ACKNOWLEDGEMENTS	16
REFERENCES	16
APPENDIX A.....	21
Chapter 2. DISTRIBUTION SYSTEM WATER AGE CAN CREATE PREMISE PLUMBING CORROSION HOTSPOTS.....	28
ABSTRACT.....	28
INTRODUCTION	29
MATERIALS AND METHODS.....	31
<i>Simulated Distribution System (SDS)</i>	31
<i>Corrosion Evaluation Rig (CER)</i>	32
<i>Statistical Analyses</i>	33
RESULTS AND DISCUSSION.....	34
<i>Simulated Distribution System (SDS)</i>	34
<i>Pipe Main Material and Water Age Effect on Metal Release</i>	35
<i>Corrosion Evaluation Rig (CER) Field Study</i>	38
<i>Impact of Treatment Process on Metals Release</i>	44
<i>Sample Site Selection Criteria</i>	44
CONCLUSIONS.....	45
ACKNOWLEDGEMENTS	45
REFERENCES	45
APPENDIX B	53
Chapter 3. INCREASED LEAD IN WATER ASSOCIATED WITH IRON CORROSION	57
ABSTRACT.....	57
INTRODUCTION	58
MATERIALS AND METHODS.....	60
<i>Profile Sampling</i>	60
<i>Sample Analysis</i>	61
<i>Bench Scale Testing</i>	61

<i>Phase 1: Effects of pH on iron corrosion</i>	61
<i>Phase 2: Impact of Iron on Lead Corrosion</i>	62
<i>Phase 2a: Conditioning of Lead Pipes</i>	62
<i>Phase 2b: Exposure of Lead Pipes to Iron Particulates</i>	62
<i>Statistical Analysis of Results</i>	62
RESULTS AND DISCUSSION	63
<i>Bench Scale Testing</i>	63
<i>Profile Sampling</i>	66
CONCLUSIONS	69
<i>Bench Scale</i>	69
<i>Profile and Utility Sampling</i>	69
ACKNOWLEDGEMENTS	69
REFERENCES	70
APPENDIX C	74
Chapter 4. SEASONAL VARIATIONS IN TEMPERATURE INFLUENCE LEAD RELEASE	82
ABSTRACT	82
INTRODUCTION	83
MATERIALS AND METHODS	84
<i>Lead Mineral Solubility Experiments and Theoretical Model Comparisons</i>	84
<i>Providence Simulated Water Bench Scale Testing</i>	85
<i>Field Sampling: Providence Rhode Island and Washington Aqueduct</i>	85
RESULTS AND DISCUSSION	86
CONCLUSIONS	90
APPENDIX D	97
Chapter 5. INHERENT VARIABILITY OF LEAD AND COPPER CONCENTRATIONS COLLECTED DURING STANDARDIZED SAMPLING	105
ABSTRACT	105
INTRODUCTION	106
MATERIALS AND METHODS	109
<i>Corrosion Evaluation Rigs (CERs)</i>	109
<i>Data Analyses</i>	111
RESULTS	111
<i>Contribution of Particulate Lead to Variability</i>	114
DISCUSSION	118
<i>Practical and Regulatory Implications of Variability and Particulate Lead Release</i>	118
CONCLUSIONS	119
ACKNOWLEDGMENTS	120
REFERENCES	120
APPENDIX E	126

LIST OF FIGURES

Figure 1-1: Schematic of simulated drinking water distribution system (SDS). SDSs consisted of PVC pipe fitted with iron, concrete or PVC coupons in triplicate and receiving chlorine or chloramine disinfectant (18 SDSs total).....	4
Figure 1-2: pH profile as a function of water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent standard error from triplicate pipes.....	6
Figure 1-3: Redox profiles as represented by depletion of oxidizing species (dissolved oxygen and chlorine) in chlorinated simulated drinking water distribution systems with (a) PVC (b) Cement and (c) Iron pipe materials. Nitrogen species were below detection. Errors bars represent standard error from triplicate pipes.	7
Figure 1-4: Redox profiles as represented by depletion of oxidizing species (dissolved oxygen and chlorine) and shifts in nitrogen species in chloraminated simulated drinking water distribution systems with (a) PVC (b) Cement and (c) Iron pipe materials. Errors bars represent standard error from triplicate pipes. Error bars for nitrite gradient not included since some measurements were close to the detection limit.....	8
Figure 1-5: Gene copy numbers of nosZ, which catalyzes conversion of N ₂ O to N ₂ in some denitrifying bacteria: (a) chlorinated SDS biofilm and (b) chloraminated SDS biofilm. Errors bars represent standard error from triplicate pipes.	9
Figure 1-6: Average weight change for iron coupons in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent standard error from triplicate pipes.....	11
Figure 1-7: Pitting corrosion in chloraminated system.....	12
Figure 1-8: Comparison of pitting corrosion rate in chlorinated and chloraminated iron SDSs. Each dot represents an individual pit.....	12
Figure A1: Photograph illustrating design of simulated distribution system (SDS).....	26
Figure A2: Iron release as a function of water age in the chlorinated and chloraminated Iron-PVC systems. Error bars represent 95% confidence intervals from weekly composite samples from each triplicates collected over 10 weeks (<i>n</i> =30).....	26
Figure A3: Change in calcium concentration in (a) chlorinated and (b) chloraminated simulated distribution systems. Error bars represent 95% confidence intervals from weekly composite samples from each triplicates collected over 10 weeks (<i>n</i> =30).....	27
Figure A4: Change in magnesium concentration in (a) chlorinated and (b) chloraminated simulated distribution systems. Error bars represent 95% confidence intervals from weekly composite samples from each triplicates collected over 10 weeks (<i>n</i> =30).....	27
Figure 2-1. Schematic of simulated drinking water distribution system (SDS) and transfer of water to premise plumbing batch reactors. SDSs consisted of PVC pipe fitted with iron, concrete or PVC coupons in triplicate and receiving chlorine or chloramine disinfectant (18 SDSs total).....	32

Figure 2-2: Copper release from copper with lead solder coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.....	37
Figure 2-3: Lead release from brass coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.....	38
Figure 2-4: Influence of water age on copper release from (a) copper with lead solder (b) lead-copper and (c) brass test rigs at 5 utilities. Error bars represent 95% confidence intervals where n is between 33 and 36.	42
Figure 2-5. Influence of water age on lead release from (a) copper with lead solder (b) lead-copper and (c) brass test rigs at 5 utilities. Error bars represent 95% confidence intervals where n is between 33 and 36.	43
Figure B1. Copper release from brass coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.....	54
Figure B2. Lead release from copper with lead solder coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.....	54
Figure B3. Lead release from lead coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 3.....	54
Figure 3-1: Providence, RI, Lead and Copper Rule compliance between 1997 and 2014. Beginning in 2006, after lowering pH from 10.3 to 9.7, there was a significant increase in the 90 th percentile lead levels.....	60
Figure 3-2: Average iron concentration after iron release stabilized (weeks 6-24). Error bars represent 95% confidence intervals.	63
Figure 3-3: Comparison of representative coupons at (a) pH 8.3 and (b) pH 10.3.	64
Figure 3-4: Average lead concentration after lead release stabilized (week 6-24). Error bars represent 95% confidence intervals.	65
Figure 3-5: Cumulative mass of soluble and particulate lead in triplicate samples (week 20 and 25).	65
Figure 3-6: Relationship between iron and lead.	66
Figure 3-7: Stacked bar chart comparing the average soluble and particulate lead at low, moderate, and high flow rates for representative sites.....	68
Figure C1: Illustration of sequential profile water sampling collected in each home. One-liter water samples were successively collected at low, moderate, and high flow after at least 6 hours of stagnation.....	79
Figure C2: Mixed water from batch reactors with and without iron coupon (control) from Phase 1 were transferred to Pb pipes in Phase 2.....	79

Figure C4: Correlation between particulate lead and particulate iron in bench scale test (Week 20 & 25).....	80
Figure C5: Relationship between iron and lead at a) moderate and b) high flow at Site B.....	81
Figure 4-1: Dissolution of lead carbonate, lead oxide, chloropyromorphite and lead orthophosphate.....	87
Figure 4-2: Seasonal variation in temperature and average lead in the Washington Aqueduct pipe loop study and one of the houses in the Providence, RI, field sampling.....	88
Figure D1. Seasonal variation in temperature and average dissolved lead in the Washington Aqueduct pipe loop study.....	102
Figure D2. Average total lead release from triplicate pipes.....	103
Figure D3. Average soluble lead release from triplicate pipes.....	104
Figure 5-1 Corroded Pb ²⁺ can contaminate potable water or attach to pipes, creating an accumulating rust layer which can be detached by hydraulic disturbances or high flow conditions.....	108
Figure 5-2 Average RSD from Individual LCR Sampling Sites at Three Participating Utilities. Only sites that were sampled three or more times are included in this analysis. ‘n’ indicates the total number of LCR sites that were sampled at least three times.....	112
Figure 5-3 Average monthly RSD for (a) copper and (b) lead for Corrosion Evaluation Rigs. Horizontal black bar indicates average RSD for all utilities (WTP = water treatment plant; DS = distribution system).....	113
Figure 5-4 Lead data for lead-copper test pieces at the WTP and DS for utility A (modified from Parks et al. (2014)).....	115
Figure 5-5 Average percent particulate lead and RSD from lead-copper samples for three threshold ranges at (a) all utilities, (b) Utility A and (c) Utility B.....	116
Figure 5-6 Impact of sample flow rate on lead release from (a) brass, (b) copper-solder, and (c) lead copper test pieces.	117
Figure E1 Lead and copper concentration for (a) brass, (b) copper with solder and (c) copper-lead pipe pretest coupons.....	127
Figure E2 Corrosion evaluation rig.....	128

LIST OF TABLES

Table A1: Key drinking water quality parameters in Blacksburg tap water	22
Table A2: Physiochemical parameters in chlorinated SDS (\pm standard deviation).....	22
Table A3: Physiochemical parameters in chloraminated SDS (\pm standard deviation).....	23
Table A4: Average percent weight change (\pm 95% confidence intervals).....	23
Table A5: Comparison of percent weight loss in chlorinated and chloraminated at a given water age (p-values based on non-parametric Kruskal-Wallis test).....	24
Table A6: Summary of pitting corrosion in chlorinated and chloraminated DWDSs.....	25
Table 2-1. Water quality issues associated with water age and their concomitant impact on lead and copper corrosion.....	30
Table 2-2. Summary of characteristics of drinking water utilities.....	33
Table 2-3. Physiochemical parameters in the SDSs (\pm standard deviation).....	34
Table 2-4. Summary of Statistical Analyses from Simulated Distribution Systems.....	36
Table 2-5. Comparison of water quality parameters of drinking water utilities (\pm standard deviation).	40
Table 2-6. Summary of statistical analyses from Corrosion Evaluation Rigs.....	41
Table B1. Comparison of average lead and copper release between Utilities C and D.....	56
Table 3-1. Cumulative mass of soluble and particulate lead in triplicate samples (Week 25).	65
Table C1: Providence finished water quality Pre (2011) and Post (2013) pH increase to ~10.3..	75
Table C2: Synthetic Providence water recipe (modified from Wang et a. 2012).....	75
Table C3: Elemental composition of iron coupon.....	75
Table C4: Summary of lead and iron concentration from profile sampling.....	76
Table C5: Ratio of particulate lead to particulate iron in 3 rd and 5 th liter profile samples.....	78
Table C6: Average soluble and particulate lead in 3 rd and 5 th liter profile samples.....	78
Table 4-1. Change in soluble lead concentration with temperature.....	87
Table 4-2. Correlation (Spearman's Rho) between temperature and lead release from the service line and copper from first draw samples.....	89
Table D1. Synthetic Providence water recipe.....	98
Table D2. Summary of sample site characteristics.....	98
Table D3. Providence finished water quality.....	99
Table D4. Summary of Washington Aqueduct water quality.....	99
Table D5. Change in lead concentration with temperature (bold indicates statistical significance at the 95% confidence level).....	100

Table D6. Comparison of average lead and copper at each site during the summer and winter (bold and italics indicates a statistically significant difference at the 95% confidence level).....	101
Table 5-1. Summary of Sources of Lead and Copper Variability and How a Pipe Rig Can Minimize These With Respect to Consumer Home Sampling	107
Table 5-2. Summary of RSD Data for Homes from Selected Cities Evaluated by Marcus et al. (1990).....	109
Table 5-3. Summary of Lead and Copper LCR Results from Five Participating Utilities	111
Table E1 Summary of Lead and Copper Statistics for the Carefully Constructed Test Pieces...	129
Table E2 Summary of characteristics of drinking water utilities.....	130
Table E3 Comparison of water quality parameters of drinking water utilities (\pm standard deviation).....	131
Table E4 Summary of Average RSD at each Utility.....	132

CHAPTER 1. REDOX GRADIENTS IN DISTRIBUTION SYSTEMS INFLUENCE WATER QUALITY, CORROSION, AND MICROBIAL ECOLOGY

Sheldon Masters, Hong Wang, Amy Pruden, and Marc A. Edwards

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ABSTRACT

Simulated distribution systems (SDSs) defined the interplay between disinfectant type (free chlorine and chloramines), water age (1 - 10.2 days), and pipe material (PVC, iron and cement surfaces) on water chemistry, redox zones and infrastructure degradation. Redox gradients developed as a function of water age and pipe material affected the quality of water consumers would receive. Free chlorine was most stable in the presence of PVC while chloramine was most stable in the presence of cement. At a 3.6 day water age the residual in the chlorinated PVC SDS was more than 3.5 times higher than in the chlorinated iron or cement systems. In contrast, the residual in the chloraminated cement SDS was more than 10 times greater than in the chloraminated iron or PVC systems. Near the point of entry to the SDSs where disinfectant residuals were present, free chlorine tended to cause as much as 4 times more iron corrosion when compared to chloramines. Facultative denitrifying bacteria were ubiquitous, and caused complete loss of nitrogen at distal points in systems with iron, and these bacteria co-occurred with very severe pitting attack (1.6-1.9 mm/year) at high water age.

KEYWORDS: Distribution system, disinfectant, cement, PVC, iron, denitrification

INTRODUCTION

Properly operated and maintained distribution systems protect public health (Committee on Public Water Supply Distribution Systems, 2005) and deliver safe, pressurized, non-corrosive and aesthetically pleasing drinking water to consumers. However, distribution systems can also be thought of as complex biological and chemical reactors (Awwa Research Foundation, 2007) in which deficiencies including disinfectant decay, long detention times, corrosion, and microbial activity can deteriorate the quality of water delivered to consumers (U.S. Environmental Protection Agency, 2002a; Zhang et al., 2009; Nguyen et al., 2011).

The type of pipe material and disinfectant stability play a critical role in maintaining drinking water quality (Hallam et al., 2002; Clark and Haught, 2005; Tamminen et al., 2008; Munavalli et al., 2009; Clark, 2011). Drinking water distribution system pipes in the U.S. are typically cementitious (concrete, asbestos cement, or cement-mortar lined), plastic (polyvinyl chloride, chlorinated polyvinyl chloride or high density polyethylene) or lined or unlined iron (cast, ductile, or steel) (Tombouliau et al., 2004; Folkman et al., 2012; Tang et al., 2013). Each pipe material can be categorized as having relatively high (e.g., unlined iron mains) or low (PVC, medium-density polyethylene, or cement-lined pipes) chemical reactivity to disinfectants (Hallam et al., 2002). Leaching of free lime from the cement can cause significant increases in pH, calcium, hardness and alkalinity, especially in long pipelines or parts of the distribution system with low flow regions in poorly buffered water (Byfors et al., 1986; Douglas et al., 1996; Leroy et al., 1996; American Water Works Association, 1999; Berend and Trouwborst, 1999; Bos and Rosenthal, 2000; Taylor et al., 2003; Montgomery Watson Harza, 2005). Bacteria that grow on less reactive pipe surfaces, such as PVC, are often more susceptible to inactivation by free chlorine and monochloramine, while more disinfectant is needed to achieve the same level of microbial inactivation growing on iron surfaces (LeChevallier et al., 1990; Zhang et al., 2009).

Chlorine and chloramines are the most commonly used secondary disinfectants in distribution systems to prevent re-growth of bacteria (Vasconcelos et al., 1997; Jegatheesan et al., 2000; Maier et al., 2000; Vikesland et al., 2001; Munavalli et al., 2009). These disinfectants can dissipate (i.e., decay) with increasing water age, resulting in lower residual disinfectant in distal parts of the distribution system (Lu et al., 1995; DiGiano et al., 2005). However, compared to chlorine, chloramines form fewer regulated disinfectant by-products and are generally more persistent in the distribution system (Neden et al., 1992; Norton and LeChevallier, 1997). Chloramines have also been reported to be more effective than free chlorine at reducing heterotrophic plate counts (HPC) in drinking water systems (Neden et al., 1992). For all of these reasons the use of chloramines as a disinfectant has increased in recent years at U.S. water utilities (Seidel et al., 2005; Nguyen et al., 2011). In some situations; however, use of chloramines can trigger nitrification, which can accelerate chloramine decay. Chloramine decay due to nitrification been associated with adverse effects on metallic corrosion, microbial growth, pH, taste and odor (Zhang et al., 2009).

In contrast to nitrification, the occurrence and impact of denitrification has received relatively little study and detection of denitrifying bacteria has rarely been reported in distribution pipelines (Lee et al., 1980). Generally, denitrifiers are assumed to be essentially irrelevant to potable water systems, residing only deep within iron pipe scale (Zhu et al., 2014). However, one recent study identified denitrifiers at high levels in a building plumbing system that had problems with taste and odors, elevated lead, rapid losses in chloramine disinfectant residuals and higher pH after stagnation (Nguyen et al., 2012). Baron et al. (2014) also quantified a significant increase of genera related to denitrification in a hospital water system following the introduction of on-site monochloramine disinfection. Denitrification requires nitrate or other oxidized nitrogen species as an electron acceptor and also generally thrive under conditions of low dissolved oxygen (DO) and high levels of organic matter (Knowles, 1982; Zumft, 1997; Baribeau, 2006), although some autotrophic denitrifiers can use H₂ as an electron donor (Knowles, 1982; Koch et al., 2014). Kielemoes et al. (2000) and Till et al. (1998) demonstrated a relationship between autotrophic denitrification and accelerated hydrogen evolution associated with iron corrosion in lab-scale reactors. This suggests that similar undesirable reactions might occur in water mains; however, significant denitrification has not been reported in studies of either simulated or full-scale potable water main distribution systems.

The purpose of this study was to characterize the chemical and biological gradients that develop as water passes through water distribution systems. Triplicate simulated distribution systems (SDSs) equipped with PVC, iron and cement surfaces were compared with the goal of defining the interplay between disinfectant type (free chlorine and chloramines), water age (1 - 10.2 days), and pipe material on the water chemistry, redox zones and materials corrosion. Implications for microbial growth, aesthetics and corrosion in building plumbing systems are considered, with particular attention on the potential for denitrifying bacteria to exacerbate such problems.

MATERIALS AND METHODS

Simulated Drinking Water Distribution Systems (SDSs)

SDSs were used to compare two types of disinfectants (chlorine and chloramines) and three types of typical distribution system materials: concrete, cast iron, and polyvinyl chloride (PVC) (Figure 1-1). Each distribution system was examined in triplicate, resulting in 18 total SDSs. The SDSs were constructed by epoxying iron, PVC, and cement coupons into a cumulative length of 158 cm long and placing them inside a 3.8 cm diameter PVC pipe (ASM D1785 Schedule 40). This created a surface:volume ratio of 0.12 cm⁻¹ of coupons per unit volume; which is equivalent to 34.3 cm diameter pipe main. Each sleeve was conditioned by soaking in a pH 12 solution of sodium hydroxide for half an hour to ensure each material had the same starting surface conditions and to simulate higher pH conditions present during shock chlorination (Raetz, 2010). Prior to the operation of the SDS, all systems were disinfected using a 500 mg/L sodium hypochlorite solution in order to satisfy chlorine demand and reduce background microorganisms. Ports in the SDS allowed for sample collection at water ages of approximately 1, 2.3, 3.6, 5.7 and 10.2 days from the point of entry. Five distinct SDS

segments were created using threaded check-valves to reduce back-mixing or short-circuiting (Figure A1). The total volume of each 5 segment SDS was 5.6 L. Water was pumped continuously from a 20 L polyethylene reservoir using a 12-channel low-speed digital peristaltic pump (Ismatec, Vancouver, WA) with a flow rate of 0.40 ± 0.005 mL/min (Reynolds number = 0.25).

TREATED BLACKSBURG

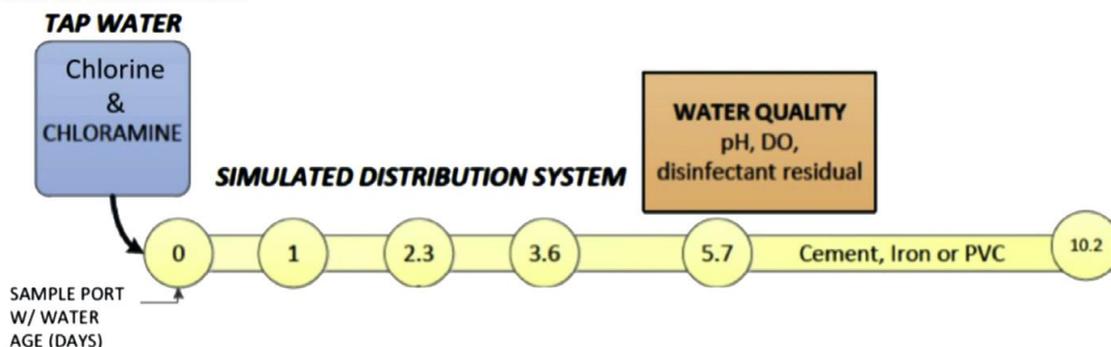


Figure 1-1: Schematic of simulated drinking water distribution system (SDS). SDSs consisted of PVC pipe fitted with iron, concrete or PVC coupons in triplicate and receiving chlorine or chloramine disinfectant (18 SDSs total).

The efficacy of two types of disinfectants was compared in this study using Blacksburg, VA tap water (Table A1). The normal chloramine residual and ammonia was first removed from the water by breakpoint chlorination. Thereafter, a chloramine solution of ~ 4.0 mg/L was made using the procedure outlined in the Standard Methods for the Examination of Water and Wastewater (American Public Health Association et al., 2005) at a pH of ~ 8.0 . For comparison, a ~ 4.0 mg/L solution of free chlorine (pH ~ 8) was used for the other condition. Prior to the exposure of the coupons to the test waters, each sleeve was weighed to the nearest 0.1 mg using an analytical balance. After continuously monitoring and operating all the systems for 15 months, the coupons were removed and air-dried for at least two-weeks. The corrosion scales were then physically removed and the sleeves were reweighed to calculate material weight loss.

Water Quality Parameters

Water quality parameters (i.e., pH, disinfectant concentration and dissolved oxygen (DO)) were measured every 2 weeks. Free chlorine and chloramine were measured using a DR2700 spectrophotometer (HACH, Loveland, CO). DO was measured using an Orion Star DO probe (Thermo Scientific, Beverly, MA) and pH was measured using a pH 110m (Oakton Research, Vernon Hills, IL). Nitrifying and Denitrifying Biological Activity Reaction Tests (BARTs) were used to examine the presence of active nitrifying and denitrifying bacteria. After operating the system for 1-year, weekly composite samples were collected over a 10-week period from each port and analyzed for iron, magnesium and calcium by inductively coupled plasma mass spectrometry (ICP-MS) using Standard Method 3125B (American Public Health Association, 2005).

Microbial Analyses

SDS biofilm samples were taken by swabbing the inner area of the sampling ports. The details of biofilm sampling and DNA extraction procedures were described previously (Wang et al., 2012). Quantitative polymerase chain reaction (q-PCR) was used to enumerate nitrous oxide reductase genes using degenerate primers nosZ1F-nosZ1R as an indicator of denitrifying bacteria (Henry et al., 2006; Nogales et al., 2002; Throbäck et al., 2004). All q-PCR reactions were performed in triplicate on a Bio-Rad CFX96 Real-time thermal cycler in a 10 μ L reaction mixture, which contained 5 μ L of 2 \times SsoFast Evagreen Supermix (Bio-rad), 400 nM each primer, and 1 μ L of DNA template. Negative controls (i.e., sterilized nanopure water) and a 10-fold series dilution of standard DNA (derived from cloned *nosZ1* genes amplified from an environmental sample) were included in each q-PCR run. The thermal cycling conditions were: an initial cycle of 98°C for 2 min; 6 cycles of 98 °C for 5 s, 68 °C for 30 s with a touchdown of 1 °C by cycle, 72 °C for 5 s, and 81 °C for 5 s; 45 cycles of 98 °C for 5 s and 62 °C for 5 s, 81 °C for 8 s; and 1 cycle at 65 °C for 5 s, to 95°C for 5 s. The specificity of the assay was demonstrated by cloning and sequencing q-PCR products from select positive samples (i.e., 2 samples from chloraminated SDSs, two samples from chlorinated SDSs).

Statistical Analyses

A Shapiro-Wilks test was used to assess normality of the data. Analysis of variance (ANOVA) and Kruskal Wallis rank sum test were used to determine the difference between the means of physiochemical parameters based on the normality of the data. Linear regressions were used to determine if various physiochemical parameters increased or decreased in association with water age. Statistical analyses were performed in R (<http://www.r-project.org/>) with significance defined as $p < 0.05$.

RESULTS AND DISCUSSION

Chemistry and Redox Gradients

pH. SDSs with cement had a significantly higher pH than systems with iron or PVC due to the leaching of lime. In the cement SDSs, pH steadily increased by up to 2.1 units with increasing water age while the pH decreased slightly in the chlorinated PVC and iron conditions and by as much as 1.3 units in the chloraminated PVC and iron conditions ($p < 0.05$). The lower pHs in the PVC and iron systems were consistent with increased CO₂ from microbial respiration, as pH dropped without significant changes in alkalinity. In general, the pH values in the chlorinated systems were higher than the chloraminated systems. The lower pH in the chloraminated system is likely due to acid production from nitrification as documented later in this paper. Comparing the cement SDSs, the pH was higher in the chlorinated systems by as much as 1.3 pH units (Figure1-2, Table A2 and A3). Comparing the PVC SDSs, the pH was higher in the chlorinated condition between 1 and 10.2 day water ages by as much as 1 pH unit ($p < 0.05$). A similar trend was also observed in the iron SDS where the pH was lower in the chloraminated system by as much as 0.7 pH units.

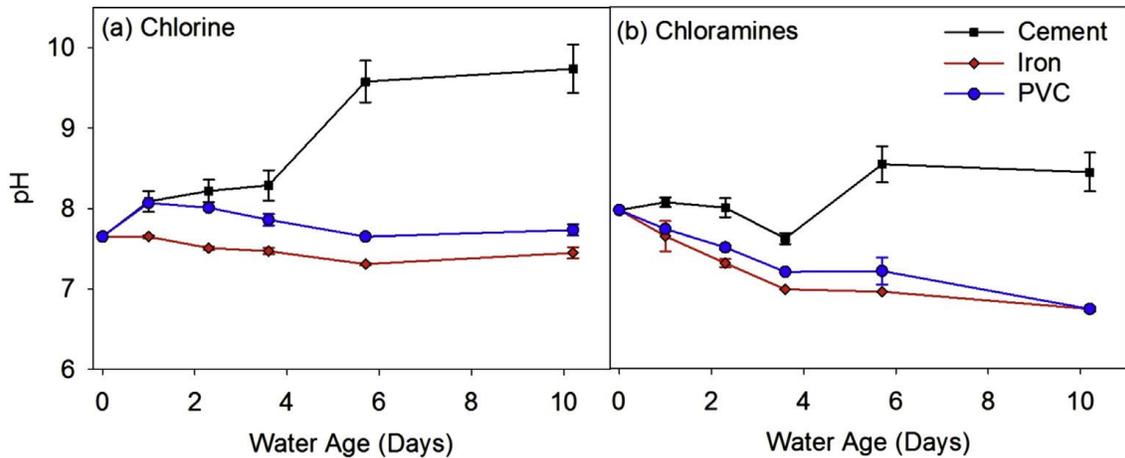


Figure 1-2: pH profile as a function of water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent standard error from triplicate pipes.

Disinfectant. Even though chloramine is known to be more persistent than chlorine, in this work the disinfectant residual decayed faster in the chloraminated system due to nitrification (Figure 1-3 and Figure 1-4). At day 2.3 in the chlorinated SDSs, the residual was 1.5-6.5 times higher in the PVC condition when compared to the cement and iron conditions ($p < 0.05$) (Table A2). At water ages of 3.6 and 5.7 days, the residual in the chlorinated PVC SDS was > 3.5 higher than in the chlorinated iron or cement systems. While PVC was the most inert material in terms of reaction with free chlorine, cement was the least reactive material in terms of reaction with chloramines. At day 3.6, the residual in the chloraminated cement SDS was at least 1.5 times higher than in the chloraminated iron or PVC systems.

Dissolved Oxygen. Dissolved oxygen concentration decreased with increasing water age in all SDSs (Figure 1-3 and Figure 1-4). Between water ages of 1 and 5.7 days, DO levels were lower in the chlorinated cement SDS compared to PVC and iron conditions. There was no difference between the DO in the chloraminated PVC and cement SDSs ($p > 0.05$). DO levels in the iron systems were as much as 75% lower than SDSs with cement or PVC, consistent with oxygen consumption via iron corrosion.

Nitrogen. Characterization of changes in nitrogen species (i.e., ammonia, nitrite, and nitrate) provide insight to redox, nitrification and denitrification. In the chlorinated systems there were no detectable (< 0.2 mg/L) levels of nitrogen species. In the chloraminated iron system, ammonia disappeared at a significantly faster rate when compared to the PVC and cement SDSs ($p < 0.001$) (Figure 1-4 and Table A3). For example, at 5.7 day water age, the ammonia levels in the iron system were 89% and 91% lower than in the cement and PVC SDSs, respectively. In the iron system, ammonia was completely oxidized by a water age of 10.2 days. Ammonia losses co-occurred with higher nitrate and nitrite, consistent with nitrification. Biological Activity Reaction Tests for nitrifying Bacteria (N-BARTs) were used to assay the presence of nitrifying bacteria at 5.7 day water age in all systems, and active nitrifiers were not detectable in the chlorinated systems but were observed in the chloraminated SDSs (~ 1000 cfu/mL).

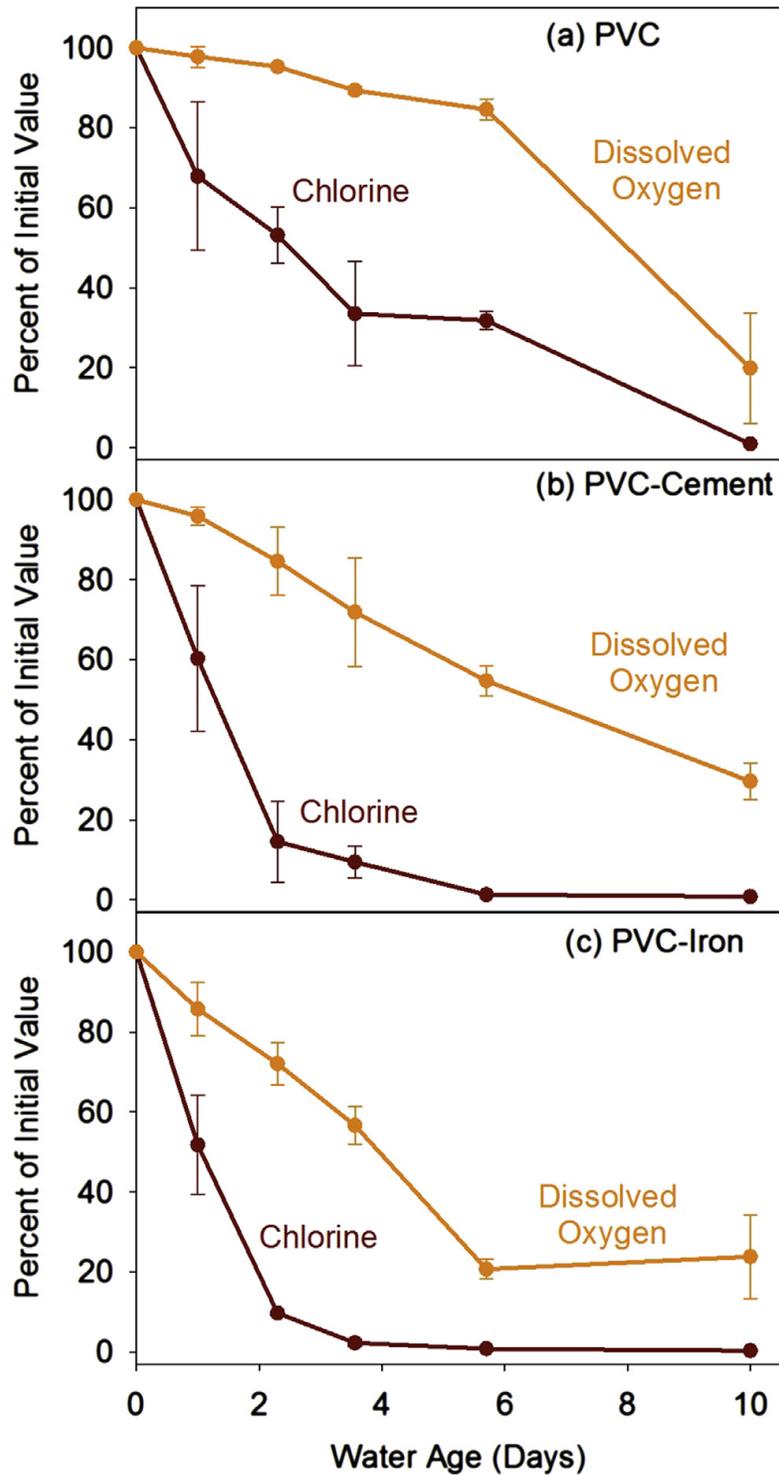


Figure 1-3: Redox profiles as represented by depletion of oxidizing species (dissolved oxygen and chlorine) in chlorinated simulated drinking water distribution systems with (a) PVC (b) Cement and (c) Iron pipe materials. Nitrogen species were below detection. Errors bars represent standard error from triplicate pipes.

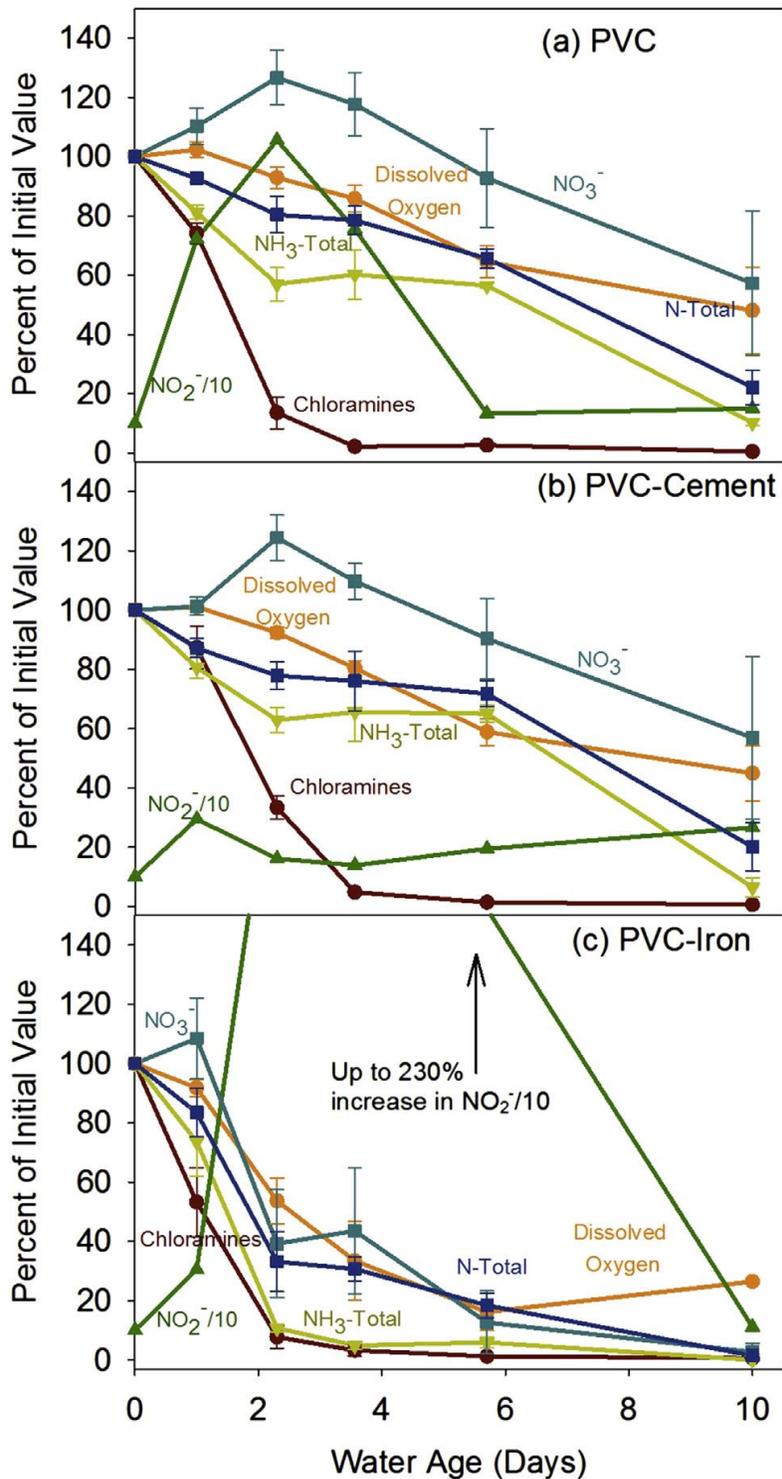


Figure 1-4: Redox profiles as represented by depletion of oxidizing species (dissolved oxygen and chlorine) and shifts in nitrogen species in chloraminated simulated drinking water distribution systems with (a) PVC (b) Cement and (c) Iron pipe materials. Errors bars represent standard error from triplicate pipes. Error bars for nitrite gradient not included since some measurements were close to the detection limit.

There was a trace of nitrite in the water from the feed reservoir (0.012 mg/L), which increased 1.4 to 3 times at water ages of 1-10.2 days in the chloraminated cement system. Nitrite levels peaked at 10.5 times higher than influent values in the PVC system and 23 times higher in the iron system, and decreased as the nitrite was oxidized to nitrate via nitrification. In all chloraminated SDSs, the nitrate concentration and total-N tended to decrease with water ages beyond 2.3 days, and total-N was completely removed in the iron system, consistent with denitrification. This prompted further examination of denitrifying bacteria, indicators, and potential impacts.

Denitrifying Bacteria. As an indicator of relative levels of denitrifying bacteria potential, q-PCR was used to enumerate *nosZ* genes, which encode nitrous oxide reductase, which catalyzes conversion of N_2O to N_2 in both heterotrophic and autotrophic denitrification pathways. In all SDSs, *nosZ* gene levels increased with water age (Figure 1-5). In the chlorinated SDSs, the *nosZ* gene concentrations increased by ~3 log units in the PVC and Iron SDSs and 1.4 log units in the cement SDSs between water ages of 1 and 5.7 days. At the same time, there was also an increase in total bacteria as indicated by 16S rRNA genes (3.5 logs in cement SDSs, 3.2 logs in iron SDSs, and 2.4 logs in the PVC SDSs) (Wang et al. 2012). The highest average amount of *nosZ* gene copies were observed in the PVC and iron SDSs (1.77×10^5 and 1.84×10^5 gene copies/ cm^2 respectively) which was ~ 1.9 log units more than in the cement SDS ($p < 0.001$). The overall results in the chlorinated system, indicates that bacteria with the capability for denitrification were growing facultatively even in the SDS without significant denitrification.

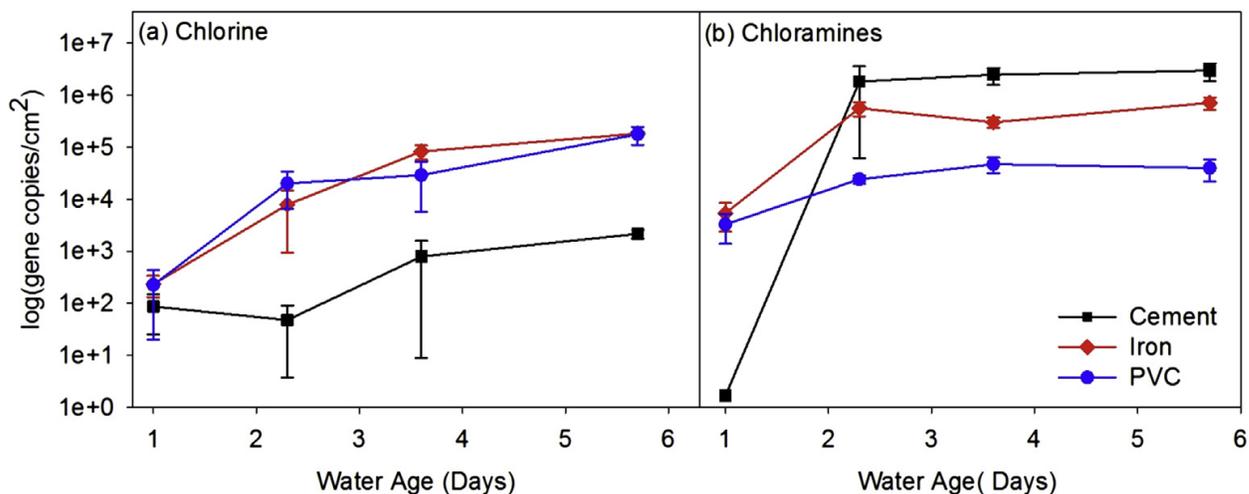


Figure 1-5: Gene copy numbers of *nosZ*, which catalyzes conversion of N_2O to N_2 in some denitrifying bacteria: (a) chlorinated SDS biofilm and (b) chloraminated SDS biofilm. Errors bars represent standard error from triplicate pipes.

In the chloraminated SDSs, between water ages of 1 and 5.7 days, *nosZ* gene copy numbers increased by 1 log in the PVC systems, 2 logs in the iron systems, and 6.25 logs in the cement systems. This corresponded to an increase in 16S rRNA genes (2.6 logs in the cement SDSs, 1.8 logs in the iron SDSs, and 1.9 logs in the PVC SDSs) (Wang et al. 2012). At 1 day water age in cement SDSs, *nosZ* was 1 log unit higher in chlorinated versus chloraminated conditions ($p = 0.04$), and by 5.7 days the *nosZ* concentration was

more than 3 logs higher in the chloraminated versus chlorinated conditions ($p < 0.001$). Between 3.6 and 5.7 days water age, the *nosZ* gene concentration was also 0.6 log units higher in the chloraminated versus the chlorinated system ($p = 0.034$ and $p = 0.024$ respectively). Overall, while there were many instances when the *nosZ* gene concentration was not significantly higher in the chloraminated system (with quantifiable denitrifier activity as measured by total-N loss) versus chlorinated system (with no detectable N-loss), there was a tendency for higher *nosZ* gene concentrations in the chloraminated system. Furthermore, presence of active denitrifying bacteria were detected by positive DN-BARTs, only in the chloraminated SDSs.

Drinking Water Infrastructure

Changes in Mass of Materials with Time. As expected given its relatively inert character, the mass (i.e., weight) of the PVC coupons remained relatively constant regardless of residence time or disinfectant type (Table A4). The cement coupons in the chlorinated and chlorinated systems increased in mass by as much as 2% consistent with minimal mass loss and possible hydration of the cement (Table A4), consistent with observations of (Parks et al., 2012).

For iron coupons there were noteworthy differences for chlorine versus chloramine with water age, which depended on the observed disinfectant or oxygen levels. At water ages of 1 and 3.6 days, when higher levels of disinfectant were observed in the chlorine versus chloramine system ($p < 0.05$, Table A5), iron exposed to the free chlorine oxidant had higher mass loss (Figure 1-6). At moderate water age of 5.7 days, when there was no longer a disinfectant residual in either system, there was no significant difference in iron mass loss with respect to disinfectant type ($p = 0.51$). But at the highest water age of 10.2 days, the iron weight loss was more than 3 times higher in the SDSs with chloramines (0.5% in the chlorinated system versus 1.6% in chloraminated system, $p < 0.05$). At first glance this is counter-intuitive because iron corrosion rates would generally be expected to be higher in the chlorine system, which tended to have higher redox and O_2 concentrations. This raised prospects that anaerobic iron corrosion pathways were important in the chloramine system (Speller, 1951; Uhlig & Revie, 1985; Benjamin et al., 1996; Sun & Edwards, 2002; Sun et al., 2002; Zhang & Edwards, 2007).

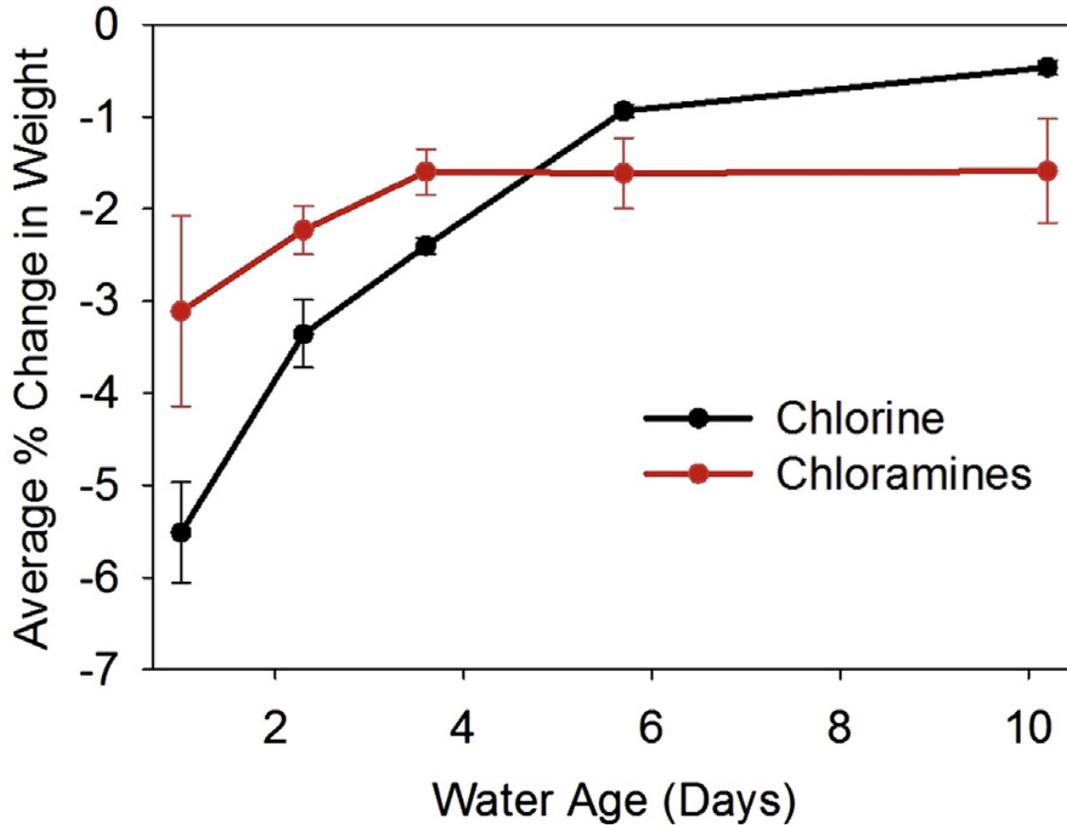


Figure 1-6: Average weight change for iron coupons in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent standard error from triplicate pipes.

Pitting Corrosion. While the total iron corrosion rate is best characterized by the total loss of mass, the life expectancy of the pipe is more strongly indicated by leaks due to pitting or non-uniform corrosion (Figure 1-7). In terms of pitting corrosion, between 2.3 and 5.7 days water age, the chlorinated and chloraminated system both had three pits on coupons removed from the SDSs (Figure 1-8 and Table A6). At 5.7 days water age, two of the three large pits identified were in chloraminated systems versus only one in a chlorinated system. But at 10.2 day water age, there were 3 very large pits identified in the system with chloramine versus none in the system with chlorine. The rate of pitting (1.6-1.9 mm/year) at the high water age in the chloraminated system was extremely high (Figure 1-8).

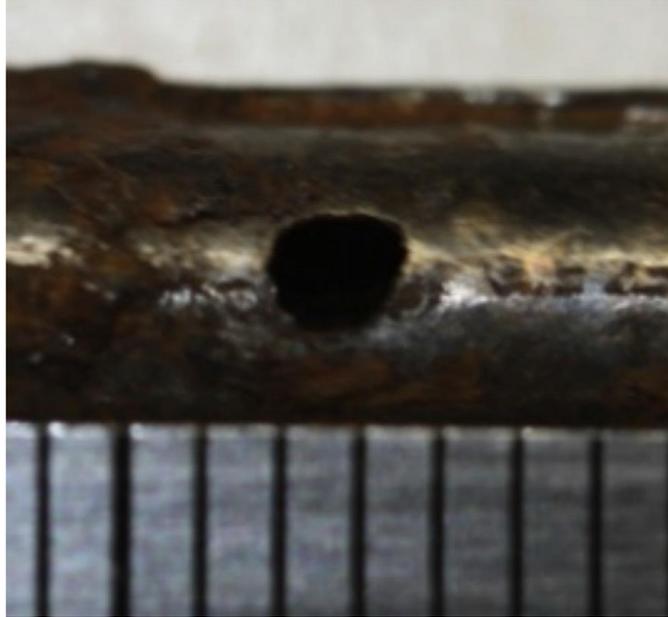


Figure 1-7: Pitting corrosion in chloraminated system.

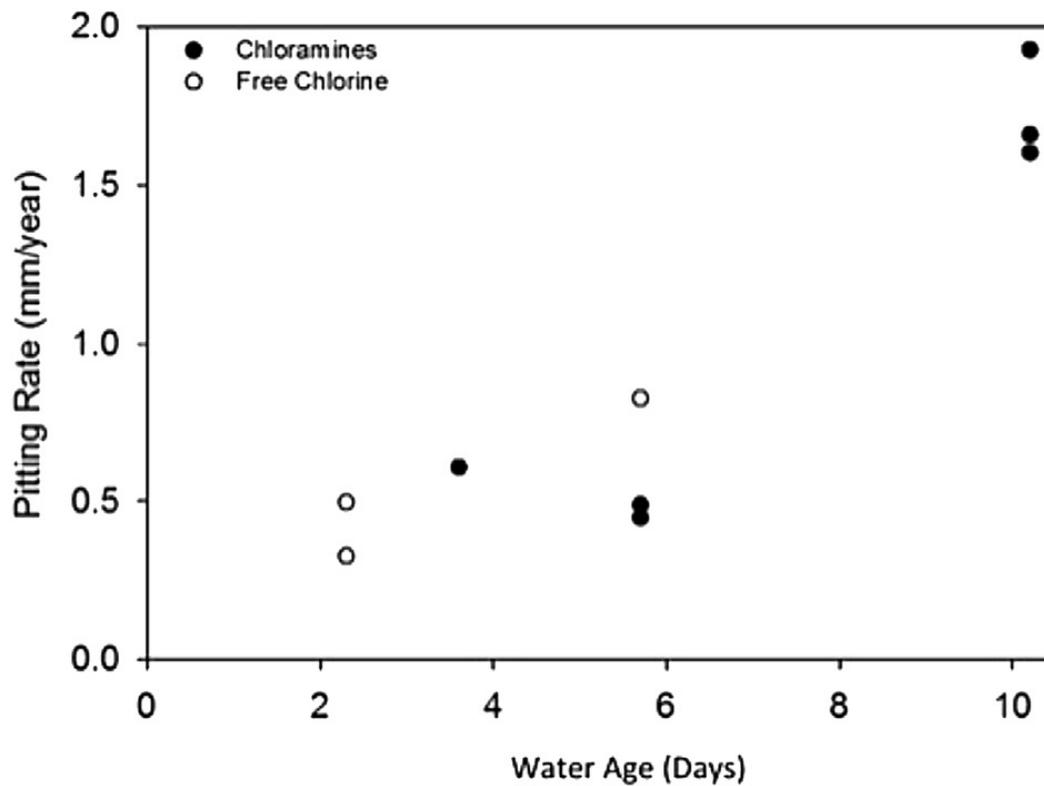


Figure 1-8: Comparison of pitting corrosion rate in chlorinated and chloraminated iron SDSs. Each dot represents an individual pit.

Red Water and Aesthetics. At day 1 water age, the total iron release was 5.7 mg/L in the chlorinated SDSs versus 1.5 mg/L in the chloraminated SDS (Figure A2). By 10.2 day water age, the total iron release decreased to ~0.6 mg/L in both the chlorinated and chloraminated iron SDSs. The release of total iron in the chlorinated system correlated

with presence of oxidants such the disinfectant ($R^2 = 0.99$) and DO ($R^2 = 0.78$). Similar trends were observed in the chloraminated system (DO $R^2 = 0.75$, chloramines $R^2 = 0.70$).

Other Indicators of Concrete Infrastructure Degradation. In PVC and iron SDSs, calcium levels were stable throughout the distribution system. However, in cement SDSs between 0 and 10.2 days water age, calcium concentrations increased by 144% in the chlorinated system and 151% in the chloraminated system, consistent with leaching of lime from the cement to water (Figure A3). There was not statistical difference between the leaching of calcium in the chlorinated and chloraminated cement systems.

In the PVC and iron SDSs, magnesium concentrations remained relatively stable throughout the distribution system. Between 0 and 5.7 days water age, magnesium concentrations were constant in the cement systems, but at 10.2 days decreased by 18% ($p < 0.001$) in the chlorinated and chloraminated systems (Figure A4).

DISCUSSION

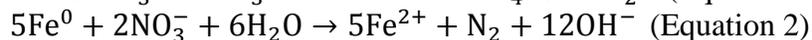
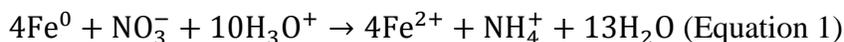
Water Chemistry and Microbial Growth

The goal of this study was to characterize the chemical and biological gradients that develop in distribution systems and their practical consequences. In terms of disinfectant stability, chloramines decayed faster than free chlorine across all SDSs due to nitrification in the chloraminated system. Zhang and Edwards (2009) also reported a similar occurrence of rapid nitrification resulting in chloramines being less persistent than free chlorine even in relatively inert materials (e.g., PVC, copper with epoxy coating, stainless steel). The lowest disinfectant residuals were consistently found in the iron conditions, which supports the expectation that iron will readily react with these oxidants via corrosion and reactions with the array of minerals in iron rusts (LeChevallier et al., 1990; Hallam et al., 2002; Munavalli et al., 2009). Additionally, because iron is a highly reactive material and iron corrosion itself consumes oxygen, the lowest DO levels were noted in the chlorinated and chloraminated iron systems. In the chlorinated SDSs, PVC was the most inert material in terms of reaction with free chlorine, while cement was the least reactive material in terms of reaction with chloramines. This latter observation could be due to the higher pH inhibiting nitrification or differences in the microbial community structure, which were noted in a prior microbial characterization of these SDSs (Wang et al., 2014) (Figure 1-4, Table A3 and A4).

Nitrogen species (i.e., ammonia, nitrite, and nitrate) also provide insight into the relative redox conditions, as well as the tendency for nitrification and denitrification. Nitrification was only noted in the chloraminated systems, given that there were no detectable nitrogen levels in the chlorinated systems. The highest rate of nitrification in chloraminated systems was observed in the chloraminated iron SDS. By 10.2 day water age, all the ammonia in the iron SDSs was completely removed. Theoretically, approximately 8.8 mg/L as CaCO_3 of bicarbonate would have been consumed in completely oxidizing the ammonia via nitrification, which would likely result in a decrease in pH (Gujer and Jenkins, 1975). In addition to loss of chloramine residual, nitrification can also have adverse impacts with respect to lead and copper corrosion in consumers homes due to this

potential drop in alkalinity and pH (U.S. Environmental Protection Agency, 2002b; Zhang et al., 2009).

In the presence of zero-valent iron, abiotic nitrate reduction will result in conversion of nitrite and nitrate to ammonia (Van Hecke et al., 1990; Murphy, 1991; Choe et al., 2000; Devlin et al., 2000; Huang et al., 2003; Ginner et al., 2004; Huang and Zhang, 2004) (Equation 1), but without significant loss of total nitrogen, which is generally mediated by denitrifying bacteria (Equation 2). Denitrification has only rarely been reported in drinking water distribution systems (Baron et al., 2014) and no significant adverse consequences have yet been reported with its occurrence. When iron metal is present in water under anaerobic conditions autotrophic denitrifying bacteria can utilize nitrate as an electron acceptor and H₂ derived from iron as an electron donor. This hydrogenotrophic reduction of nitrate and oxidation of Fe⁰ can result in elevated pH (Equation 2) (Kielemoes, 2000) and can potentially enhance corrosion of iron.



Denitrifying bacterial functional genes increased with water age in all SDSs, including the chlorinated systems where no measureable denitrification was occurring. Similarly, Baron et al. (2014) detected denitrifiers in a hospital hot water system when free chlorine disinfectant was used, as well as after the introduction of on-site monochloramine disinfection. Interestingly, the authors found that the highest relative abundance of denitrifying bacterial genera occurred during a spike in nitrate levels. Furthermore, relative abundance of these bacteria was also substantial at relatively low nitrate levels, implying that alternative constituents influenced their relative abundance.

Even though denitrifying functional genes were detected in all systems, positive BARTs were only observed in the chloraminated SDSs. This implies that there was a lack of activity in the denitrifying bacteria community in the absence of oxidized nitrogen species. Based on the redox gradients, the highest rate of denitrification was observed in the chloraminated iron system. However, *nosZ* gene copy numbers were not significantly higher in the iron systems. This discrepancy could be due to the fact that the biofilm was sampled from the PVC surfaces, and not the iron coupons. In any case, the widespread presence of *nosZ* genes suggests that bacteria capable of denitrification are ubiquitous in drinking water distribution systems, even in systems without measureable denitrification. This suggests that the potential for denitrification by facultative bacteria is pervasive and will likely ensue whenever redox conditions are favorable and sufficient organic matter and nitrogen species are present, or if nitrogen species are present and H₂ is available from corrosion of materials such as iron.

Impact of Redox Gradients on Drinking Water Infrastructure

Weight loss of pipe materials provides one perspective on degradation of drinking water infrastructure. Not surprisingly, the mass of the PVC remained stable with increasing water age in both chlorinated and chloraminated SDSs. This is consistent with previous studies that have found relatively minute changes (maximum of -0.08%) in the mass of

PVC gas pipe samples submerged in water (Scholten and Wolters, 2011). In the cement SDS there was an increase in mass due to hydration reactions that typically take place in cementitious pipe, which overwhelms any weight loss due to material degradation. Significant cement degradation from nitrification could also not be detected by measurements of calcium and magnesium, consistent with findings of Zhang et al. (2010) that lower pHs due to nitrification had little impact in chloraminated systems.

Several studies examining the impact of disinfectants on iron corrosion have yielded divergent results (Treweek et al., 1985; LeChevallier et al., 1990; Eisnor and Gagnon, 2004). LeChevallier et al. (1990) found that chlorine produced a higher iron corrosion rate than chloramine, whereas Eisnor and Gagnon (2004) found the opposite effect and Treweek et al., 1985 found no difference between the two disinfectants. In our study, all three of these outcomes were reproduced dependent on the water age. Specifically, there was greater iron weight loss in chlorinated SDSs versus chloraminated SDSs at water ages between 1 day and 3.6 day when a free chlorine residual was still present and no difference in weight loss between the two disinfectants at day 5.7. For day 10.2, when there was no longer a disinfectant residual, the weight loss in the chloraminated iron SDSs was 3 times greater than in the chlorinated iron SDSs. This might possibly reflect the fact that the pH was more than 0.70 pH units lower in the chloraminated system due to nitrification.

At day 1, there was also a 290% increase in total iron release to the water in the chlorinated system compared to the chloraminated system (Figure A2), which is consistent with the trend reported by Eisnor and Gagnon (2004). However, at longer water ages there was no statistical difference in terms of total iron release to water. This confirms that consumers drawing water from different points in the distribution system could have large differences in terms of iron release.

Even though weight loss is commonly used to characterize iron corrosion rates, measurement of wall penetration and pitting better indicates the impact of corrosion on the life-span of the infrastructure. While there was no detectable differences in pitting at lower water ages, at day 10.2 a very high rate of pitting was only observed in the chloraminated systems (1.6-1.9 mm/year). At this linear penetration rate, it would take less than 6.5 years to completely penetrate a cast iron pipe with a wall thickness of 1 cm. Under abiotic nutrient limited conditions, previous studies have demonstrated that nitrate tends to accelerate uniform corrosion of iron and inhibits pitting corrosion (Ma et al., 2003). In our study, it is not clear whether the extremely high rates of pitting, which co-occurred in parts of the SDS associated with denitrification, are due to microbial corrosion associated with denitrification or if it resulted from other unknown factors associated with rapid anaerobic corrosion, such as sulfate reducing bacteria (SRB). However, SRB presence as indicated by q-PCR and activity as detected by BARTs, were very low and chemical spot tests for sulfide minerals were negative.

CONCLUSIONS

An improved understanding of chemical and biological gradients in drinking water distribution systems has real and important practical benefits in terms of providing safe drinking water and addressing localized corrosion problems and aesthetic complaints. The specific conclusions of this study are summarized as follows:

- Under comparable SDS conditions, chloramines can disappear faster than free chlorine due to nitrification.
- In sections of the SDSs where disinfectant residuals were present, the use of chlorine disinfectant produced a higher iron weight loss versus chloramines.
- Denitrification, a phenomenon only rarely reported in drinking water, actively occurred in chloraminated distribution systems, particularly at higher water age. The potential for denitrification is relatively widespread, according to molecular evidence, and has important implications for water quality, infrastructure integrity, and corrosion.
- The worst localized attack on iron materials occurred at high water age in the system with chloramine, at which point denitrification was essentially complete as measured by complete loss of total N. Denitrifiers have been noted to play a role in iron corrosion for pure cultures, and future work should examine this potential linkage more carefully.
- The interplay between disinfectant type, water age, and pipe material created unique redox gradients and water chemistries that can potentially affect the aesthetics and quality of water consumers receive.

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APPENDIX A

Supporting Information for Chapter 1

Redox Gradients in Distribution Systems Influence Water Quality, Corrosion, and Microbial Ecology

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KEYWORDS. Distribution system, disinfectant, cement, PVC, iron, denitrification

Table A1: Key drinking water quality parameters in Blacksburg tap water.

Parameter	Concentration (mg/L)
Na	8.84±1.1
Mg	4.54±0.3
Al	0.032±0.01
Si	3.81±0.32
P	0.32±0.03
Ca	10.9±0.99
Alkalinity (as CaCO ₃)	~40

Table A2: Physiochemical parameters in chlorinated SDS (± standard deviation)

	Disinfectant Concentration (mg/L)	pH	Dissolved Oxygen (mg/L)
Iron 0d	4.08±0.00	7.65±0.00	8.42±0.00
Iron 1d	2.11±0.88	7.65±0.03	7.22±0.96
Iron 2.3d	0.40±0.04	7.51±0.04	6.07±0.77
Iron 3.6d	0.09±0.06	7.47±0.07	4.77±0.68
Iron 5.7d	0.03±0.01	7.31±0.03	1.74±0.36
Iron 10.2d	0.01±0.01	7.45±0.11	2.01±1.52
Cement 0d	4.08±0.00	7.65±0.00	8.42±0.00
Cement 1d	2.46±1.29	8.09±0.22	8.08±0.34
Cement 2.3d	0.59±0.72	8.22±0.25	7.12±1.24
Cement 3.6d	0.39±0.28	8.29±0.33	6.05±1.98
Cement 5.7d	0.05±0.04	9.58±0.44	4.61±0.55
Cement 10.2d	0.03±0.02	9.74±0.53	2.49±0.67
PVC 0d	4.08±0.00	7.65±0.00	8.42±0.00
PVC 1d	2.77±1.31	8.07±0.03	8.24±0.38
PVC 2.3d	2.17±0.49	8.01±0.03	8.03±0.06
PVC 3.6d	1.37±0.92	7.86±0.12	7.53±0.15
PVC 5.7d	1.30±0.16	7.65±0.01	7.13±0.38
PVC 10.2d	0.04±0.01	7.73±0.12	1.68±2.01

Table A3: Physiochemical parameters in chloraminated SDS (\pm standard deviation)

	Disinfectant Concentration (mg/L)	pH	Dissolved Oxygen (mg/L)	Total Ammonia (mg/L)	Nitrite (mg/L)	Nitrate (mg/L)
Iron 0d	4.32 \pm 0.00	7.98 \pm 0.00	8.06 \pm 0.00	1.24 \pm 0.00	0.012 \pm 0.000	0.38 \pm 0.00
Iron 1d	2.30 \pm 0.87	7.65 \pm 0.34	7.40 \pm 0.40	0.91 \pm 0.25	0.037 \pm 0.028	0.41 \pm 0.09
Iron 2.3d	0.33 \pm 0.28	7.31 \pm 0.08	4.33 \pm 1.08	0.13 \pm 0.03	0.258 \pm 0.144	0.15 \pm 0.12
Iron 3.6d	0.14 \pm 0.14	6.98 \pm 0.01	2.70 \pm 1.86	0.06 \pm 0.03	0.275 \pm 0.066	0.16 \pm 0.14
Iron 5.7d	0.05 \pm 0.01	6.95 \pm 0.01	1.30 \pm 0.88	0.07 \pm 0.04	0.183 \pm 0.010	0.05 \pm 0.07
Iron 10.2d	0.03 \pm 0.01	6.73 \pm 0.03	2.13 \pm 0.10	0.00 \pm 0.00	0.013 \pm 0.001	0.01 \pm 0.02
Cement 0d	4.32 \pm 0.00	7.98 \pm 0.00	8.06 \pm 0.00	1.24 \pm 0.00	0.012 \pm 0.000	0.38 \pm 0.00
Cement 1d	3.77 \pm 0.54	8.08 \pm 0.11	8.15 \pm 0.04	1.00 \pm 0.08	0.035 \pm 0.039	0.38 \pm 0.02
Cement 2.3d	1.44 \pm 0.30	8.01 \pm 0.21	7.44 \pm 0.25	0.78 \pm 0.09	0.019 \pm 0.005	0.47 \pm 0.05
Cement 3.6d	0.21 \pm 0.05	7.62 \pm 0.12	6.48 \pm 0.34	0.81 \pm 0.21	0.017 \pm 0.003	0.41 \pm 0.04
Cement 5.7d	0.06 \pm 0.03	8.56 \pm 0.40	4.75 \pm 0.63	0.81 \pm 0.06	0.023 \pm 0.004	0.34 \pm 0.09
Cement 10.2d	0.03 \pm 0.03	8.46 \pm 0.43	3.62 \pm 1.30	0.08 \pm 0.07	0.032 \pm 0.011	0.22 \pm 0.18
PVC 0d	4.32 \pm 0.00	7.98 \pm 0.00	8.06 \pm 0.00	1.24 \pm 0.00	0.012 \pm 0.000	0.38 \pm 0.00
PVC 1d	3.20 \pm 0.26	7.74 \pm 0.02	8.25 \pm 0.36	1.01 \pm 0.05	0.087 \pm 0.023	0.42 \pm 0.04
PVC 2.3d	0.59 \pm 0.40	7.51 \pm 0.05	7.49 \pm 0.50	0.71 \pm 0.12	0.127 \pm 0.064	0.48 \pm 0.06
PVC 3.6d	0.09 \pm 0.03	7.20 \pm 0.03	6.92 \pm 0.62	0.75 \pm 0.18	0.091 \pm 0.074	0.44 \pm 0.07
PVC 5.7d	0.11 \pm 0.06	7.21 \pm 0.30	5.20 \pm 0.75	0.70 \pm 0.02	0.016 \pm 0.003	0.35 \pm 0.11
PVC 10.2d	0.02 \pm 0.00	6.73 \pm 0.06	3.88 \pm 2.04	0.13 \pm 0.02	0.018 \pm 0.003	0.22 \pm 0.16

Table A4: Average percent weight change (\pm 95% confidence intervals)

Water (Days)	PVC	Cement	Iron
Chlorinated SDS			
1	-0.095 \pm 0.068	0.313 \pm 0.277	-5.515 \pm 1.07
2.3	-0.025 \pm 0.024	0.565 \pm 0.168	-3.358 \pm 0.722
3.6	-0.063 \pm 0.065	0.708 \pm 0.094	-2.399 \pm 0.169
5.7	0.067 \pm 0.037	0.789 \pm 0.157	-0.935 \pm 0.135
10.2	0.05 \pm 0.024	1.649 \pm 0.168	-0.461 \pm 0.148
Chloramination SDS			
1	-0.047 \pm 0.018	1.971 \pm 3.016	-3.111 \pm 2.029
2.3	0.074 \pm 0.041	0.674 \pm 0.063	-2.23 \pm 0.517
3.6	0.018 \pm 0.074	0.827 \pm 0.087	-1.595 \pm 0.486
5.7	0.021 \pm 0.034	0.67 \pm 0.163	-1.61 \pm 0.757
10.2	0.101 \pm 0.01	1.654 \pm 0.025	-1.587 \pm 1.111

Table A5: Comparison of percent weight loss in chlorinated and chloraminated at a given water age (p-values based on non-parametric Kruskal-Wallis test).

	p-value
Iron 1d	<0.05
Iron 2.3d	<0.05
Iron 3.6d	<0.05
Iron 5.7d	0.51
Iron 10.2d	<0.05
Cement 1d	0.28
Cement 2.3d	0.51
Cement 3.6d	0.28
Cement 5.7d	0.28
Cement 10.2d	0.51
PVC 1d	0.51
PVC 2.3d	<0.05
PVC 3.6d	0.13
PVC 5.7d	0.13
PVC 10.2d	<0.05

Table A6: Summary of pitting corrosion in chlorinated and chloraminated DWDSs.

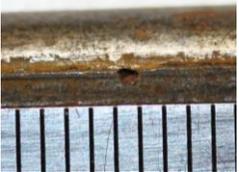
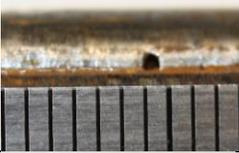
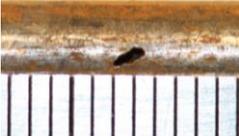
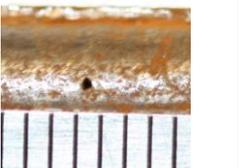
Pit ID	Replicate	Disinfectant	Water Age (Days)	Pit Depth (mm)	Picture
A	1	Chloramine	3.6	1.216	
B	1	Chloramine	5.7	0.897	
C	1	Chloramine	5.7	0.975	
D	3	Chloramine	10.2	2.890	
E	3	Chloramine	10.2	2.404	
F	3	Chloramine	10.2	2.485	
G	1	Chlorine	2.3	0.993	
H	3	Chlorine	2.3	0.656	
I	3	Chlorine	5.7	1.652	



Figure A1: Photograph illustrating design of simulated distribution system (SDS).

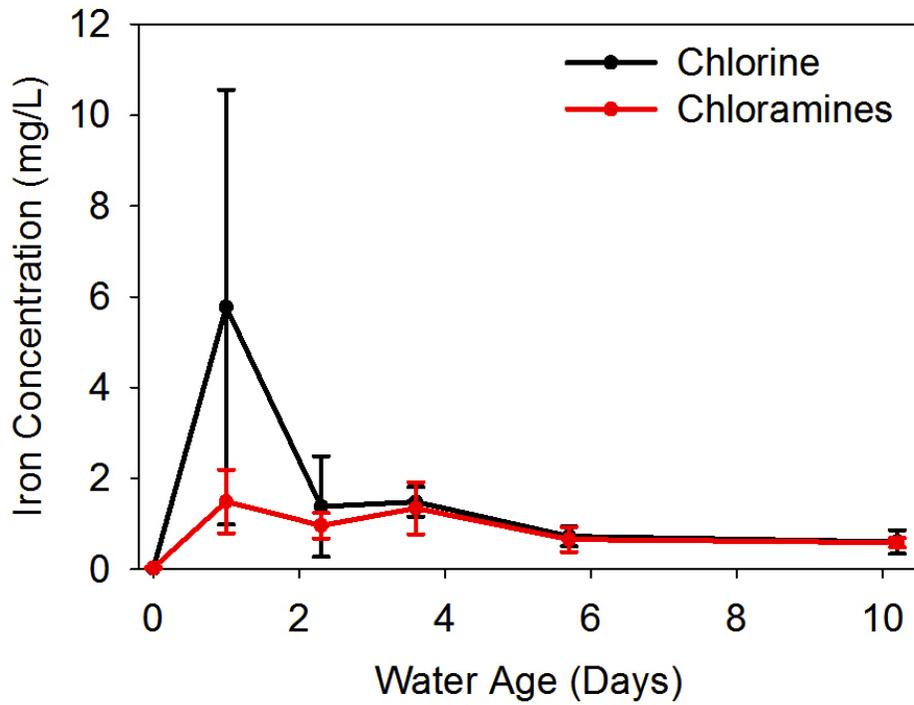


Figure A2: Iron release as a function of water age in the chlorinated and chloraminated Iron-PVC systems. Error bars represent 95% confidence intervals from weekly composite samples from each triplicates collected over 10 weeks ($n=30$).

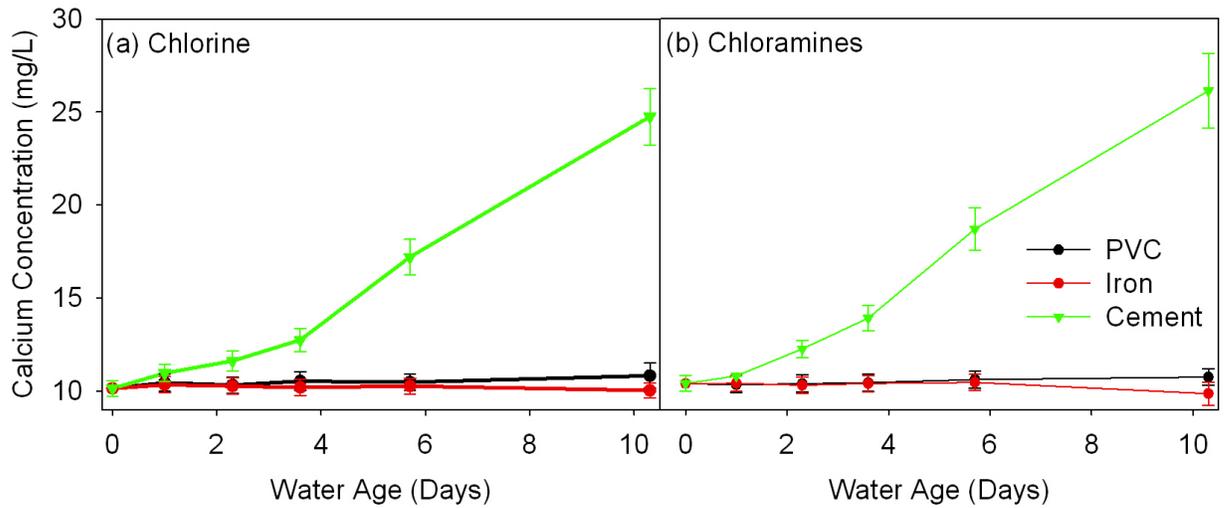


Figure A3: Change in calcium concentration in (a) chlorinated and (b) chloraminated simulated distribution systems. Error bars represent 95% confidence intervals from weekly composite samples from each triplicates collected over 10 weeks ($n=30$).

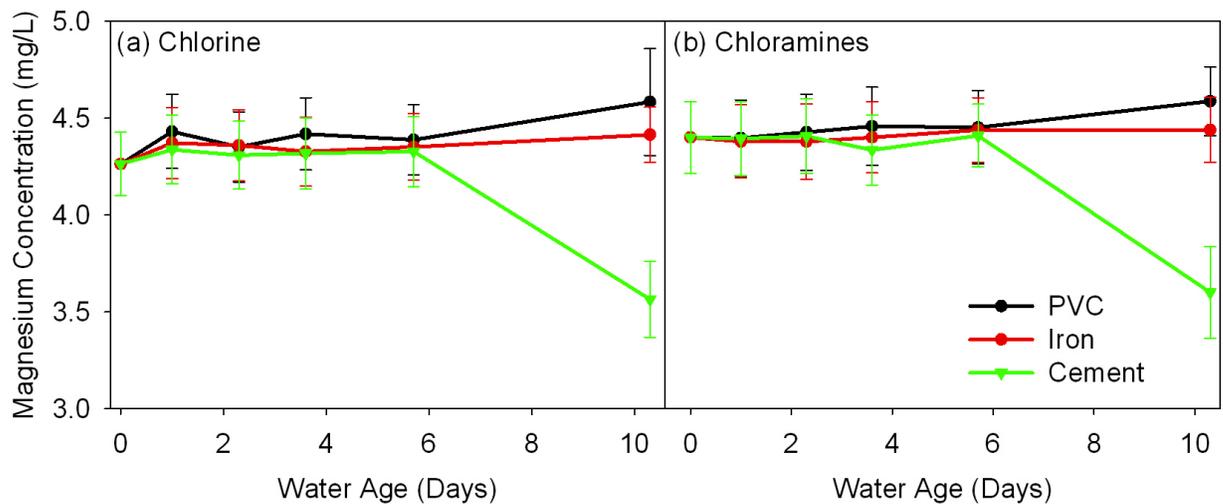


Figure A4: Change in magnesium concentration in (a) chlorinated and (b) chloraminated simulated distribution systems. Error bars represent 95% confidence intervals from weekly composite samples from each triplicates collected over 10 weeks ($n=30$).

CHAPTER 2. DISTRIBUTION SYSTEM WATER AGE CAN CREATE PREMISE PLUMBING CORROSION HOTSPOTS

Sheldon Masters, Jeffrey Parks, Amrou Atassi and Marc A. Edwards

ABSTRACT

Cumulative changes in chemical and biological properties associated with higher “water age” in distribution systems may impact water corrosivity and regulatory compliance with lead and copper action levels. The purpose of this study was to examine the effects of water age and chemistry on corrosivity of various downstream premise plumbing pipe materials and configurations using a combination of controlled laboratory studies and a field survey. Examination of lead pipe, copper pipe with lead solder, and leaded brass materials in a replicated lab rig simulating premise plumbing stagnation events indicated that lead or copper release could increase as much as ~440% or decrease as much as 98% relative to water treatment plant effluent. In field studies at 5 utilities, trends in lead and copper release were highly dependent on circumstance; for example, lead release increased with water age in 13% of cases and decreased with water age in 33% of conditions tested. Levels of copper in the distribution system were up to 50% lower and as much as 30% higher relative to levels at the treatment plant. In many cases, high-risks of elevated lead and copper did not co-occur, demonstrating that these contaminants will have to be sampled separately to identify “worst case” conditions for human exposure and monitoring.

KEYWORDS: Water age, corrosion, lead, copper

INTRODUCTION

Drinking water distribution systems (DS) are complex networks of pipes and storage tanks delivering treated water to consumers. Water quality can deteriorate in the distribution system via reactions between the water and pipe surfaces and the bulk water itself during transport (U.S. Environmental Protection Agency 2002b). These concerns are exacerbated at higher water age (i.e., water residence time) and can include disinfectant decay, nitrification, pipeline corrosion, biofilm formation and microbial regrowth (Table 2-1). Water age can be managed by system design and operation within limitations of infrastructure constraints (Committee on Public Water Supply Distribution Systems 2005) and the variable nature of water demand (Besner et al. 2001; DiGiano et al. 2005; Committee on Public Water Supply Distribution Systems 2005; Grigg 2010; Machell and Boxall 2012).

Water age and its associated cumulative impacts on biology and chemistry, is suspected to significantly impact metal corrosion and lead/copper levels in consumers homes (Table 2-1). However, the influence of water age on pipeline corrosion is related to site-specific factors such as local water quality conditions and the type of pipe materials. For example, case studies have shown that lead and copper levels can vary dramatically within the distribution system even when utilities meet the Lead and Copper Rule (LCR) (Cantor et al. 2003; Imran et al. 2005; Stith et al. 2006; Renner 2006; Gronberg 2007; Scardina et al 2008; HDR 2011; Hill and Cantor 2011; Arnold et al. 2012; Edwards 2014; Wang et al. 2014). Wang et al. (2014) recently used GIS in Raleigh, NC, to determine that higher water age to buildings tended to increase lead leaching. Many studies have also found associations between corrosion problems and the water-age related levels of residual disinfectant in the water. In some cases the complete absence of chlorine triggered Type III copper pitting with elevated levels of copper (> 6 mg/L), blue ice and blue staining, and pinhole leaks (Edwards et al. 2000; Cantor et al. 2003; Scardina et al. 2008), but in other cases the highest levels of pitting were reported in parts of the distribution system with higher free chlorine and the lowest water age (Rushing and Edwards 2004; Scardina et al. 2008; Kleczyk and Bosch et al. 2008; Sarver et al. 2011). In the latter case the pitting attack is largely chemical in nature and is driven by high levels of free chlorine oxidants, whereas the former case is believed to be consistent with bio-corrosion encouraged by the absence of disinfectant.

In addition to suspected impacts on copper pitting, changing disinfectant levels influence copper and lead solubility. Higher levels of free chlorine can sometimes decrease copper or lead solubility by producing lower solubility surface solids (Lytle and Schock 2005; Nguyen et al. 2011a), or increase copper leaching in some cases by accelerating copper corrosion rates (Boulay and Edwards 2001). Rahman et al. (2007) observed that even though both chlorine and chloramines reduced copper release relative to a control without disinfectant, chloramines induced more copper release than the free chlorine conditions. Higher levels of chloramine have also been associated with increased lead levels in some cases (Edwards and Dudi 2004; Triantafyllidou et al. 2012), or higher levels of copper and lead if nitrification depresses pH (Douglas et al. 2004; Zhang et al. 2008; Zhang et al. 2009; Zhang and Edwards 2009; Nguyen et al. 2012).

Table 2-1. Water quality issues associated with water age and their concomitant impact on lead and copper corrosion.

Parameter	Trend with Water Age	Reference	Impact on Pb Release	Reference	Impact on Cu Release	Reference
Physiochemical						
Disinfectant	Decrease in disinfectant concentration.	Lu et al. (1995); Kiene et al. (1998); U.S. Environmental Protection Agency (2002b); Digiano et al. (2005); Al-Jasser (2007)	Loss of Cl ₂ can cause much higher solubility in some systems, higher chloramine may slightly increase lead leaching	Schock et al. (1996); Lin et al. (1997); Edwards and Dudi (2004); Zhang et al. (2009)	In some waters higher chlorine and chloramine can increase Cu corrosion/pitting and copper release, but in other conditions with MIC even trace levels of disinfectant can solve pitting and by-product release problems.	Boulay and Edwards (2001); Bremer et al. (2001); Zhang et al. (2002); Cantor et al. (2003); Cantor et al. (2006); Rahman et al. (2007); Nguyen et al. (2011); Sarver and Edwards (2012)
Corrosion inhibitor	Removal of orthophosphate by pipes and reversion of polyphosphate to orthophosphate.	Zinder et al. (1984); Goldberg (1995); Edwards et al. (2001); U.S. Environmental Protection Agency (2002b); Holm and Edwards (2003)	Possible increase in lead release due to reduced concentration of orthophosphate inhibitor.	Holm and Schock (1991); Dodrill and Edwards (1995); Schock et al. (1996); Cantor et al. (2000)	Possible decrease in copper corrosion due to formation of insoluble phosphate scale.	Holm and Schock (1991); Dodrill and Edwards (1995); Schock et al. (1996); Cantor et al. (2000)
Dissolved Oxygen	Microbial activity and interactions with pipe materials decrease DO.	Sarin et al. (2004); Masters et al. (2015)	Lead corrosion may decrease at lower DO.	Sarin et al. (2004); Jung et al. (2009)	While higher oxygen fuels copper corrosion, anaerobic corrosion via sulfides is associated with pitting corrosion. Low DO can decrease copper release.	Werner et al. (1994); Edwards et al. (1994a); Ferguson et al. (1996); Schock et al. (1998); Sorg et al. (1999); Edwards and Sprague (2001); Scardina et al. (2008)
Iron	Increased iron release and consumer red water complaints.	Imran et al. (2005); Mutoti et al. (2007)	Increased lead corrosion due to formation of lead and iron particles, reduced levels of phosphate inhibitor.	Hulsmann (1990); De Rosa and Williams (1992); HDR (2009); Lytle et al. 2005; Camara et al. (2013) Masters and Edwards (2015)	Higher iron can increase copper release similar to lead.	
Microbial						
Biofilm formation & Microbial regrowth	Increase in biofilm formation and microbial regrowth due to loss of disinfectant residuals.	Kerneis et al. (1995); Crozes and Cushing (2000); U.S. Environmental Protection Agency (2002b)	Increase in lead release due to microbial induced corrosion (MIC)	Garret (1891); Larson et al. (1956); Guo et al. (2002); Sundberg et al. (2003); Zhang (2008); Zhang et al. (2009)	Increase copper corrosion and pitting due to MIC.	Edwards et al. (2000); Bremer et al. (2001); Cantor et al. (2003); Cantor et al. (2006)
Nitrification	Increased nitrification potential.	U.S. Environmental Protection Agency (2002b) Zhang et al. (2009); Masters et al. (2015)	Increase in lead release due to MIC and decrease in pH; alkalinity; and DO. Nitrite catalyzed stress failures.	Garret (1891); Larson et al. (1956); Guo et al. (2002); Sundberg et al. (2003); Zhang (2008); Zhang et al. (2009)	Increase copper corrosion and pitting due to MIC and decrease in pH; alkalinity; and DO. Nitrite may catalyze stress failures.	Pugh et al. (1966); Murphy et al. (1997); Edwards et al. (2000); Cantor et al. (2006); Scardina et al. (2008).

In many cases, inhibitors are used in public water systems to mitigate some of these corrosion concerns, but their concentration and speciation can also vary with water age. Orthophosphate can generally decrease copper and lead levels (Holm and Schock 1991; Dodrill and Edwards 1995; Schock et al. 1996; Cantor et al. 2000), but in some cases the phosphate inhibitor can be consumed by prolonged contact with unlined iron pipe (McNeill and Edwards 2002; Lytle et al. 2005). Polyphosphate inhibitors, which tend to increase lead and copper solubility, can hydrolyze and revert to orthophosphate with higher water age (Zinder et al. 1984; Goldberg 1995; Edwards et al. 2001; U.S. Environmental Protection Agency 2002b; Holm and Edwards 2003).

Even as populations in many urban areas have increased, water efficiency and conservation initiatives have decreased water usage (and increased water age) (U.S. Environmental Protection Agency 2002a and 2002b; Rhoads and Edwards 2013; Rhoads et al. 2015), resulting in increased corrosion problems in at least some water systems (Salleh 2012). While rigorous lab and field data are lacking (Grigg 2010), there is concern that implementation of water conservation and higher water ages may be creating hotspots of lead and copper corrosion in distribution systems (Arnold et al. 2012; Del Toral et al. 2013) that might influence childhood lead poisoning risks and selection of “worst case” sites for monitoring (Edwards et al. 2009; Edwards 2014; U.S. Environmental Protection Agency 2014).

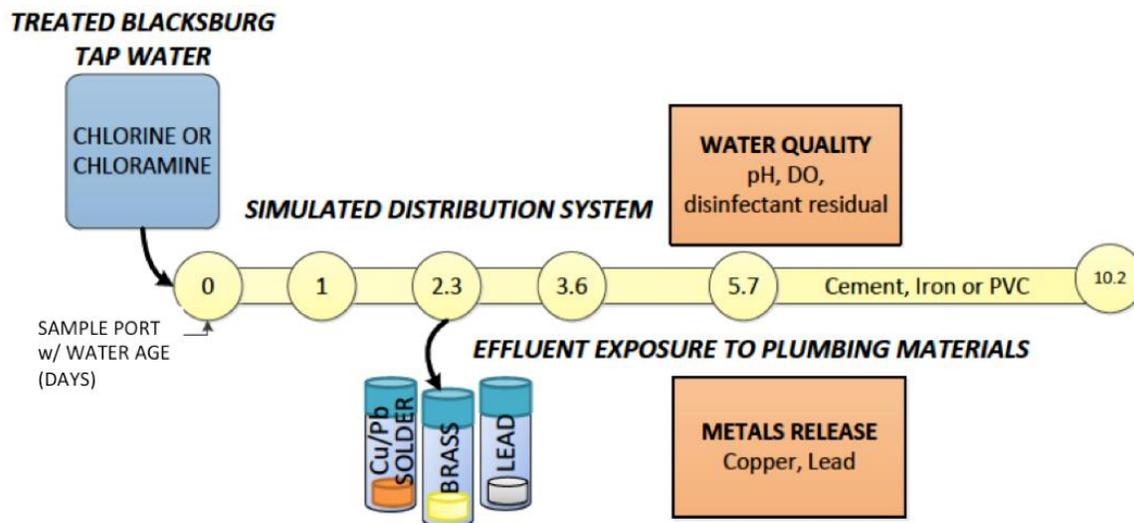
This study examines the impact of water age on lead and copper release during stagnation events in well-controlled field and laboratory studies. The goal was to determine 1) if water age can significantly impact lead/copper release, and 2) if the effects of water age vary with distribution system and premise plumbing material. At the laboratory scale, triplicate simulated distribution systems (SDSs) were used to examine the effect of distribution system water age (0-10.2 days), distribution system material (PVC, cement, iron), and disinfectant type (free chlorine and chloramines) on the lead and copper release from standard premise plumbing materials (copper with lead solder, lead, and brass) of concern. The same materials were examined in triplicate using large pipe loops at 5 utilities, comparing metal release in water treatment plant effluent to the same water after traveling a short distance into the water distribution system.

MATERIALS AND METHODS

Simulated Distribution System (SDS)

Changes in microbiology and chemistry of water as it passed through a simulated water distribution system (SDS) were investigated over a 15 month period and are described elsewhere (Wang et al. 2012 and 2014; Masters et al. 2015). Briefly, in those studies 6 triplicate SDSs with two types of disinfectants (chlorine and chloramines) and three types of typical distribution system materials [polyvinyl chloride (PVC), cement, and cast iron] were operated to generate samples with 0, 1, 2.3, 3.6, 5.7, and 10.2 days of water age. After operating the SDSs continuously for 1-year, 10-mL of water was collected from each sample port and transferred to batch reactors containing standardized premise plumbing materials consisting of 1) copper with lead solder coupon, 2) lead coupon, or 3) brass coupon, for a total of 324 batch reactors (Figure 2-1). Each batch reactor thus served as an analog to the premise plumbing materials located in homes throughout a

municipality, that come in contact with water from a treatment plant as modified by the chemical and biological reactions occurring as water flows through long distribution systems comprised of PVC, cement, or iron pipe. The metal surface area:volume ratio in the premise plumbing batch reactors was 5.6 cm^{-1} . Complete water changes carried out three times per week (MWF) using a dump-and-fill protocol, and weekly composite samples were collected over a 10-week period and analyzed for metals using inductively coupled plasma mass spectrometry (ICP-MS) using Standard Method 3125B (American Public Health Association 2005). A total of 3240 samples were analyzed for lead and copper during this 15 month study.



6 SAMPLE PORTS x 3 PIPE MATERIALS x TRIPLICATES x 2 DISINFECTANTS x 3 PLUMBING MATERIALS = 324 CONDITIONS
Adapted from Masters et al. (2015)

Figure 2-1. Schematic of simulated drinking water distribution system (SDS) and transfer of water to premise plumbing batch reactors. SDSs consisted of PVC pipe fitted with iron, concrete or PVC coupons in triplicate and receiving chlorine or chloramine disinfectant (18 SDSs total).

Corrosion Evaluation Rig (CER)

Portable pipe loop racks, henceforth referred to as a Corrosion Evaluation Rigs (CER), were deployed to detect changes in metal leaching propensity at water treatment plant (WTP) effluents compared to a point within a distribution system (DS). In fall 2011, ten CERs were installed at five utilities representing a variety of treatment processes, disinfectants, corrosion control strategies, water qualities, and distribution system corrosion issues (Table 2-2). All the utilities consistently met the copper action level (AL), while two of the participating utilities had issues with lead compliance. Utility C and D shared the same source water, which allowed for comparison of slightly different treatment processes on metal leaching propensity of the treated water. The distribution system CERs were located in buildings under water utility control that tended to have relatively low water age (<1-5 days), which makes trends reported herein a lower bound to those expected in practice when water age can be higher by an order of magnitude or more.

Each CER consisted of 5 total feet lengths of copper tube with lead solder, lead pipes galvanically connected to copper tube, or PVC pipe with brass rod inserts for a total of 9 lengths of pipe. Each type of pipe was tested in triplicate with a design flow rate of 10 L/min (~2 fps) to simulate typical premise plumbing flow conditions. These rigs were sampled monthly over a one year period. During operation, every 8 hours solenoid valves were opened for 10 minutes for flushing. Samples were collected after a 6 to 8 hour stagnation period in the pipes. All samples were digested using 2% nitric acid and analyzed for lead and copper using ICP-MS. A more detailed report of the design, construction, and operation of the CERs are reported in Parks et al. (2014).

Table 2-2. Summary of characteristics of drinking water utilities.

Utility	Treatment Process	LCR Compliance History	Utility Interest in Project
A	Conventional treatment with chlorine disinfection/Lime and CO ₂ for water stability/no corrosion inhibitor	Out of compliance: 2006-2011; part of 2012	Lead compliance problems; large fraction of unlined iron distribution system
B	Conventional treatment/UV and chloramine disinfection/no corrosion inhibitor	In compliance	Multi-source water with large distribution system; some nitrification and copper corrosion issues
C	Conventional treatment plus GAC contactors/Chlorine disinfection and corrosion inhibitor	In compliance	Use of testing technique to evaluate corrosion issues in distribution system
D	Three treatment plants with conventional treatment/Chlorine disinfection and corrosion inhibitor	In compliance	Difficult to find LCR volunteers. Variable water quality.
E	Conventional treatment plus ultra-filtration membranes/Chlorine disinfection and corrosion inhibitor	Out of compliance: 2004-2007	Past lead corrosion problems; old distribution system

Statistical Analyses

A Shapiro-Wilks test was used to test for normality of the data. A *t*-test on normalized data or a non-parametric Wilcoxon test was used to compare the difference ($p < 0.05$) between two groups while a Kruskal-Wallis test or an analysis of variance (ANOVA) on normalized data was used to perform multiple comparisons. Linear regressions were used

to determine if the lead and copper concentration tended to increase or decrease with increasing water age in the SDSs. To have a common basis of comparison from one utility to another and to quantify the magnitude of the effect, the increase in metal release with water age (e.g., $\mu\text{g Pb L}^{-1}\text{day}^{-1}$) is calculated as the slope of the regression line from a graph of metal concentration versus water age in days.

RESULTS AND DISCUSSION

After briefly summarizing the influence of water age on water chemistry and the propensity to leach lead and copper from materials in SDS rigs, key results of field studies in relationship to the lab studies are presented. A final section discusses practical implications.

Simulated Distribution System (SDS)

Chemistry and Redox Gradients in SDS. The pH in SDSs with cement increased by as much as 2.1 units with increasing water age due to release of lime to water, while the pH decreased by as much as 1.3 units in the PVC and iron systems (Table 2-3). In general, chlorinated SDSs had a higher pH when compared to the parallel system with chloramine due to nitrification. Nitrification also produced faster disinfectant decay for chloramine versus the system with free chlorine. Dissolved oxygen (DO) levels decreased by as much as 80% with increasing water age (Table 2-3), and total nitrogen decreased with increasing water age in chloraminated SDSs with the most significant loss occurring in the iron system due to denitrification (Masters et al. 2015).

Table 2-3. Physiochemical parameters in the SDSs (\pm standard deviation)

Materials	Disinfectant Conc. (mg/L)		Disinfectant Conc. at Day 3.6 (mg/L)	pH		Dissolved Oxygen (mg/L)		Total-N (mg/L)	
	Initial	Final		Initial	Final	Initial	Final	Initial	Final
Chlorine									
Iron		0.01 \pm 0.01	0.09 \pm 0.06		7.45 \pm 0.11		2.01 \pm 1.52		BDL
Cement	4.08 \pm 0.00	0.03 \pm 0.02	0.39 \pm 0.28	7.65 \pm 0.00	9.74 \pm 0.53	8.42 \pm 0.00	2.49 \pm 0.67	BDL	BDL
PVC		0.04 \pm 0.01	1.37 \pm 0.92		7.73 \pm 0.12		1.68 \pm 2.01		BDL
Chloramines									
Iron		0.03 \pm 0.01	0.14 \pm 0.14		6.73 \pm 0.03		2.13 \pm 0.10		0.02 \pm 0.01
Cement	4.32 \pm 0.00	0.03 \pm 0.03	0.21 \pm 0.05	7.98 \pm 0.00	8.46 \pm 0.43	8.06 \pm 0.00	3.62 \pm 1.30	1.63	0.33 \pm 0.23
PVC		0.02 \pm 0.00	0.09 \pm 0.03		6.73 \pm 0.06		3.88 \pm 2.04		0.36 \pm 0.16

Influence of Disinfectant on Metals Release. Only one disinfectant is typically used within a given distribution system, with exceptions for rare changeovers from one disinfectant type to another, or during annual “free chlorine burns” of chloraminated systems (Odell et al. 1996; Vikesland et al. 2001; Carrico et al. 2008). In the laboratory study, an extreme outbreak of nitrification was experienced in the SDS with chloramine, which is atypical of full-scale distribution systems in which chloramine is relatively stable. Water quality impacts in the chlorine system were also reflective of much higher water ages in full-scale chlorinated distribution systems. The lack of similitude between the SDS used herein and full-scale distribution systems, deserves further study and is likely due to the very low velocities and relatively high surface area:volume of PVC used in each rig. Overall, the water quality trends reported for the SDS herein likely represent an upper bound to those expected in typical full scale distribution systems.

At day 0, before the water came in contact with any of the pipe main materials, copper release was 67% higher with the chloramine disinfectant when compared to free chlorine ($p < 0.05$). In the chloraminated SDSs, there was no significant increase or decrease in copper release with increasing water age for any of the main materials tested. At day 0, there was no statistical difference between the average copper release from brass due to chloramines or chlorine ($p = 1$). At day 0, lead from solder was more than 70% higher with chlorine as opposed to chloramines ($p < 0.05$) while there no significant impact on the amount of lead leached from brass ($p > 0.05$). Similar to the lead release associated with solder, the lead coupons had 3 times more lead leaching with the free chlorine disinfectant at day 0 compared to the chloramines ($p < 0.001$). However, numerous studies have demonstrated that chlorine disinfection is normally associated with lower lead levels due to the formation of insoluble lead oxide scale (Schock et al. 1996; Lin et al 1997; Edwards and Dudi 2004). In our study the higher levels of lead in the chlorinated system is likely due to the fact that the lead coupons were new and the experimental time-scale was too short to allow for the complete formation of a passivating scale (Arnold 2011).

Pipe Main Material and Water Age Effect on Metal Release

Copper Release

Copper. The concentration of copper in water was influenced by water age and pipe main material (Figure 2-2 and Table 2-4). In the chlorinated SDSs copper increased with water age for the PVC and iron SDSs with slope = $5.2 \mu\text{gL}^{-1}\text{day}^{-1}$ ($p = 0.02$) and slope = $34.5 \mu\text{gL}^{-1}\text{day}^{-1}$ ($p = 0.004$), respectively. By day 10.2, the average copper release was 91% and 439% higher for the PVC and iron SDSs when compared to day 0 (Figure 2-2). On the other hand, copper decreased by as much as 30% with increasing water age for the cement SDSs (Slope = $-5.3 \mu\text{gL}^{-1}\text{day}^{-1}$, $p = 0.001$), likely due to the 2.1 unit increase in pH as water passed through this system (Masters et al. 2015; Shull and Becker 1960; Edwards et al. 1996; Ferguson et al. 1996, Boulay and Edwards, 2001). Thus, after 10.2 days transport, the same water transported through cement had at least 45% less copper than for iron, demonstrating the hypothesized effect of main material and water age on metal leaching propensity of the water.

Between day 1 and 3.6, copper release due to water in contact with the chloraminated iron SDSs was at least 1.5 times higher than PVC and cement SDSs ($p < 0.05$). Between days 5.7 and 10.2 there was no difference in copper corrosion associated with any of the pipe main materials (Figure 2-2). There was also no difference between the amounts of copper release associated with the chlorinated or chloraminated cement SDSs at corresponding water ages. On the other hand, between days 3.6 and 10.2, the water from the chlorinated iron SDSs resulted in 1.5 to 5 times more copper leaching from the copper coupons when compared to the chloraminated system ($p < 0.05$).

Table 2-4. Summary of Statistical Analyses from Simulated Distribution Systems.

Condition	Change in Metals Concentration with Increasing Water Age	Percent Change	Slope ($\mu\text{gL}^{-1}\text{day}^{-1}$)	Linear Regression p-value
Copper Release				
Copper with Lead Solder				
Free chlorine PVC	Increase	-3% to 91%	5.2	0.02
Free chlorine Cement	Decrease	-38% to 38%	-5.3	0.001
Free chlorine Iron	Increase	181% to 439%	34.5	0.004
Chloramines PVC	No change	-	0.11	0.96
Chloramines Cement	No change	-	-2.5	0.20
Chloramines Iron	No change	-	0.40	0.91
Brass				
Free chlorine PVC	Increase	-11% to 66%	10.5	0.001
Free chlorine Cement	Decrease	0% to -44%	-6.8	0.001
Free chlorine Iron	No change	-	-12.3	0.39
Chloramines PVC	No change	-	-0.08	0.13
Chloramines Cement	Decrease	-3% to -56%	-10.1	0.001
Chloramines Iron	No change	-	-5.9	0.13
Lead Release				
Copper with Lead Solder				
Free chlorine PVC	No change	-	-19.3	0.45
Free chlorine Cement	Decrease	5% to -75%	-100.0	0.003
Free chlorine Iron	No change	-	-36.1	0.33
Chloramines PVC	Increase	-6% to 149%	167.9	0.01
Chloramines Cement	Decrease	-68% to 447%	-140.5	0.026
Chloramines Iron	No Change	-	10.00	0.79
Lead				
Free chlorine PVC	Decrease	-62% to -92%	-236.8	< 0.001
Free chlorine Cement	Decrease	16% to -98%	-268.7	< 0.001
Free chlorine Iron	Decrease	-63% to -96%	-274.0	< 0.001
Chloramines PVC	No change	-	54.27	0.26
Chloramines Cement	No change	-	-75.54	0.21
Chloramines Iron	Decrease	-86% to 189%	-227.1	0.0034
Brass				
Free chlorine PVC	No change	-	0.54	0.30
Free chlorine Cement	Decrease	-43% to -61%	-1.0	0.03
Free chlorine Iron	Increase	9% to 360%	10.0	< 0.001
Chloramines PVC	Increase	13% to 382%	7.7	0.04
Chloramines Cement	No change	-	-2.4	0.17
Chloramines Iron	No change	-	2.0	0.25

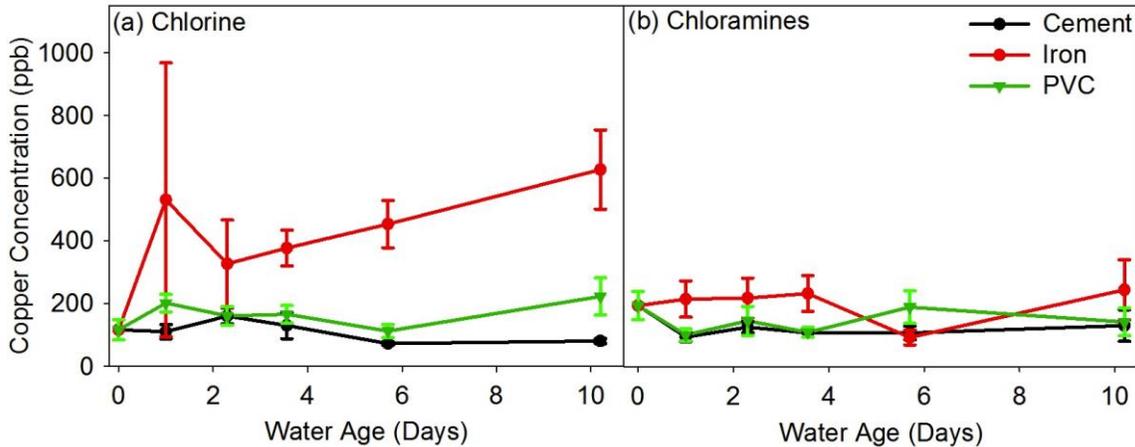


Figure 2-2: Copper release from copper with lead solder coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.

Brass. Copper leaching from brass decreased with increasing water age for both chlorinated and chloraminated cement SDSs with slope = $-6.8 \mu\text{gL}^{-1}\text{day}^{-1}$ and $-10.1 \mu\text{gL}^{-1}\text{day}^{-1}$ ($p = 0.001$), consistent with the trend for copper metal (Figure B1). Meanwhile, copper associated with the chlorinated PVC SDSs increased by as much as 66% with increasing water age (Slope = $10.5 \mu\text{gL}^{-1}\text{day}^{-1}$, $p = 0.001$).

Lead Release

In general, the highest relative lead release was associated with the pure lead coupons, followed by the copper with lead solder coupons, and then brass. The average lead levels varied over a 12X range (11-124 ppb) for leaded brass, a 7X range (407-2926 ppb) for lead solder, and a 28X range (144-4090 ppb) for lead pipe.

Copper with lead solder. Lead leaching from copper with lead solder coupons decreased with increasing water age for the chlorinated and chloraminated cement SDSs (Figure B2) ($p < 0.05$). By day 10.2, water from the chlorinated and chloraminated cement SDSs had a 65% reduction in average lead leaching compared to the treated effluent water ($p < 0.05$), probably due to the higher pHs after contacting the cement (Schock et al. 1996; Kim et al. 2011; Masters and Edwards, 2015). There was no statistically significant increase or decrease in lead with increasing water age for the chlorinated or chloraminated iron SDSs ($p > 0.05$) (Figure B2).

Lead. Lead leaching from lead coupons decreased with increasing water age for all chlorinated SDSs ($p < 0.05$) (Figure B3a, Table 2-4). By day 10.2, lead release from lead coupons exposed to water from the chlorinated SDSs was as much as 98% lower when compared the average lead concentration at day 0 ($p < 0.05$). Water from the chloraminated iron SDSs resulted in an initial 190% increase in average lead corrosion between day 0 and day 1 ($p < 0.01$); but by day 10.2 the average lead concentration decreased by 86% from the starting concentration ($p < 0.05$) (Figure B3). There was no statistically significant increase or decrease with increasing water age for lead release

from lead coupons in the chloraminated PVC or cement SDSs with slope = $54 \mu\text{gL}^{-1}\text{day}^{-1}$ ($p = 0.26$) and slope = $-76 \mu\text{gL}^{-1}\text{day}^{-1}$ ($p = 0.21$) respectively.

Brass. The change in average lead leaching from brass with increasing water age depended on the type of disinfectant and pipe main material (Figure 2-3). Water from the chlorinated cement SDSs resulted in a 50% decrease in lead leaching by day 10.2 ($p < 0.05$) (Figure 2-3). However, lead from brass increased between 9% and 360% with increasing water age for the chlorinated iron SDS. There was no significant increase or decrease in lead release from brass with increasing water age for the chlorinated PVC SDSs (Slope = $0.54 \mu\text{gL}^{-1}\text{day}^{-1}$, $p = 0.30$) and the chloraminated cement and iron SDSs (Slope = $-2.4 \mu\text{gL}^{-1}\text{day}^{-1}$, $p = 0.17$ and Slope = $2.0 \mu\text{gL}^{-1}\text{day}^{-1}$, $p = 0.25$). Between days 3.6 and 10.2, water from the iron system resulted in 2 to 9 times more lead release from brass compared to the cement or PVC system.

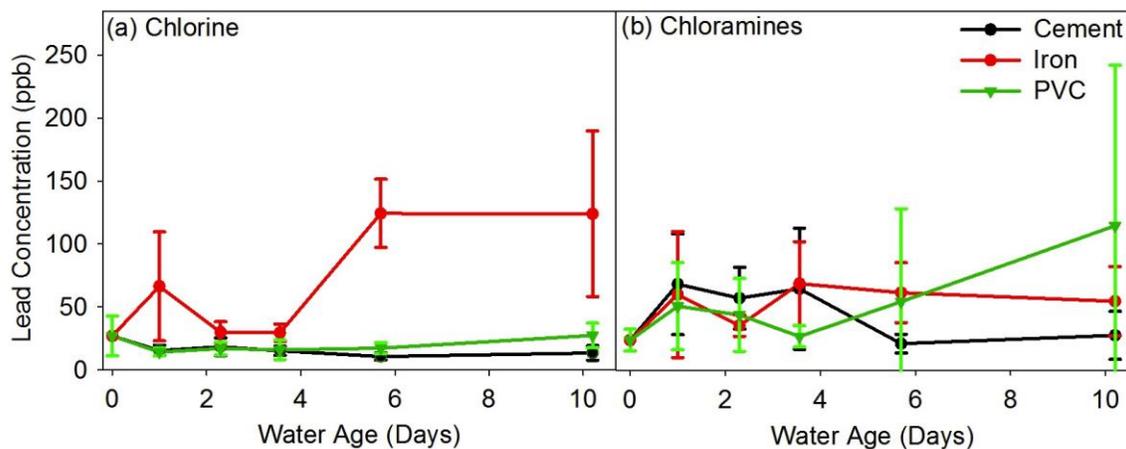


Figure 2-3: Lead release from brass coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.

Corrosion Evaluation Rig (CER) Field Study

CERs were installed at the WTP and a point in the DS at 5 utilities that characterize various water quality conditions (Table 2-5). As noted previously, the water ages between the WTP and DS CER in this study of 0.5-5 days are relatively short compared to the maximum range observed in most distribution systems, making the observed trends in corrosion by-product release closer to the minimum or average of the range likely to be encountered in practice.

Field Stations: Chemical Changes in Water Quality. At 4 utilities (A, B, C, and E), disinfectant residuals were 15-45% lower in the distribution system compared to the WTP ($p < 0.05$), whereas utility D had no statistical difference in disinfectant levels at the WTP versus the DS (both 1.7 mg/L). Even though there was less disinfectant residual in the DS compared to the WTP at most utilities, there was no statistical difference in terms of the total bacteria ($p > 0.05$) (P. Ji, personal communication).

The alkalinity at the utilities can be categorized as low (Utility A), moderate (Utility C, D and E), and high (Utility B). Utility A had a slight, but statistically significant decrease in

alkalinity from 19 mg/L as CaCO₃ at the WTP to 17 mg/L as CaCO₃ in the DS ($p = 0.026$) and a slight corresponding decrease in pH from 9.9 at the WTP to 9.7 in the DS ($p = 0.001$). There was no significant decrease in alkalinity and pH at the other utilities ($p > 0.05$). Utility C doses sodium hexametaphosphate for corrosion control while utilities D and E use a blended phosphate. Between the WTP and DS the total phosphate levels remained stable at these three utilities ($p > 0.05$).

The WTP nitrate levels at utility B were at least 3 times higher than other utilities. Utility B was also the only site where there was a statistically significant difference between the levels of nitrate at the WTP (2.0 mg/L) versus the DS (0.84 mg/L). The average chloride concentration at utility B was also 2 times higher than the other sites and was also the only case where the chloride concentration was statistically different at the WTP when compared to the DS ($p = 0.002$). Since there were multiple points of entry at utility B (5 groundwater plants and 4 large surface water plants), this was considered proof that the water at the DS CER was not entirely comprised of water leaving the WTP.

A relatively high chloride-sulfate mass ratio (CSMR) has been linked to lead corrosion issues especially in low alkalinity waters (Edwards and Triantafyllidou 2007; Nguyen et al. 2010b; Stone et al. 2011; Nguyen et al. 2011b). All the utilities had a CSMR greater than 0.2 which, according to Nguyen et al. (2010b), poses a “significant concern” for utilities with lead solder or partially replaced lead pipes. There was no statistically significant difference between the CSMR at the WTP compared to the DS for all 5 utilities; however, the CSMR did vary significantly from one utility to another (Table 2-5). Two utilities (A and B) had detectable levels of iron and each in case there was 5 times more iron in the DS when compared to the WTP ($p < 0.0001$). Finally, there was no statistical difference between the levels of aluminum at the WTP and DS at all the utilities. Overall, the observed changes are consistent with expectations for low water ages.

Copper Corrosion. The overall copper release was strongly dependent on utility location with a range of 6-181 ppb for brass, 21-689 ppb for lead-copper and 40-1073 ppb for copper (Table 2-6). The relative increase in the DS compared to the WTP ranged from -50-30%. The influence of water age on copper corrosion varied based on the water utility and was dependent the type of premise plumbing material (Figure 2-4). In the copper with lead solder test pieces, 2 utilities (B and E) had higher copper levels in the distribution system when compared to the WTP while utility C had higher copper release at the WTP ($p < 0.05$). Copper leaching from the galvanically connected copper and lead pipes was higher at the WTP for utility A and D and in the DS for B and E. Finally, copper release from the brass sections was statistically higher at the WTP for utility B, C, and D while there was no statistical difference at the other two utilities.

Table 2-5. Comparison of water quality parameters of drinking water utilities (\pm standard deviation).

Parameter	Utility A			Utility B			Utility C			Utility D			Utility E		
	WTP	DS	p-val.	WTP	DS	p-val.	WTP	DS	p-val.	WTP	DS	p-val.	WTP	DS	p-val.
pH	9.9 \pm 0.13	9.7 \pm 0.1	0.001	7.60 \pm 0.11	7.6 \pm 0.1	0.64	8.6 \pm 0.1	8.6 \pm 0.1	0.69	7.4 \pm 0.1	7.3 \pm 0.1	0.06	8.01 \pm 0.1	8.07 \pm 0.1	0.08
Alkalinity (mg/L as CaCO ₃)	19.0 \pm 1.7	17.3 \pm 1.4	0.026	218.3 \pm 27.0	206.5 \pm 25.9	0.39	79*	N/M	-	54.3 \pm 24.7	53.2 \pm 24.4	0.77	106.5 \pm 1.8	106.9 \pm 2.3	0.57
Total Chlorine (mg/L as Cl ₂)	1.1 \pm 0.3	0.6 \pm 0.1	<0.0001	1.8 \pm 0.3	1.0 \pm 0.3	0.0001	1.1 \pm 0.1	0.9 \pm 0.1	0.001	1.7 \pm 0.2	1.7 \pm 0.2	0.74	1.3 \pm 0.2	1.1 \pm 0.1	0.003
Total Phosphate (μ g/L)	-	-	-	-	-	-	131.9 \pm 23.7	137.5 \pm 20.3	0.51	228.5 \pm 40.9	223.8 \pm 38.1	0.67	281.0 \pm 19.6	276.1 \pm 27.5	0.80
Iron (μ g/L)	12.8 \pm 12.6	64.6 \pm 63.1	<0.0001	4.8 \pm 3.7	22.4 \pm 11.0	<0.0001	-	-	-	-	-	-	-	-	-
Aluminum (μ g/L)	2.3 \pm 1.4	3.0 \pm 2.2	0.10	74.7 \pm 40.6	54.2 \pm 28.0	0.11	63.6 \pm 34.9	61.8 \pm 36.6	0.64	17.3 \pm 15.5	17.6 \pm 15.6	0.93	5.0 \pm 2.8	3.3 \pm 1.30	0.10
Nitrate (mg/L as N)	0.09 \pm 0.16	0.11 \pm 0.15	0.93	1.98 \pm 1.00	0.84 \pm 0.51	0.004	0.66 \pm 0.26	0.70 \pm 0.41	0.84	0.59 \pm 0.27	0.55 \pm 0.31	0.89	0.36 \pm 0.18	0.36 \pm 0.18	1
Chloride (mg/L)	22.0 \pm 2.7	21.9 \pm 2.8	0.66	105.7 \pm 23.5	67.5 \pm 10.5	0.002	30.6 \pm 16.9	31.1 \pm 17.0	0.98	32.8 \pm 13.7	32.7 \pm 13.1	0.86	18.21 \pm 3.3	18.5 \pm 3.5	0.88
Sulfate (mg/L)	33.2 \pm 7.6	33.4 \pm 7.4	0.98	116.2 \pm 62.1	97.6 \pm 60.0	0.02	104.8 \pm 47.2	105.4 \pm 49.2	1	111.9 \pm 42.6	112.1 \pm 44.7	0.89	25.0 \pm 3.0	25.0 \pm 2.8	0.95
CSMR [#]	0.68 \pm 0.10	0.67 \pm 0.9	0.98	0.99 \pm 0.27	0.83 \pm 28	0.17	0.29 \pm 0.05	0.29 \pm 0.05	0.80	0.29 \pm 0.10	0.29 \pm 0.10	0.93	0.73 \pm 0.13	0.75 \pm 0.14	0.74
TOC (mg/L as C)	2.0 \pm 0.7	1.6 \pm 0.7	0.04	2.2 \pm 0.7	2.3 \pm 0.8	0.61	1.2 \pm 0.9	1.0 \pm 0.7	0.45	1.5 \pm 0.7	1.6 \pm 0.5	0.77	1.61 \pm 0.48	1.62 \pm 0.47	0.77
Pb-Cu Pipe Galvanic Current (μ A)	24.8 \pm 4.5	19.7 \pm 3.7	<0.0001	36.3 \pm 13.9	51.3 \pm 14.7	0.0003	36.0 \pm 3.0	35.3 \pm 6.6	0.60	31.9 \pm 6.9	33.1 \pm 6.7	0.44	23.1 \pm 10.1	42.5 \pm 10.8	<0.0001
Water Age (Days)	0	0.75	-	<1	3	-	0	4-5	-	0	<1	-	0	0.5-0.75	-

*Average of 2010 data #Chloride:Sulfate Mass Ratio

Table 2-6. Summary of statistical analyses from Corrosion Evaluation Rigs.

Utility	WTP Avg. Pb Conc. (ppb)	DS Avg. Pb Conc. (ppb)	Pb Result	Pb p-value	WTP Avg. Cu Conc. (ppb)	DS Avg. Pb Conc. (ppb)	Cu Results	Cu p-value
Copper Solder								
A	4.8	3.5	No difference	0.21	43	40	No difference	0.26
B	3297	345	WTP greater	<0.0001	826	1073	DS greater	0.0003
C	12.9	7.6	No difference	0.11	96	90	WTP greater	0.034
D	2.0	1.9	No difference	0.20	293	275	No difference	0.19
E	6.8	2.7	WTP greater	<0.0001	294	327	DS greater	0.013
Traditional Lead and Copper LSL								
A	202	217	No difference	0.58	26	21	WTP greater	0.0017
B	2445	12807	DS greater	<0.0001	537	689	DS greater	0.004
C	294	220	No difference	0.25	44	41	No difference	0.47
D	265	130	WTP greater	0.0015	189	127	WTP greater	<0.001
E	1793	118	WTP greater	0.007	163	183	DS greater	0.0032
PVC and Brass								
A	3.8	3.8	No difference	0.42	5.8	6.4	No difference	0.074
B	10.1	13.3	DS greater	0.0014	181	152	WTP greater	0.015
C	2.7	13.1	No difference	0.08	19	11	WTP greater	<0.0001
D	16.7	4.9	No difference	0.57	98	49	WTP greater	<0.0001
E	118	4.9	WTP greater	0.0019	44	47	No difference	0.12

Lead Corrosion. In 33% of cases lead went down in the DS and increased in 13% of cases (Table 2-6). At utility B and E, lead leaching from copper pipes with lead solder was 9.5 and 2.5 times higher at the WTP respectively when compared to the DS (Figure 2-5) ($p < 0.0001$). On the other hand, there was no statistical difference for the other three utilities. Compared to the other 4 sites, Utility B had as much as 1650 times more lead release from solder.

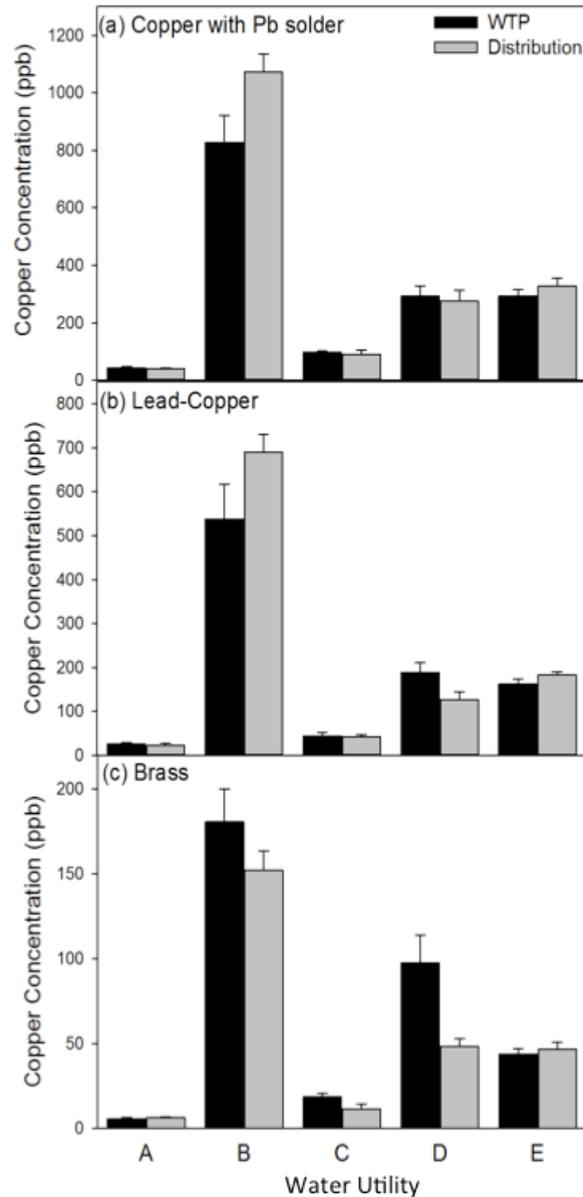


Figure 2-4: Influence of water age on copper release from (a) copper with lead solder (b) lead-copper and (c) brass test rigs at 5 utilities. Error bars represent 95% confidence intervals where n is between 33 and 36.

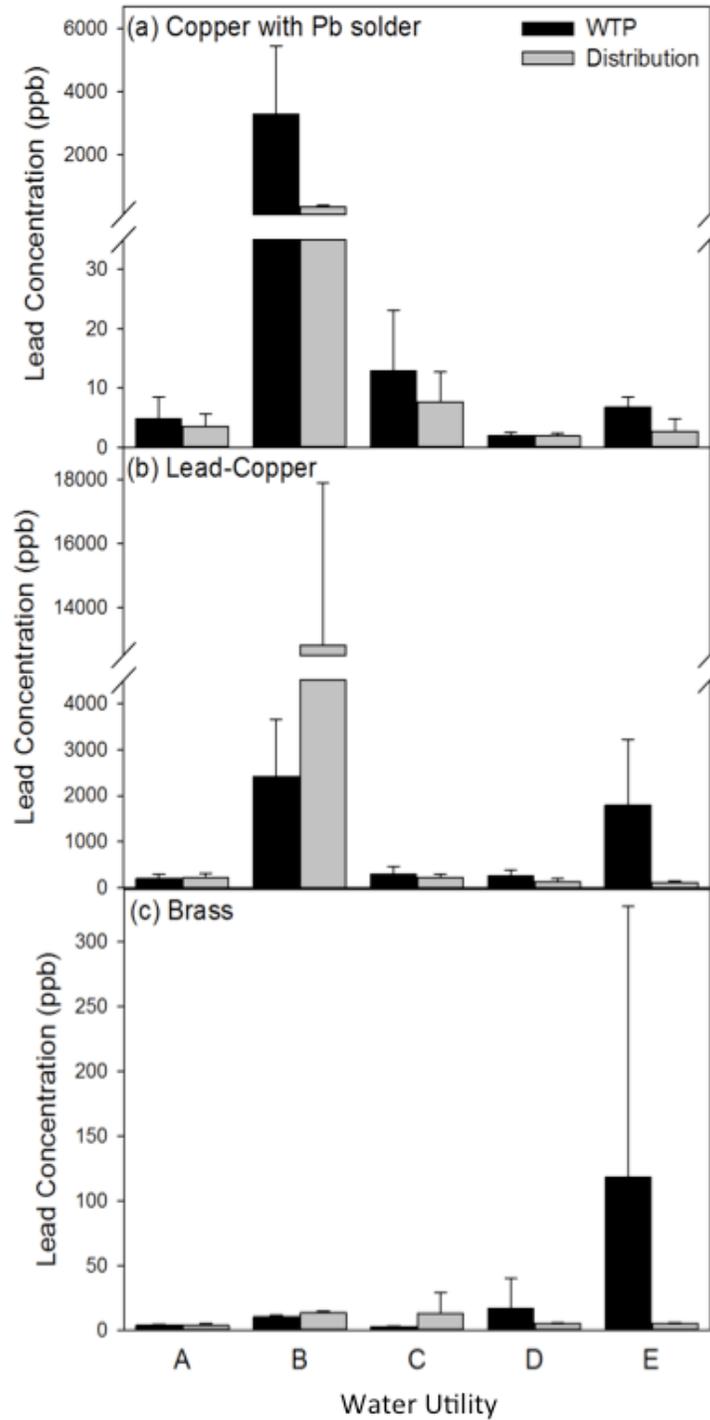


Figure 2-5. Influence of water age on lead release from (a) copper with lead solder (b) lead-copper and (c) brass test rigs at 5 utilities. Error bars represent 95% confidence intervals where n is between 33 and 36.

Lead release from galvanically connected lead and copper was 2 and 15 times higher at the WTP for utility D and E respectively. However, at utility B, average lead levels for the lead-copper test pieces was more than 5 times higher in the DS compared to the WTP

($p < 0.0001$). Similar to the copper leaching results, the highest average lead release occurred at utility B, which was as much as 110 times higher compared to the other sites. Probably the most significant water quality difference at utility B relative to the other 4 sites is that it was the only utility that used chloramines and also had the highest chloride, nitrate, and CSMR (Table 2-5). The significantly higher levels of lead at utility B are most likely due to the high CSMR, which has been shown to significantly increase lead corrosion of lead galvanically connected to copper (Nguyen et al. 2010b; Triantafyllidou and Edwards 2010 & 2011). At utility E, similar to the lead release from solder or lead-copper pipes, lead levels from brass test pieces were higher at the WTP compared to the DS ($p = 0.002$). At utility B, lead from brass was 32% higher in the DS compared to the WTP ($p = 0.001$) while there was no difference in lead levels between the WTP and DS at the other sites (Utility A, C and D).

Impact of Treatment Process on Metals Release

Utility C and D had the same source water but the different treatment processes resulted in slightly different chemistry and differences between the amount of lead and copper released (Table B3). Both utilities had relatively stable water quality between the WTP and DS (Table 2-5). However, utility C had a higher finished water pH (8.6 versus 7.4), a lower disinfectant concentration (1.1 mg/L versus 1.7 mg/L), lower total phosphate (132 $\mu\text{g/L}$ versus 229 $\mu\text{g/L}$), and lower aluminum (17 $\mu\text{g/L}$ versus 64 $\mu\text{g/L}$). Copper leaching was significantly higher at utility D for all materials ($p < 0.0001$). Average lead release from copper with lead solder was 7.5 times higher at the Utility C WTP compared to Utility D WTP ($p < 0.001$). However, comparing the DS lead levels, even a difference of 4X more lead was not statistically significant at 95% confidence for utility C and D for lead solder ($p = 0.07$) due to the extreme variability in lead release for this condition. Lead leaching from brass was 6.2 times higher at site D WTP compared to the Utility C WTP ($p < 0.001$). On the other hand, lead leaching from brass was 2.7 times higher at the Utility C DS relative to Utility D ($p = 0.02$). Comparing the DS, average lead leaching from the copper-lead pipes was 70% higher at C compared to D ($p = 0.02$).

Sample Site Selection Criteria

The existing and proposed U.S. E.P.A LCR is intended to target sampling at “worst case” sites. In the past, selection of “worst case” sites has focused exclusively on identifying homes with the highest propensity to leach lead from plumbing based on a tier system of age and lead bearing materials that are present in homes (Ferguson et al. 1996; Broo et al. 1997; Friedman et al. 1999; Edwards et al. 2001; Rajaratnam et al. 2002; Schock and Sandvig 2009; Turek et al. 2011; Grace et al. 2012). It has recently been acknowledged that other risk factors in homes can be of equal or greater importance including the length of lead service lines (Kuch and Wagner 1983; Cardew 2006; Cartier et al. 2011), whether the service line has been disrupted by a partial replacement or other activities (Boyd et al. 2004; Sandvig et al. 2008; Triantafyllidou and Edwards 2011; Cartier et al. 2012; Del Toral et al. 2013), and even water use rates in the home (Arnold and Edwards 2012; Del Toral et al. 2013). This research unambiguously demonstrates that the location of a home in a given water distribution system can also influence lead leaching, creating hot-spots of corrosion that are associated with greater incidence of childhood lead poisoning and even fetal death (Stith et al. 2006; Renner 2006; Gronberg 2007; Edwards et al. 2009;

HDR 2011; Wang et al. 2014; Edwards 2014). As a part of this study, we examined whether high-risk sites for lead are likely to also be high-risk sites for copper. There were two occasions where lead and copper were both statistically higher at the same location: lead and copper release from the lead-copper pipes were both statistically higher in the DS at Utility B and Utility D WTP. On the other hand, there were 4 cases where lead and copper were statistically higher at different sites within the same distribution system. This confirms reasonable expectations that risks of elevated lead and copper are unlikely to occur at the same location, even without consideration of water age (Schock and Sandvig 2009). Furthermore, in order to identify “worst case” homes, sampling of lead and copper will have to be conducted separately.

CONCLUSIONS

- Water age and associated changes in biology/chemistry can be important factors influencing corrosion in water distribution systems and in identifying hotspots for consumer exposure to lead and copper. This study demonstrates that water corrosivity can vary significantly throughout the distribution system with increased water age; however, whether the corrosivity increases or decreases is site-specific and ultimately determined by the specifics of plumbing, microbiology and chemistry.
- In the SDSs and CERs, the highest relative lead release was associated with pure lead, followed by lead solder connected to copper and then leaded brass pipes. In the SDSs, the copper and lead release pattern ranged from –98% lower to 440% higher than day 0 and was dependent on circumstance.
- Across the 5 utilities, lead and copper release was not consistently higher in the distribution system when compared to the treatment plant. Furthermore, in many cases, high-risk of elevated lead and copper did not co-occur which suggests that these contaminants will have to be sampled separately to identify “worst case” homes for lead or copper.
- Two utilities that shared the same water source but different treatment processes had markedly different levels of lead release, confirming that drinking water treatment processes and finished water quality can have significant effects on corrosion control.

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APPENDIX B

Supporting Information for Chapter 2 Distribution System Water Age Can Create Premise Plumbing Corrosion Hotspots

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KEYWORDS. Water age, corrosion, lead, copper

Figures

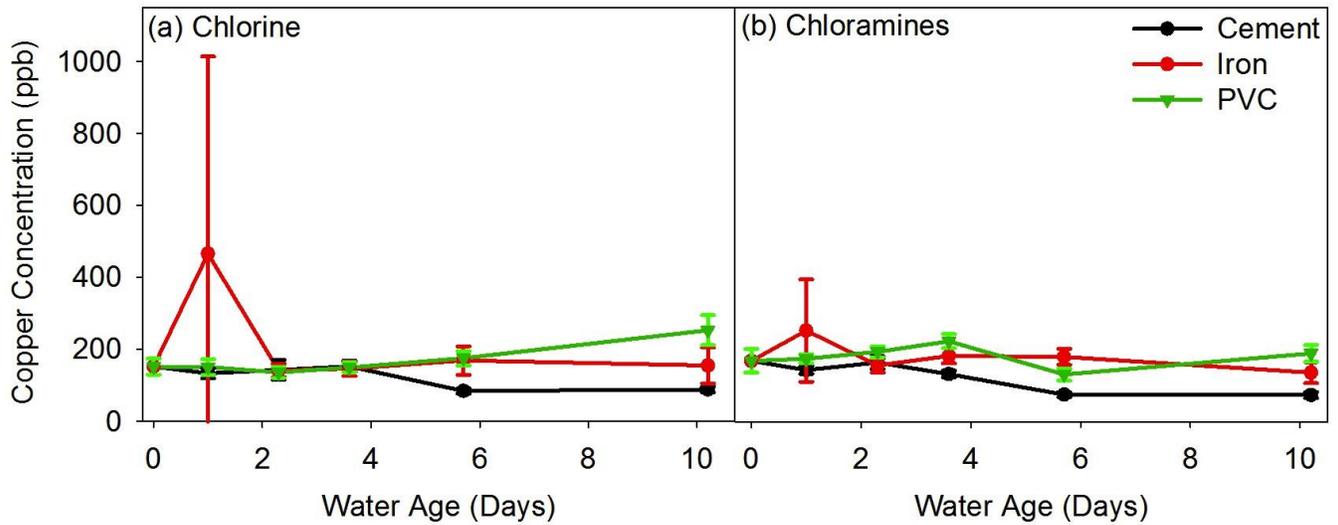


Figure B1. Copper release from brass coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.

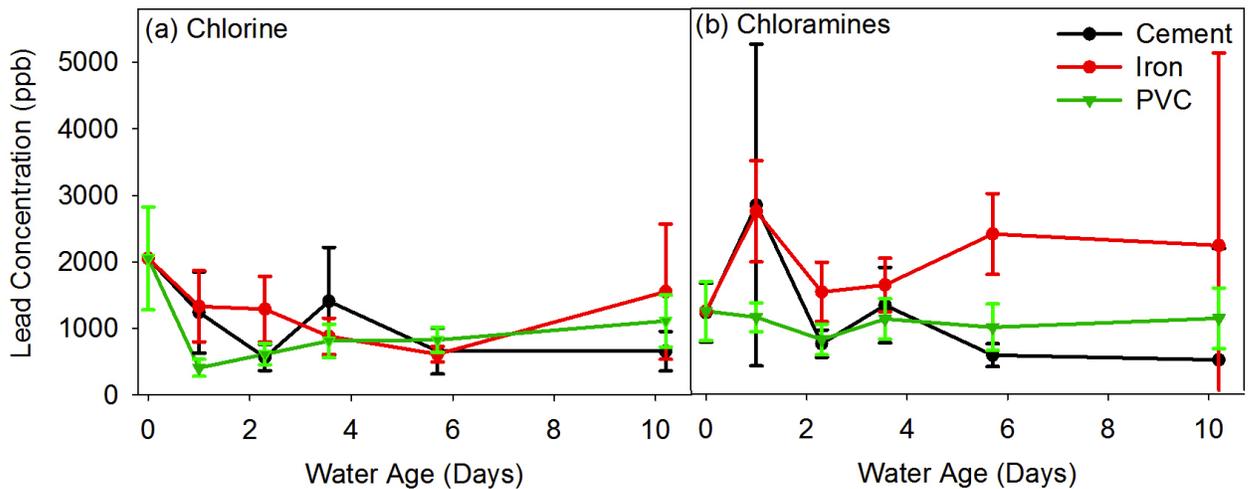


Figure B2. Lead release from copper with lead solder coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 30.

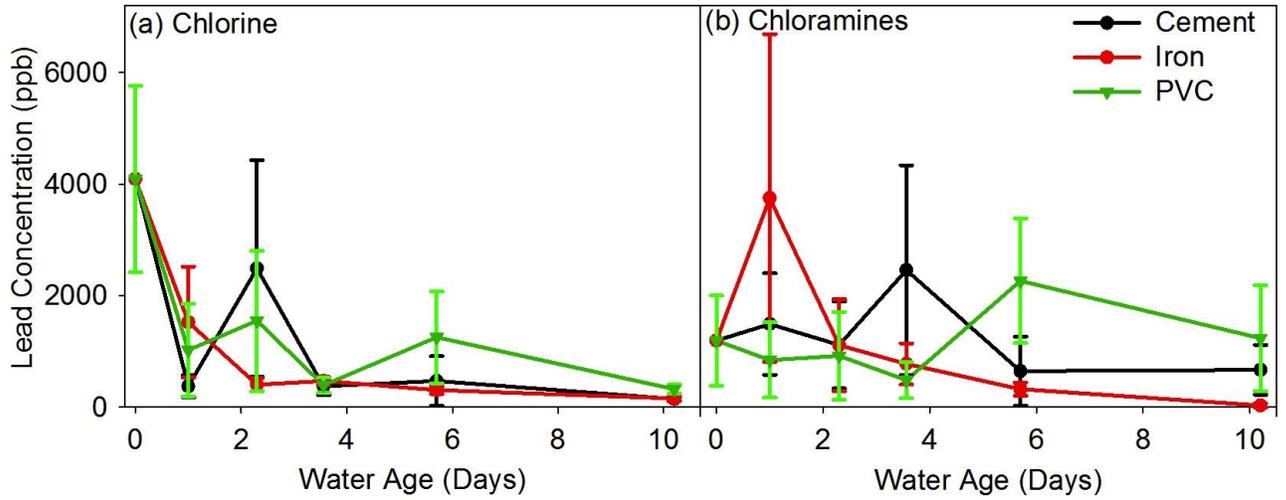


Figure B3. Lead release from lead coupons as a function of pipe main material and water age in (a) chlorinated and (b) chloraminated simulated drinking water distribution systems. Error bars represent 95% confidence intervals where n is 3.

Table

Table B1. Comparison of average lead and copper release between Utilities C and D.

Metals	WTP				DS			
	Utility C	Utility D	Comparison	p- value	Utility C	Utility D	Comparison	p-value
Lead Comparison								
Copper-Solder	12.9	2.0	C Higher	<0.001	7.6	1.9	No difference	0.07
Copper-Lead	294	265	No difference	0.07	220	130	C Higher	0.02
Brass	2.7	16.7	D Higher	<0.001	13.1	4.9	C Higher	0.02
Copper Comparison								
Copper-Solder	96	293	C Higher	< 0.0001	90	275	C Higher	< 0.0001
Copper-Lead	44	189	C Higher	< 0.0001	41	127	C Higher	< 0.0001
Brass	19	98	C Higher	< 0.0001	11	49	C Higher	< 0.0001

CHAPTER 3. INCREASED LEAD IN WATER ASSOCIATED WITH IRON CORROSION

Sheldon Masters and Marc A. Edwards

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ABSTRACT

When attempting to reduce lead solubility by lowering the finished water pH in Providence, RI from ~10.3 to 9.7, consumer “red water” complaints and overall lead levels increased, prompting bench scale tests and intensive field sampling into possible associations between higher particulate iron and particulate lead. At pH 10.3, iron release to water was as much as 35% lower in bench scale tests and 99% lower in field samples when compared to pH 9.7. The lower levels of particulate iron released at higher pH, translated to lower levels of particulate lead release after contacting downstream plumbing in bench testing. Although a significant decrease in distribution system iron at pH 10.3 did not immediately translate to decreased lead levels at all field-sampling sites, the complementary laboratory and field studies demonstrate that lead corrosion control is sometimes strongly linked to iron corrosion control.

KEYWORDS: corrosion; iron; particulate lead, profile sampling

INTRODUCTION

The release of lead into drinking water due to the corrosion of lead bearing pipe materials continues to be a major public health concern (Edwards et al., 2009; Brown et al., 2011; Triantafyllidou and Edwards, 2012; Edwards, 2014). In general, water utilities have controlled the release of lead from plumbing materials by maintaining water conditions such as pH and alkalinity that suppress lead dissolution (Sheiham and Jackson, 1981; Schock and Gardels, 1983; Schock et al., 1996). However, in some cases, a majority of lead in potable water has been identified as particulate rather than soluble lead (Reiber et al., 1997; McNeill, 2000; Triantafyllidou, 2006). Past studies have found that plumbosolvency can be significantly reduced by increasing the finished water pH to 9 or above in the presence of low levels of inorganic carbon (Schock and Gardels, 1983; Dodrill and Edwards, 1995; Tam and Elefsiniotis, 2009; Xie et al., 2010; Kim et al., 2011; Xie and Giammar, 2011), even as particulate lead has been found to be more important at higher pH conditions (Kim et al., 2011; Xie and Giammar, 2011).

Exactly how particulate lead is formed and released to water is relatively poorly understood, and quantification of this problem is highly sensitive to nuances of sampling including flow rate during sampling (Reiber et al., 1997; Triantafyllidou and Edwards, 2012; Clark et al., 2014). Obviously, the durability and adherence of lead rust/scale to pipes is one key factor, although as a practical matter, little is known about factors that control these characteristics (McNeill and Edwards, 2004). Anecdotally, several studies have identified links between high levels of particulate lead and particulate iron in both natural and engineered systems, suggesting that mitigation of particulate lead problems might sometimes be associated with reducing other particulates present in the distribution system (Hulsmann, 1990; Erel et al., 1991; De Rosa and Williams, 1992; Erel and Morgan, 1992). More recent studies have elucidated more definitive links between elevated particulate lead and particulate iron in drinking water (HDR, 2009; Deshommes et al., 2010; Camara and Gagnon, 2012; Triantafyllidou and Edwards, 2012; Camara et al., 2013; Schock et al., 2014; Knowles et al., 2015). Given that more than a quarter of the distribution system in the United States is unlined iron (Baird, 2011), a better understanding of the potential link between lead and particulate iron is important.

Links between Pb:Fe in natural and engineered systems

Erel et al. (1991) and Erel and Morgan (1992) found that naturally occurring lead in the Sierra Nevada watershed was sorbed by particulate iron oxide surfaces at a relatively consistent rate. The authors speculated that the mechanism of removal by sorption resulted in a correlation between iron and lead particulates. It is logical to think that a similar phenomenon may also occur in certain lead service lines, when particulate iron is either present in the distributed water or formed in the distribution system by corrosion of iron water mains. Field studies conducted by WRC Group in the United Kingdom in 1987 found that elevated particulate lead levels were associated with elevated levels of particulate iron and organic matter (De Rosa and Williams, 1992; Hulsmann, 1990). Water supplied in these areas had low alkalinity, low hardness, discoloration and high concentrations of natural organic matter, and poor pH control (De Rosa and Williams, 1992; Hulsmann, 1990). It was speculated (De Rosa and Williams, 1992) that particulate iron released from mains was transported to lead service lines, where dissolved lead was

adsorbed to the surface of iron particulates. The iron with sorbed lead may then be mobilized or released to potable water by turbulence when the consumer draws water, resulting in “excess” lead in the water relative to that which would be present by dissolution alone. This particulate lead problem was eventually solved by measures that reduced particulate iron, including the use of corrosion inhibitors and systemic cleaning of the distribution system (Hulsmann, 1990). Although the link between iron corrosion and particulate lead problems was only circumstantial, this study raised prospects that lead corrosion issues must sometimes be solved by reducing iron corrosion.

Similar findings were made in 2008, when the District of Columbia Water and Sewer Authority found that at least 75% of homes that exceeded the lead action level (LAL) for either first and/or second draw samples also had elevated levels of iron (i.e., > 79 ppb) (HDR, 2009). It was hypothesized that galvanized iron pipes installed in homes during the mid-twentieth century could be a persistent source of high lead even after the removal of the lead service line (McFadden et al., 2011). Studies by Deshommes et al. (2010) of random daytime samples collected from 45 homes with lead service lines (LSLs) also found situations in which particulate lead and particulate iron from the distribution system were correlated ($R = 0.58$). More recently, researchers using a Dalhousie pipe loop found that particulate iron from iron corrosion in the distribution system caused more lead release from 50/50 Pb/Sn solder in simulated home plumbing (Camara and Gagnon, 2012). The researchers hypothesized that the release of iron rust to the lead soldered copper pipes, with subsequent sorption of lead to the iron and then entrainment into flowing water, was a viable explanation for these observations. The authors also conducted bench scale adsorption tests demonstrating very strong sorption of lead to iron oxides, including magnetite and goethite, confirming a mechanistic basis for this hypothesis. Camara et al. (2013) also found trends similar to that of WRc Group, in that areas served by tuberculated cast-iron mains had increased lead release in homes. Other iron solids transported to lead plumbing, including those from carryover of ferric coagulant from water treatment processes, have also been associated with mobilization of lead (Knowles et al., 2015).

The Case of Providence, RI highlights research need

Prior to 2005, Providence Water was close to, but always under, the US EPA Lead and Copper Rule (LCR) Action Level. Desk-top studies based on conventional lead corrosion control by minimizing lead solubility predicted that lead release would be further reduced by decreasing the pH from ~10.3 to pH ~9.7. Unfortunately, when this change was implemented the opposite trend was observed (Figure 3-1) (Rego and Schock, 2007). Concomitant with the higher lead in water was a noticeable increase in “red water” consumer complaints due to higher iron levels from the more than 500 miles of unlined cast iron (Providence Water, 2013; O’Neill, 2013), highlighting gaps in understanding the interplay between iron corrosion and lead corrosion control, especially in high pH and low alkalinity water. In order to bring the finished water chemistry closer to the theoretical optimum for lead solubility in terms of pH and dissolved inorganic carbon (DIC), a carbon dioxide feed system was put into service in April 2011 (O’Brien & Gere, Inc., 2014).

The objective of this research was to examine links between iron and particulate lead release to potable water at laboratory and field scale. As part of the overall evaluation, field samples were collected from homes in the Providence, RI distribution system before and after the changes in corrosion control in June 2011 and August 2013 to assess trends in soluble and particulate metal release as a function of water flow rate.

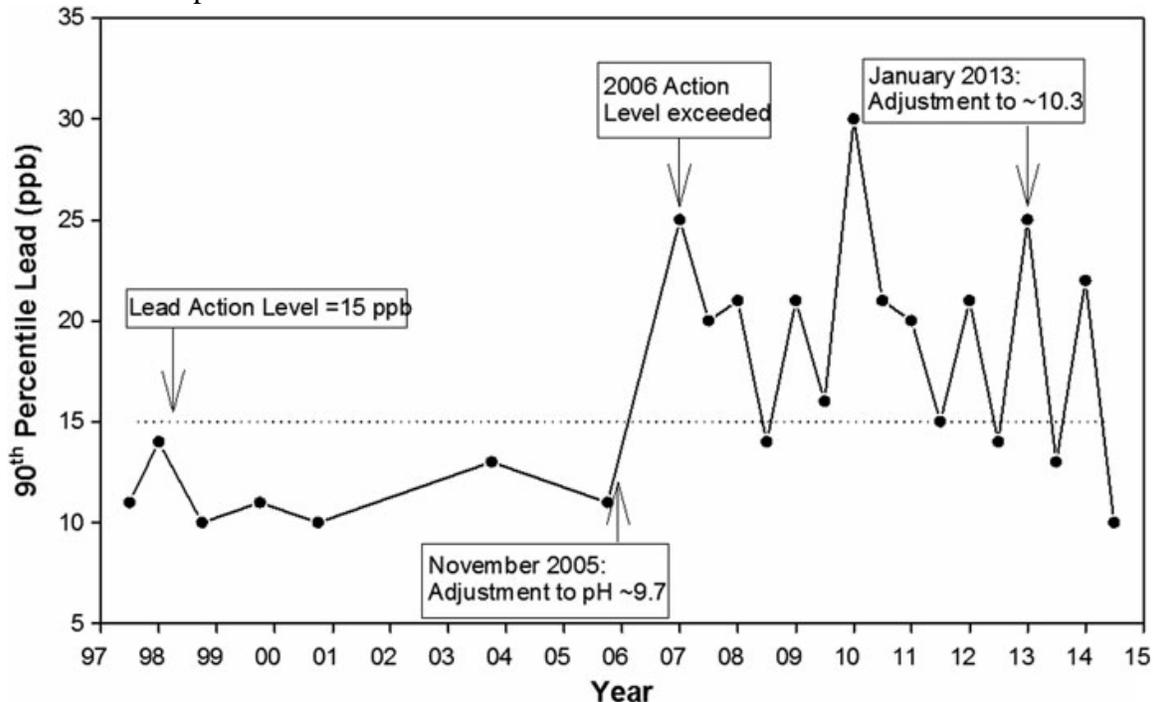


Figure 3-1: Providence, RI, Lead and Copper Rule compliance between 1997 and 2014. Beginning in 2006, after lowering pH from 10.3 to 9.7, there was a significant increase in the 90th percentile lead levels.

MATERIALS AND METHODS

Profile Sampling

The typical finished water quality conditions present in Providence during 2011 and 2013 indicate a high pH (> 9.5) and low alkalinity (< 26 mg/L as CaCO₃) distributed water consistent with corrosion control targets in each timeframe (Table C1). Conventional “profiling” involves the collection of sequential tap water samples at a fixed flow rate after a minimum of a 6-hour stagnation event. A new profile sampling protocol developed by Clark et al. (2014) was employed in the field. The protocol involves collecting sets of samples at low, moderate and then high flow rates. Comparison of the three sets of samples allows a dimension of flow rate (water velocity) in lead release to potable water flowing into homes to be elucidated.

Between June 17th and June 21st, 2011, lead and iron profiles were collected from twelve homes in Providence, RI in order to evaluate consumer exposure to lead and iron. Since January 2013, Providence Water has increased their finished water pH from 9.7 to 10.3 in an attempt to reduce distribution system corrosion. Based on this change, on August 12-13th, 2013, three homes (Site A, B, and C) which previously sampled high for iron and lead were resampled in order to compare the change in metals concentration at these three

sites. Site A had a full-lead service line while Sites B and C had partial lead service line replacements. The average temperature during the 2013 sampling period was 2.2 degrees Celsius higher than the 2011 sampling period which is likely to slightly increase lead release in 2013.

Three sequential profiles were collected after a 6-hour minimum stagnation time (Figure C1). For the low flow profile, nine sequential one-liter samples were collected at a rate between 1.3 L/min and 1.7 L/min. The tap was allowed to run for 3 minutes before collecting the tenth one-liter sample. Immediately afterwards, without allowing any stagnation time, the tap was fully opened and a moderate flow (Flow rate = 5.5 L/min to 10 L/min) sequential profile was collected. Finally, high flow (Flow rate = 6.7 L/min to 15 L/min) sequential samples were collected by removing the aerator from the faucet and opening the tap fully. A 10 mL aliquot from liters 3 and 5 in each profile was filtered in the field using a 0.45 μm pore size nylon syringe filter (Whatman) and a 10 mL BD syringe to operationally determine soluble and particulate metals in these samples (i.e., the 3rd and 5th liter). These samples were selected for filtration because the 3rd and 5th liter of a profile often contains water with soluble and particulate lead from the service lines (Cartier et al., 2012; Clark et al., 2014).

Sample Analysis

Samples were digested using 2% nitric acid and 1% hydroxylamine by volume in the original sample bottle with heated exposure of 50° C for at least 24 hours. Total metal concentrations were analyzed using a Thermo Electron X-Series inductively coupled plasma mass spectrometry (ICP-MS; Thermo Electron, Waltham, MA) based on Standard Method 3125B (Clesceri et al., 1998).

Bench Scale Testing

Bench scale testing was conducted to determine effective corrosion control strategies for low alkalinity, high pH waters analogous to Providence, RI. The overall experiment consisted of two phases. Phase 1 involved testing the effects of pH on iron release. The water derived from the Phase 1 reactors was used as the influent water for testing of lead corrosion in Phase 2, analogous to sequential exposure occurrence in a water distribution system where water first flows through iron pipe and then contacts lead pipe.

Phase 1: Effects of pH on iron corrosion

The effects of pH on iron release was examined using a synthesized water (SW) recipe developed by Wang et al. (2012) to simulate Providence tap water, but modified with the addition of 4.5 mg/L of silica as SiO₂ and 0.3 mg/L natural organic matter (NOM) as C to better match the actual Providence finished water (SW+NOM) (Table C2). The water was tested at three different pH conditions (pH 8.3, 9.7, and 10.3) using single batch reactors for each pH condition for 24 weeks. The pH in the batch reactors was adjusted using sodium hydroxide and CO₂. During week 12 of the experiment, a set of triplicate batch reactors was started in order to verify the trends in iron release observed in the individual reactors with statistical confidence. Each reactor consisted of an iron coupon (1/2-inch diameter by 1-inch long) which was epoxied to the bottom of a glass bottle with a working volume of 600 mL, resulting in an iron surface area to water volume ratio of

0.05 inch⁻¹. This ratio is roughly equivalent to that found in a 40-inch radius iron pipe. The iron coupon was an alloy which consisted of 95.3% iron (Table C3). The reactors were mixed using an orbital shaker table.

Every Monday/Wednesday/Friday, 10 mL aliquots were taken from each batch reactor to generate weekly composite samples characteristic of the influent iron concentration to each lead pipe. At the end of each week, the composite sample (30 mL) was digested using 2% nitric acid and 1% hydroxylamine by volume and the iron concentration was analyzed using inductively coupled plasma mass spectrometry (ICP-MS; Thermo Scientific Thermo Electric X Series) using Standard Method 3125B (Clesceri et al., 1998). Water taken from the batch reactors was used as the influent for the corresponding lead dump-and-fill experiment described below (Phase 2b). Since 27% (160 mL) of the water was removed, water in each batch reactor was refilled after each water transfer to the lead pipes.

Phase 2: Impact of Iron on Lead Corrosion

Phase 2 consisted of two steps which included: Phase 2a) pre-conditioning of new lead pipes, and Phase 2b) exposure of the lead pipes to water containing iron particulates generated in Phase 1.

Phase 2a: Conditioning of Lead Pipes

Eighteen 6-inch pieces of new lead pipe were conditioned for 4 weeks by pumping water continuously through the pipes in a recirculating system with the modified synthetic water (SW+NOM) described above at a high pH (i.e. 10.3). After the pipes were conditioned, they were separated into 6 groups (3 pHs x 2 levels of iron [SW+NOM+Fe]) with triplicates tested at each condition. During conditioning, the water in the reservoirs was emptied once per week and replaced with fresh water.

Phase 2b: Exposure of Lead Pipes to Iron Particulates

Water was changed for each lead pipe 3 times per week (MWF) using a dump-and-fill protocol over a 24-week period (Figure C2). As a control, water from batch reactors without any iron present was used to fill half of the lead pipes. Weekly composite samples of the entire volume of water in the lead pipes were collected and analyzed using ICP-MS. At the beginning of week 20 and 25, samples were collected and analyzed to determine the relative proportions of soluble and particulate lead in each condition. Soluble samples were collected by filtering a 10 mL aliquot using a 0.45 µm pore size nylon syringe filter (Whatman) and a 10 mL BD syringe. The remaining water was then analyzed for total metals concentration.

Statistical Analysis of Results

A Shapiro-Wilks test was used to determine if the data were normally distributed. A t-test on normalized data or a non-parametric Wilcoxon test was used to measure the difference between two groups. An analysis of variance (ANOVA) test on the log-transformed normalized data was used to determine if there was a significant difference between the means of the 3 iron conditions in Phase 1. A three-way analysis of variance (ANOVA) test was also conducted using the log-transformed lead measurements to compare the 6

different lead conditions in Phase 2 with pH, iron and water type as factors. Post-hoc analysis was conducted using Tukey HSD multiple comparison test. Pearson's rank correlation coefficient was used to measure the linear relationship between lead and iron. All statistical analyses were performed in R (<http://www.r-project.org/>) with significance defined as $p < 0.05$.

RESULTS AND DISCUSSION

After discussing results of the bench scale testing examining effects of chemistry on various aspects of iron and lead corrosion, field test results are analyzed in the context of the full-scale monitoring data and experiences of the Providence water system.

Bench Scale Testing

Iron Corrosion. Iron release stabilized after 5 weeks. Data for the steady-state period (i.e. weeks 6-24) were averaged to compare relative differences between different treatment conditions (Figure 3-2). ANOVA analysis indicated no statistical difference between the pH 8.3 and 9.7 condition ($p = 0.86$). However, the pH 10.3 conditions had as much as 35% less iron when compared to the 8.3 and 9.7 conditions ($p < 0.05$), consistent with the expectation that higher buffering capacity produced at the higher pH will reduce iron release in low alkalinity waters (Vik et al., 1996; Benson et al., 2012). This trend was confirmed in the triplicate iron batch reactors where the pH 10.3 condition had up to 63% less iron ($p < 0.05$) when compared to the pH 8.3 and 9.7 conditions (Figure C3). Additionally, the pH 10.3 conditions tended to form a denser more protective scale when compared to the pH 8.3 or 9.7 conditions (Figure 3-3). Based on these results, it would be expected that if the pH was decreased from 10.3 to 9.7 in the Providence, RI distribution system, there would be a significant increase in iron levels.

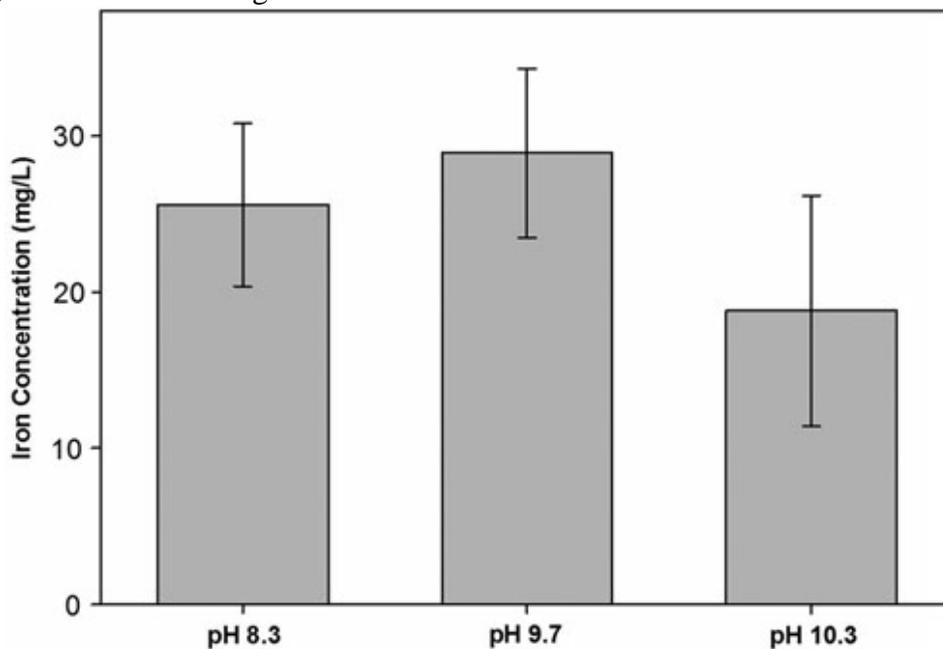


Figure 3-2: Average iron concentration after iron release stabilized (weeks 6-24). Error bars represent 95% confidence intervals.

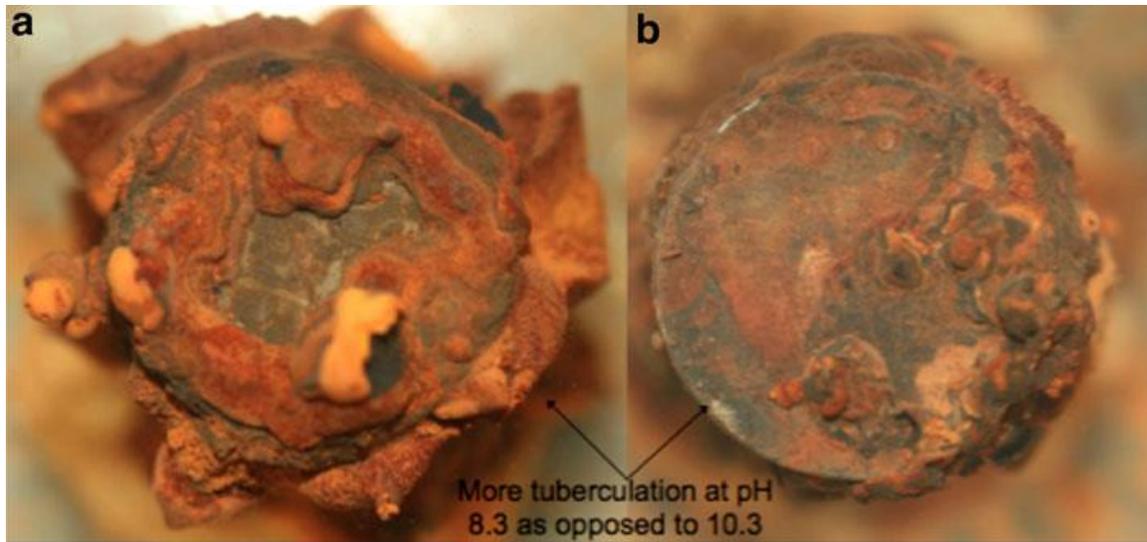


Figure 3-3: Comparison of representative coupons at (a) pH 8.3 and (b) pH 10.3.

Lead Release. Stabilization of the lead pipes took 6 weeks. The data collected after the stabilization period (i.e. week 6-24) were averaged to compare the effect of different treatments on lead corrosion (Figure 3-4). Based on the three-way ANOVA, there was a significant interaction effect between water type, pH and the presence of iron on lead corrosion. All the conditions with iron present in the influent pipes had more than 150% more lead release than the corresponding controls without iron which is likely due to the sorption and/or co-precipitation of lead onto the iron particles since more than 99.9% of the influent iron was particulate (Figure 3-4) ($p < 0.001$). This is analogous to detached iron particles from water mains flowing into a lead service line and adsorbing lead and then releasing it at consumer taps through desorption or dissolution (Camara, Montreuil, Knowles, & Gagnon, 2013; Friedman et al., 2010). The highest average lead occurred in the pH 9.7 condition with iron, while the lowest average lead levels were observed in the pH 10.3 condition without iron. This suggests that reducing corrosion of iron mains and maintaining a pH of ~ 10.3 was more effective at reducing lead release in this low alkalinity water.

Speciation of Lead. The cumulative mass of lead release from the triplicate samples were examined for soluble and particulate lead. Particulate lead species played a major role in the lead corrosion by-product release. Between 61% and 99% of the lead was determined to be particulate (Table 3-1). For the given water quality without iron (SW+NOM), soluble lead measurements were lowest at the pH 9.7 condition compared to pH 8.3 and 10.3. Soluble lead was 175% and 30% higher at the pH 8.3 and 10.3 conditions, respectively, compared to pH 9.7. This is consistent with theoretical predictions that the lowest lead solubility will occur at pH ~ 9.8 (Schock and Lytle, 2010). However, based on these results, in the case of Providence, RI, the benefits associated with decreased solubility would be outweighed by the fact the total lead would increase at pH 9.7 (Figure 3-5). Similar trends were seen for the corresponding conditions with iron where soluble lead was more than 50% lower at pH 9.7 when compared to pH 10.3.

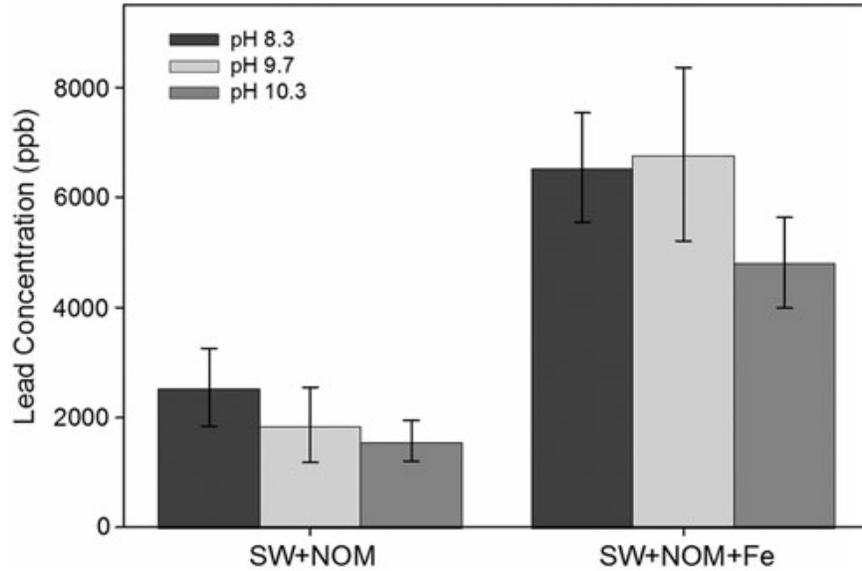


Figure 3-4: Average lead concentration after lead release stabilized (week 6-24). Error bars represent 95% confidence intervals.

Table 3-1: Cumulative mass of soluble and particulate lead in triplicate samples (Week 25).

Condition	Soluble (µg)	Particulate (µg)	Total (µg)	Percent Particulate
SW+NOM 8.3	102	109	211	52%
SW+NOM 9.7	37	92	129	71%
SW+NOM 10.3	52	125	177	71%
SW+NOM+Fe 8.3	15	1,044	1,060	99%
SW+NOM+Fe 9.7	23	540	562	96%
SW+NOM+Fe 10.3	58	398	456	87%

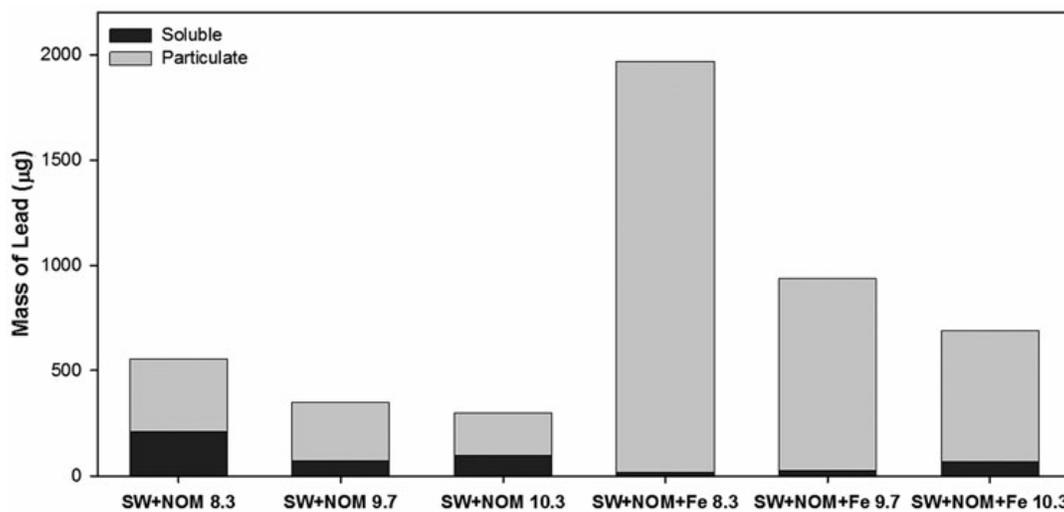


Figure 3-5: Cumulative mass of soluble and particulate lead in triplicate samples (week 20 and 25).

Relationship between Lead and Iron in Bench Scale Testing. Based on the Pearson's rank correlation coefficient, there was a statistically significant correlation between total iron and lead ($R^2= 0.54$, $p < 0.001$, Figure 3-6). There was also a strong relationship between particulate lead and iron (Figure C4, $R^2 = 0.74$). This is consistent with previous studies that have demonstrated that in both natural and engineered systems lead will tend to adsorb to iron oxide particles (Erel et al., 1991; De Rosa and Williams, 1992; HDR, 2009; Deshommes et al., 2010; Friedman et al., 2010; McFadden et al., 2011; Camara and Gagnon, 2012; Camara et al., 2013). The implication is that the presence of iron reservoirs on lead pipes, can increase lead release via lead-rich iron particulates.

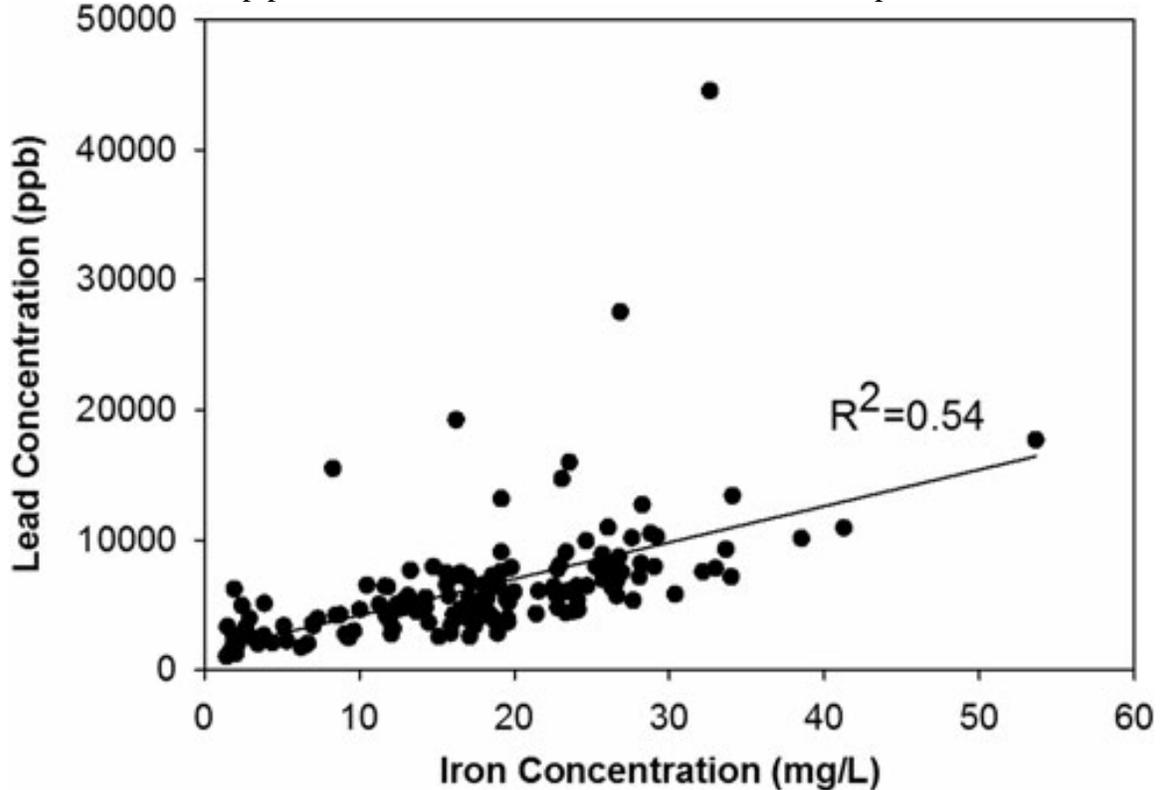


Figure 3-6: Relationship between iron and lead.

Profile Sampling

Based on results from the bench scale test and results of distribution system monitoring by others, a panel of water quality experts set up by Providence Water recommended that the finished water pH be increased to the pre-2005 level of ~10.3. Eight months after the implementation of this corrosion control strategy, profiling was conducted in order to evaluate the effectiveness of the corrosion control approach.

Iron Corrosion. The iron release from consumer taps as a function of time and flow rate was examined using profiling. Samples were collected from 12 homes in June 2011 and the 3 worst-case homes were resampled in August 2013. Data from the 3 worst-case homes were compared to each other to assess the effectiveness of the corrosion control strategy implemented by Providence Water. The cumulative iron released during low flow rate sampling decreased between 68% and 89% comparing 2013 to 2011 (Table

C4). At moderate flow, which is typical of consumer water use, iron levels were between 84% and 99% lower in 2013 than in 2011. At high flow, cumulative iron release decreased between 44% and 74%. At all sites, flushed samples (presumably representing water from the distribution system) indicated that iron levels decreased in all cases between 29% and 84% in 2013 versus 2011 (Table C4). These results are consistent with the results from the bench scale tests and theory, which predicted that pH 10.3 conditions would have significantly less iron than lower pH conditions. Furthermore, the field sampling results are consistent with the fact that there has been a 67% reduction in discolored water complaints between January and July 2013 (Welter, personal communication, September 23, 2013).

Lead Release. Given the dramatic decrease in iron that was observed between 2011 and 2013 and the literature review conducted herein, it would have been expected that a significant decrease in lead levels would have been observed in all sample sites. However, comparing the profile collected at very low flow in 2011 and 2013, cumulative lead levels only decreased between 11% and 14% at two sites (Site B and C respectively) and increased by 82% at Site A (Table C4). For the profile collected at moderate flow reflecting typical consumer use, cumulative lead release was lower at Sites A and B (58% and 72% respectively) and higher at Site C by 12%. Finally, at atypically high flow rates, lead levels were 63% lower at Site B. At the other two sites, lead levels were between 135% and 142% higher at the atypically high flow rates.

Thus, even though increasing the finished water pH from ~9.7 to ~10.3 resulted in a significant decrease in iron, unfortunately the higher pH is expected to increase the amount of lead sorbed per unit iron present (Table C5) (Schultz et al., 1987; Stumm and Morgan, 1996). At a given site, the net result depended on whether the decrease in lead due to less iron, was greater than the increased lead content per iron particle. For example, even though the ratio of particulate lead to particulate iron was 90 times higher in 2013 for the moderate flow samples at Site A, the cumulative mass of iron decreased by 99%, which resulted in a net decrease of 58% in overall lead release. On the other hand, at Site C the ratio of particulate lead to particulate iron was 7 times higher in 2013 for moderate flow samples but iron only decreased by 86%, which resulted in a net increase of 12% in overall lead. It is currently believed that a very large reservoir of iron has accumulated on the lead pipes over the years, which might take a very long time to deplete even after iron stops accumulating. This creates a longer-term problem with lead particulate release, consistent with prior research on long-term problems associated with inorganic contaminant reservoirs in distribution systems (Reiber and Dostal, 2000; Lytle et al., 2004; Schock, 2005; Cantor, 2006; Lytle et al., 2010; Deshommes et al., 2010; Schock et al., 2014).

Speciation of Lead. A filtered sample of the 3rd and 5th liter of each profile was analyzed in order to characterize the relative fraction of particulate versus soluble lead. The results for all three profile conditions seem to confirm theoretical expectations (Schock and Lytle, 2010) that the increase in finished water pH by ~0.5-pH unit could increase soluble lead (Figure 3-7). It is also possible that warmer temperatures in 2013 versus 2011 could

have also played a role in increased lead solubility. The average soluble lead in the 2013 low flow profiles was 9.0 ppb versus 16.0 ppb in 2011 ($p = 0.39$).

For the profile collected at moderate flow (with no prior stagnation), particulate lead decreased ($p = 0.04$) in 2013 (6.2 ppb) versus 2011 (29.3 ppb) (Figure 3-7 and Table C6). Average soluble lead release for moderate flow profiles was 3 times higher in 2013 compared to 2011 ($p = 0.002$). The net result is that for the total lead release at low and moderate flow, results in August 2013 had less lead than in June 2011, despite the fact that August 2013 had warmer temperatures which might be expected to increase lead release. In 2013, the average soluble lead in high flow samples was 2.0 ppb compared to 10.2 ppb in 2011 ($p = 0.07$). The average particulate lead was 66.8 ppb in 2013 versus 29.4 ppb in 2011 for samples at this atypically high flow rate ($p = 0.82$).

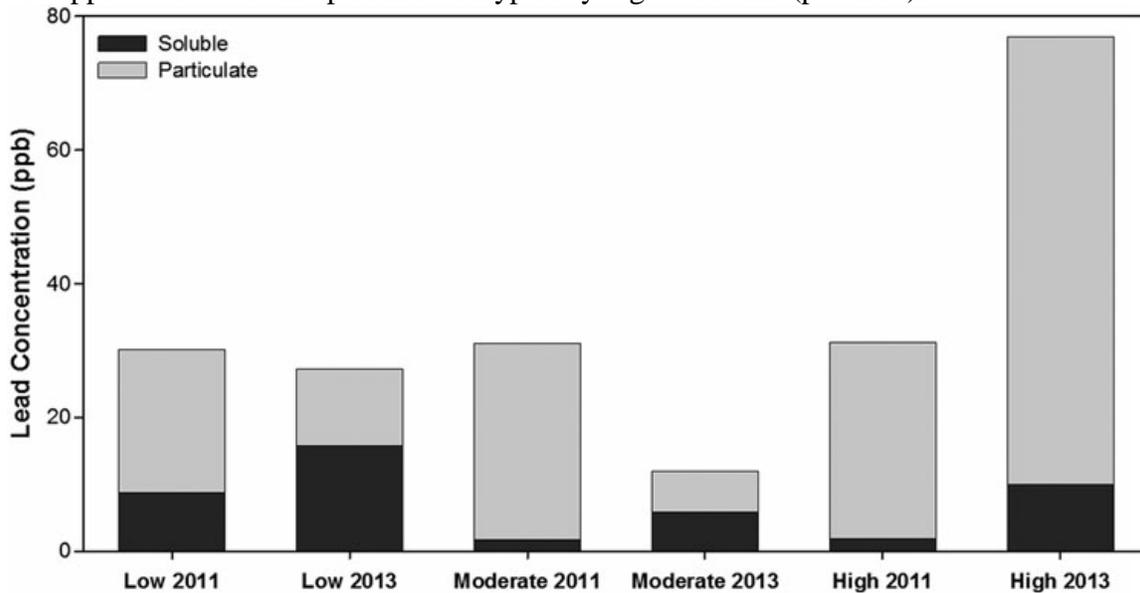


Figure 3-7: Stacked bar chart comparing the average soluble and particulate lead at low, moderate, and high flow rates for representative sites.

Relationship between Lead and Iron at Individual Homes. A strong association between lead and iron was observed from profiling at moderate flow for Site A and B in 2011. At Site A there was almost a 1:1 ($R^2 = 0.97$, $p < 0.0001$) correlation between iron and lead for samples collected at moderate flow in 2011. However, in 2013 there was no longer a significant correlation between iron and lead, perhaps because iron levels had decreased dramatically ($R^2 = 0.30$, $p = 0.40$). A similar same phenomenon was observed at Site B for samples collected at moderate flow (Figure C5). A statistically significant correlation between iron and lead was observed for high flow samples collected at Site A in 2013 ($R^2 = 0.74$, $p = 0.01$) and Site B in 2011 and 2013 (2011: $R^2 = 0.98$, $p < 0.0001$ and 2013: $R^2 = 0.91$, $p < 0.001$). Of the three homes, Site C was the only location where there was not a significant relationship between lead and iron in 2011 or 2013 (i.e. all moderate and high flow R^2 values < 0.05), and this is the site at which improved iron corrosion control did not reduce lead release in 2013 versus 2011. Overall, these results indicate that particulate lead was very strongly associated with particulate iron in 2011 at some sites,

and that this association was weakening due to the fact that both particulate iron and lead dropped in 2013.

The current study significantly advances practical knowledge and understanding of how particulate iron levels impact lead leaching in lower alkalinity waters and assist in improving LCR compliance for water utilities with similar water chemistry conditions. In several cases, there was an interplay between distribution system corrosion of iron pipe and subsequent mobilization of lead. To the extent that iron pipe corrosion can increase lead release, reducing lead in water might require upgrades to potable water infrastructure or iron corrosion control as opposed to current approaches that focus exclusively on reducing lead solubility.

CONCLUSIONS

Bench Scale

- Bench scale tests verified that reducing the finished water pH from 10.3 to 9.7 would significantly increase lead leaching and consumer red water complaints due to iron release from cast iron mains.
- Synthetic water containing particulate iron significantly increased lead release from lead pipes versus the same water without particulate iron.
- Soluble lead release was lower at the pH 9.7 conditions compared to the pH 10.3 conditions, which is consistent with theoretical predictions that the lowest lead solubility will occur at pH ~9.8. However, benefits associated with decreased solubility can be outweighed by increased particulate lead at pH 9.7 both with and without iron.

Profile and Utility Sampling

- Eight months after the finished water pH was increased back to 10.3, iron levels in profile samples decreased by as much as 99%, which also corresponds to a significant decrease in consumer red water complaints.
- The profiles indicated several instances where there was a strong relationship between particulate iron and particulate lead. These analyses suggest that rehabilitating iron mains and controlling iron corrosion can be important factors contributing to lead corrosion problems.
- In moderate flow samples typical of consumer water use, there were two cases where lead release dropped in 2013 after pH was increased, but one case where lead release increased. This suggests that in some cases, the benefits associated with corrosion control strategies can take years to realize, especially if the problems are associated with reservoirs of particulate iron on the pipe.

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APPENDIX C

Supporting Information Increased Lead in Water Associated with Iron Corrosion

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Tables

Table C1: Providence finished water quality Pre (2011) and Post (2013) pH increase to ~10.3.

Parameter	2011			2013		
	Min	Max	Average	Min	Max	Average
pH	9.6	10.4	10.0	10.2	10.5	10.4
Alk. (mg/L as CaCO ₃)	10.8	25.9	18.2	13.6	16.9	15.6
Turbidity (NTU)	0.06	0.13	0.09	0.10	0.13	0.12
Total Hardness (mg/L)	35.2	55.9	47.5	38.5	43.7	41.8
Ammonia (mg/L)	<0.1	<0.1	<0.1	N/A	N/A	N/A
Nitrate (mg/L)	0.05	0.16	0.11	N/A	N/A	N/A
Sulfate (mg/L)	25.0	30.0	27.8	N/A	N/A	N/A
Silica (mg/L)	2.6	4.1	3.6	N/A	N/A	N/A

Table C2: Synthetic Providence water recipe (modified from Wang et al. 2012).

Target water composition	Conc. (mg/L)
Total Alkalinity, as CaCO ₃	20
TDS	113
Total Hardness, as CaCO ₃	38.5
Chloride	19.4
Sulfate	21.8
Natural Organic Matter, as C	0.3
Chemicals added	
NaHCO ₃	11.76
CaCl ₂ .2H ₂ O	12.50
MgSO ₄ .7H ₂ O	55.92
MgCl ₂ .6H ₂ O	14.84
NaCl	13.44
NaNO ₃	39.95
Suwannee River Fulvic Acid (as C)	0.3
Na ₂ SiO ₃ (as SiO ₂)	4.5

Table C3: Elemental composition of iron coupon.

Element	% Mass
Cr	0.24
Cu	0.3
Fe	95.33
Mn	0.61
Ni	0.13
Zn	3.37

Table C4: Summary of lead and iron concentration from profile sampling.

Site	Sample #	Low Flow 2011		Low Flow 2013		Moderate Flow 2011		Moderate Flow 2013		High Flow 2011		High Flow 2013			
		Fe (ppb)	Pb (ppb)	Fe (ppb)	Pb (ppb)	Fe (ppb)	Pb (ppb)	Fe (ppb)	Pb (ppb)	Fe (ppb)	Pb (ppb)	Fe (ppb)	Pb (ppb)		
A	1	66.89	19.62	12.84	24.08	201.00	12.40	10.32	12.12	189.80	154.30	59.32	223.80		
A	2	47.98	21.41	5.92	30.59	370.50	17.83	6.56	11.15	155.50	63.65	131.00	147.90		
A	3	50.59	21.73	7.62	36.59	238.60	12.82	7.63	11.49	145.70	47.80	170.30	316.90		
A	4	51.12	20.68	8.45	39.93	408.00	25.84	6.69	12.09	145.90	35.82	118.80	121.70		
A	5	63.34	19.30	6.86	40.73	433.40	25.22	6.77	13.41	128.90	30.98	94.26	91.02		
A	6	46.52	16.76	16.68	39.30	620.30	28.50	7.45	13.23	126.60	33.35	59.96	54.78		
A	7	50.12	14.95	7.87	35.07	733.90	32.01	4.57	13.15	129.60	26.05	51.45	64.20		
A	8	92.34	13.38	6.02	30.51	1364.0	0	51.09	7.56	12.83	152.50	45.22	78.48	69.30	
A	9	144.50	12.07	6.05	20.99	3060.0	0	80.22	13.60	12.94	219.70	39.01	47.69	58.51	
A	10	147.80	9.76	6.71	11.42	55.62	3.96	5.14	8.56	66.59	7.59	10.71	20.70		
Cumulative Mass (µg)						7485.3	2	289.89	76.27	120.97	1460.7	9	483.77	821.97	1168.8
B	1	165.80	27.94	32.09	6.95	640.10	53.11	88.93	12.51	808.10	96.15	291.70	31.17		
B	2	130.70	5.41	35.00	7.78	731.60	76.69	94.35	13.11	773.10	105.40	130.20	16.41		
B	3	105.20	4.14	38.02	9.72	677.10	79.09	110.20	15.04	560.30	57.81	129.50	17.31		
B	4	159.00	47.99	54.47	9.05	610.90	49.61	85.45	14.23	487.50	48.61	139.00	15.63		
B	5	137.10	88.10	45.79	46.02	541.70	47.28	91.72	16.11	451.90	44.15	184.20	16.22		
B	6	158.20	35.00	47.61	71.32	503.90	38.86	86.34	12.30	423.20	37.47	124.90	16.23		
B	7	253.80	7.85	52.58	19.83	578.90	29.99	94.40	11.47	452.00	30.18	132.00	14.92		
B	8	279.70	4.90	57.45	9.71	530.00	28.36	88.32	10.55	420.80	30.56	130.80	13.85		
B	9	275.10	4.38	55.04	8.64	439.20	25.60	88.98	10.54	389.00	31.92	134.60	13.84		

B	10	263.90	3.99	62.71	8.64	295.00	12.90	79.66	9.24	285.60	13.77	201.90	27.09
Cumulative		1928.5				5548.4				5051.5		1598.8	
Mass (µg)		0	229.69	480.76	197.63	0	441.49	908.35	125.10	0	496.02	0	182.67
C	1	172.00	8.66	47.90	9.00	209.30	4.29	47.31	7.73	197.90	3.61	53.70	9.47
C	2	177.70	7.33	53.98	10.55	231.10	4.13	44.08	7.35	190.80	4.05	46.84	8.67
C	3	157.80	6.57	53.25	10.09	349.50	4.43	32.96	6.72	184.90	2.98	44.52	8.04
C	4	147.40	23.12	54.19	13.20	410.30	4.31	43.12	6.90	202.30	3.04	44.90	7.72
C	5	129.60	41.88	52.74	20.94	356.00	18.39	44.58	10.32	193.30	4.66	46.19	12.18
C	6	130.70	15.09	60.14	14.31	256.00	16.18	40.70	11.94	162.30	4.75	44.97	12.30
C	7	152.60	7.76	46.66	9.96	421.30	6.12	40.52	9.40	198.90	3.80	46.96	8.08
C	8	150.70	6.04	45.40	8.24	328.00	6.11	39.29	8.65	168.20	3.57	47.16	7.81
C	9	162.90	5.15	44.58	7.62	250.60	6.47	40.50	7.76	166.20	3.58	48.23	7.48
C	10	173.90	3.46	42.91	7.37	201.20	3.96	43.16	6.24	135.60	3.26	49.77	5.96
Cumulative		1555.3				3013.3				1800.4			
Mass (µg)		0	125.06	501.75	111.29	0	74.38	416.22	83.00	0	37.29	473.24	87.71

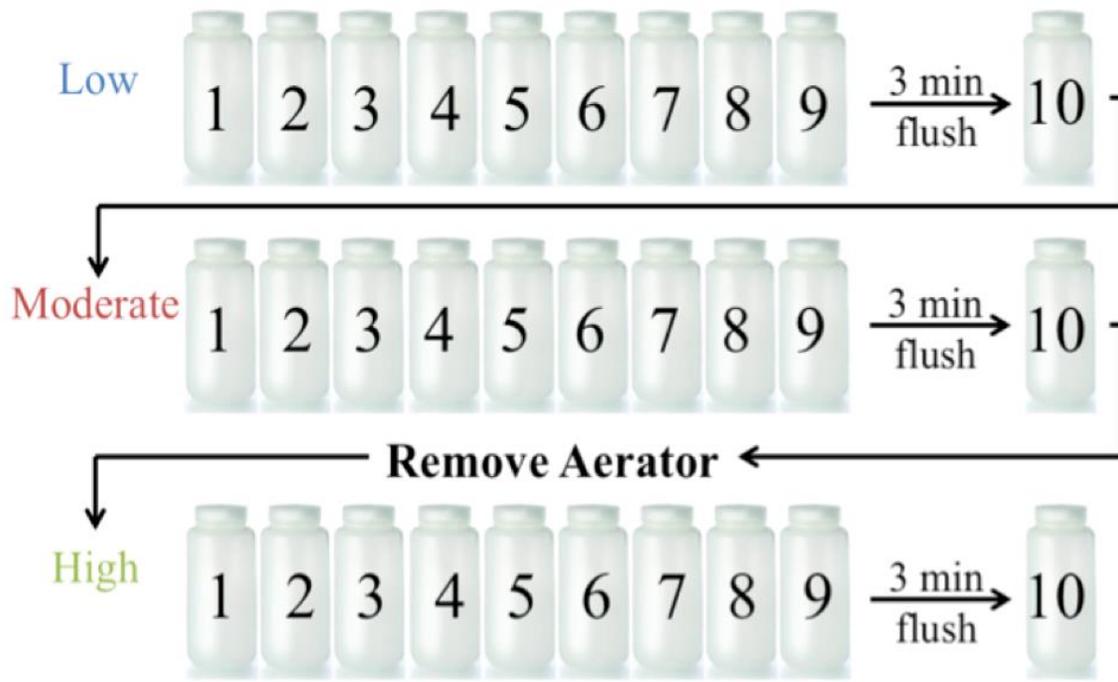
Table C5: Ratio of particulate lead to particulate iron in 3rd and 5th liter profile samples.

	Low Flow		Moderate Flow		High Flow	
	2011 Ratio	2013 Ratio	2011 Ratio	2013 Ratio	2011 Ratio	2013 Ratio
Site A	0.30	2.28	0.05	4.50	0.31	1.31
Site B	0.31	0.44	0.10	0.11	0.10	0.10
Site C	0.17	0.28	0.03	0.20	0.02	0.22

Table C6: Average soluble and particulate lead in 3rd and 5th liter profile samples.

	Soluble	Particulate	Percent Particulate
Iron			
Low Flow 2011	22.9±8.8	84.3±37.4	79%
Low Flow 2013	11.4±8.0	22.6±19.4	66%
Moderate Flow 2011	27±5.1	405.7±159.0	94%
Moderate Flow 2013	12.2±5.8	36.8±41.0	75%
High Flow 2011	25.1±5.8	254.5±187.5	91%
High Flow 2013	13.6±4.0	97.9±63.9	88%
Lead			
Low Flow 2011	9.0±7.7	21.3±24.1	70%
Low Flow 2013	16.0±12.9	11.4±8.5	42%
Moderate Flow 2011	1.9±1.0	29.3±27.7	94%
Moderate Flow 2013	6.0±2.1	6.2±3.3	51%
High Flow 2011	2.0±1.4	29.4±22.5	94%
High Flow 2013	10.2±11	66.8±116.0	87%

Figures



Modified from Clark, Masters & Edwards (2014)

Figure C1: Illustration of sequential profile water sampling collected in each home. One-liter water samples were successively collected at low, moderate, and high flow after at least 6 hours of stagnation.

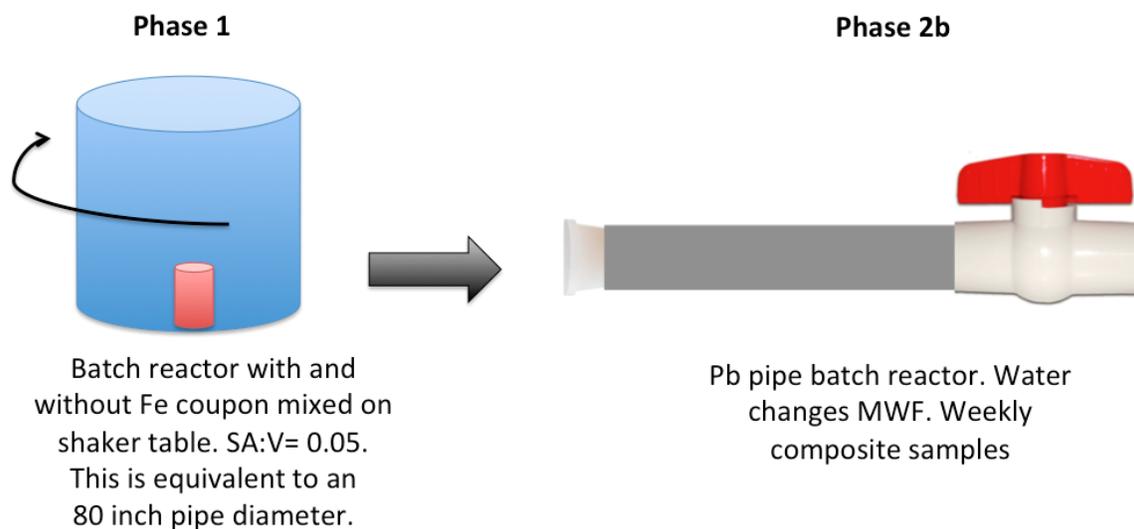


Figure C2: Mixed water from batch reactors with and without iron coupon (control) from Phase 1 were transferred to Pb pipes in Phase 2.

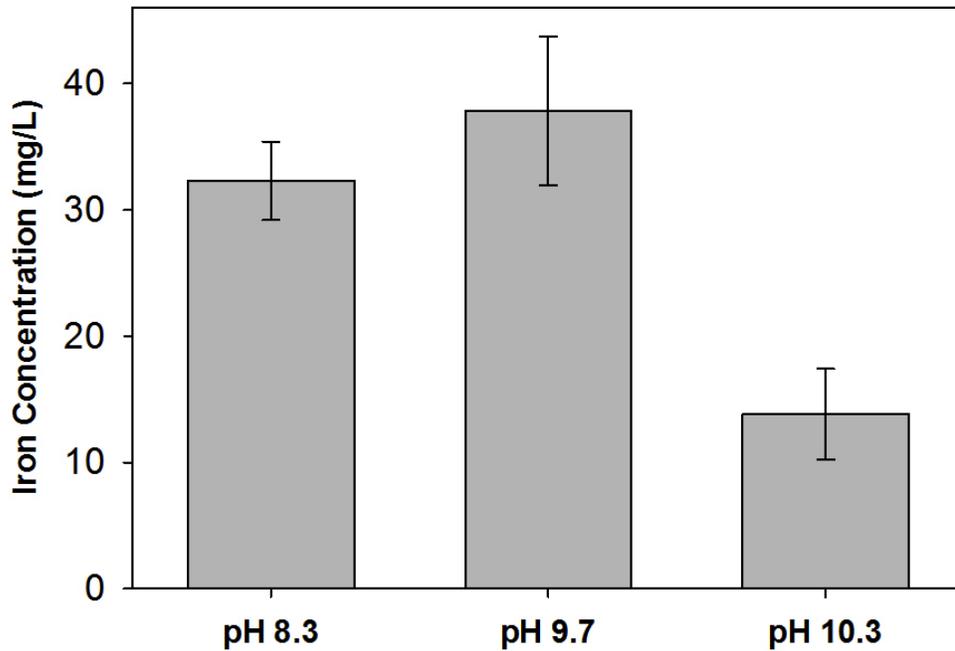


Figure C3: Average iron release from triplicate batch reactors after iron corrosion stabilized (Weeks 5-10). Error bars represent 95% confidence intervals.

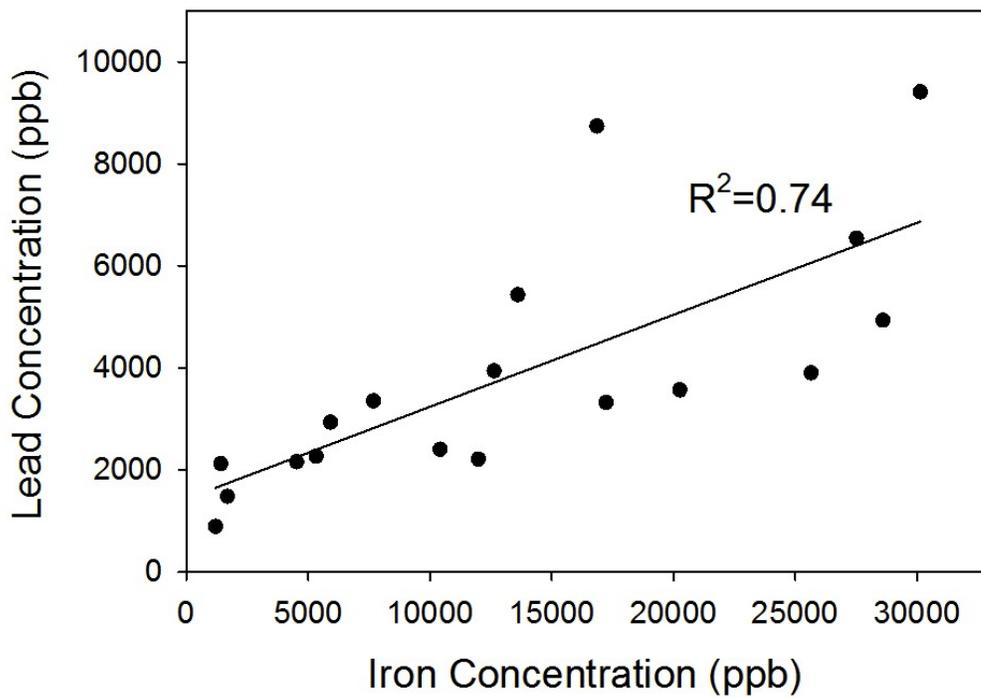


Figure C4: Correlation between particulate lead and particulate iron in bench scale test (Week 20 & 25).

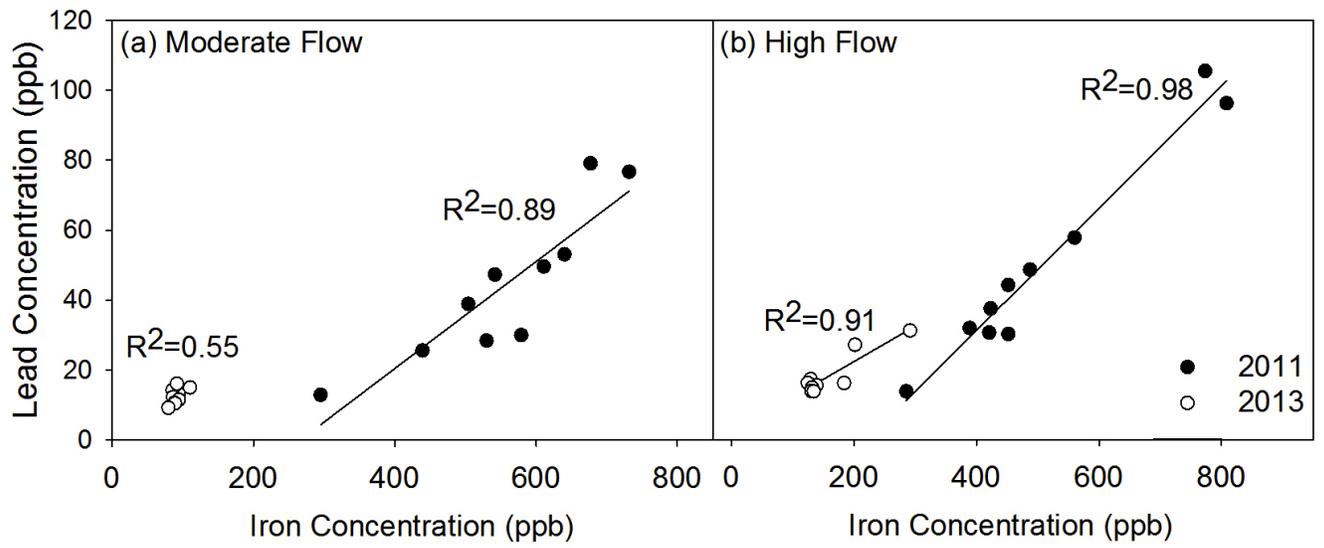


Figure C5: Relationship between iron and lead at a) moderate and b) high flow at Site B.

CHAPTER 4. SEASONAL VARIATIONS IN TEMPERATURE INFLUENCE LEAD RELEASE

Sheldon Masters, Gregory J. Welter, Melissa Wilson and Marc Edwards

ABSTRACT

The influence of temperature variations on the solubility of representative lead solids present in drinking water systems and lead release to potable water was examined. Contrary to the conventional wisdom, the solubility of lead carbonate and lead oxide decreased at higher temperature in bench scale tests with a slope of -1.95 and -1.36 ppb Pb/°C, while temperature had little effect on lead orthophosphate and chloropyromorphite solubility. In large scale pipe rigs or field testing of lead service lines in summer versus winter, total and dissolved lead release increased by 3-5X in the summer in Washington DC and up to 3X in Providence, RI. Effects other than solubility, such as scale dissolution kinetics and colloid mobilization are likely involved in higher water lead that is sometimes observed during warmer temperatures. In the Washington DC pipe loop, particulate lead was 6X higher during the summer compared to the winter and represented 74% of the total lead, indicating that higher particulate lead in water with rising temperatures is sometimes a bigger concern than soluble lead.

KEYWORDS: Solubility; lead, copper, summer, winter

INTRODUCTION

Potable water can be contaminated with lead due to the corrosion of lead bearing materials such as pipes, faucets, and fittings.¹⁻³ Human exposure to lead from drinking water in contemporary plumbing systems has been associated with higher incidence of spontaneous abortions in pregnant women and increased blood lead in children and adverse health outcomes.⁴⁻⁹ Water utilities generally attempt to control the release of lead from lead bearing pipe materials by maintaining water chemistry conditions (i.e. pH and alkalinity) that reduce the solubility of lead corrosion solids that coat plumbing materials.^{2,10}

Representative lead solids coating plumbing systems include lead phosphate, Pb(II) carbonates, and Pb(IV) oxides.¹¹⁻¹³ Pb(IV) oxides can form in distribution systems with a free chlorine residual and they have extremely low solubility.^{2,14,15} Low solubility lead phosphate scales are also formed in distribution systems that employ orthophosphate as a corrosion inhibitor,^{16,17} and if adequate levels of phosphate or free chlorine are not present higher solubility lead carbonates such as cerussite (PbCO₃) and hydrocerussite (Pb₃(OH)₂(CO₃)₂) tend to form.^{13,18,19}

The parameters that are often considered when assessing the corrosion of lead include water quality (i.e., pH, dissolved oxygen, alkalinity, buffer capacity, Langelier Saturation Index, and Calcium Carbonate Precipitation Potential). However, these factors alone cannot fully explain the observed variability in soluble metals release in real systems using simplistic models.²⁰ The seasonal variation in temperature is one potentially important factor that can influence the concentration of lead and copper in potable water. Even though the dissolution rates of lead oxide,²¹⁻²⁶ lead carbonate,^{19,27} and lead phosphate²⁸⁻³¹ have been studied under various water quality conditions, the potentially important role of temperature on the solubility of these lead solids has never been thoroughly studied.²

Nonetheless, prior practical research has often associated measured higher levels of lead in plumbing systems with higher temperature, and it is commonly believed that this is due to higher solubility and/or dissolution rates for lead solids at higher temperature.^{10,32-46} For instance, the Environmental Protection Agency warns consumers to avoid consuming hot water and recommends utility lead monitoring in the summer months, because these conditions are believed to have highest potential for lead release from plumbing.^{47,48} Anecdotally, a few studies have confirmed links between higher lead levels in water and higher seasonal temperatures.^{6,35,40,49-54} Also, observations of a higher incidence of lead poisoning during the summer months, once attributed to increased exposure from soils and lead paint⁵⁵⁻⁶³ might also be due to higher levels of lead documented in potable water in summer months.⁴⁶ Thus, the overall expectation is that higher temperatures will lead to higher levels of lead in water, although exceptions are likely to exist where the opposite trend occurs due to reduced lead solubility at higher temperatures.^{2,39,40}

The goal of this research is to address these knowledge gaps, by examining the temperature dependence of lead corrosion by-product release in representative bench,

pilot and full-scale systems. Both soluble and total lead release were examined as part of this overall evaluation, which has important implications for monitoring under a revised Environmental Protection Agency Lead and Copper Rule (EPA LCR) and human lead exposure.

MATERIALS AND METHODS

The effect of seasonal variations in temperature on lead and copper solubility and corrosion by-product release were assessed using models, bench scale tests, pipe loop studies and distribution system sampling.

Lead Mineral Solubility Experiments and Theoretical Model Comparisons

Synthesis of Lead Solids. Representative solids including lead carbonate (PbCO_3), lead oxide (PbO_2), lead orthophosphate ($\text{Pb}_3(\text{PO}_4)_2$) and lead phosphate chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) were formed using established methods. Lead carbonate was synthesized using the approach outlined by Noel et al. (2014) by simultaneously adding 0.1 M NaHCO_3 and 0.15 M $\text{Pb}(\text{NO}_3)_2$ to 3.5-L of deionized water in a well-mixed batch reactor at 20 °C. Lead oxide was produced using the method outlined by Triantafyllidou et al. (2007) by completely oxidizing a 1000 mg/L as Pb solution of lead chloride via addition of excess hypochlorous acid. Lead orthophosphate was made by slowly adding 0.1 M Na_2HPO_4 to 0.1 M lead acetate at 80 °C and maintaining a low heat on a hot plate for 3 hours.^{28,64} Finally, lead phosphate chloropyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) was synthesized by thoroughly mixing 0.25 M PbCl_2 solution with 0.15 M phosphoric acid (H_3PO_4) resulting in a white precipitate.^{29,30} After synthesis, all suspensions were adjusted to pH 7.5 and aged for 8 days before use in experiments.

Collection of Lead Solids. After measuring the concentration of both filtered (0.45 μm pore size filter) and unfiltered lead in each sample, the volume of solution that should be filtered to capture a total of 0.2 g lead on each filter was calculated.

Dissolution of Lead Solids. A dissolution experiment was conducted by adding the filter with the captured lead solids (0.2 g total Pb) into a 1 L jar containing 800 mL of synthesized tap water (Table D1) mixed at 100 rpm. The lead oxide reactors had an initial free chlorine residual of 2.7 mg/L while the lead phosphate reactors had an orthophosphate residual of 1.5 mg/L as P. Sample aliquots of 10 mL were first pre-filtered through a 0.2 μm pore size filter before final filtration through a 0.1 μm pore size filter at 2, 4, 9 and 29 hours after wasting the first 3 drops of solution. Testing using standard solutions demonstrated that the filtration using this approach did not significantly sorb more than 2 ppb lead. Each condition was tested at 4 °C and 20 °C. Metal concentrations were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) using Standard Method 3125B.⁶⁵

Solubility Model. The equilibrium solubility of 4 lead solids [lead oxide carbonate (PbO_2), ($\text{Pb}_3\text{O}_2\text{CO}_3$), lead oxycarbonate (Pb_2OCO_3), lead(II) hydroxide ($\text{Pb}(\text{OH})_2$ and cerussite] were modeled at 4 °C and 20 °C using MINEQL+ (pH = 7.5 and alkalinity = 20 mg/L as CaCO_3). In order to compare and quantify the magnitude of the temperature

effect from the bench scale test and MINEQL+ model, the increase in soluble lead with increasing temperature was calculated from the slope:

$$\text{Slope} = \frac{[\text{Soluble Pb}]_{20^{\circ}\text{C}} - [\text{Soluble Pb}]_{4^{\circ}\text{C}}}{\text{Difference in Temperature}}$$

Providence Simulated Water Bench Scale Testing

Bench testing was conducted to determine the effect of temperature on lead solubility and lead release under various water quality conditions using a synthesized water (SW) similar to treated water produced in Providence, RI (Table D1).⁶⁶ Before the start of the experiment, 54 new lead pipes were conditioned using the method outlined by Masters and Edwards (2015) by continuously pumping SW through the pipes in a recirculating system at a high pH (i.e. 10.3). The pipes were then aged using a dump and fill protocol for 6 months with water changes three times per week (Monday / Wednesday / Friday) followed by a 14 month stagnation period. After the pipes were aged, water changes were done (Monday/Wednesday/Friday) for one month at room temperature before the experiment was initiated. Triplicate 6-inch pieces of aged lead pipe were tested using unaltered SW, and alterations of the SW with various combinations of added natural organic matter (NOM, 0.3 mg/L as C) and orthophosphate (1 mg/L as P). Each water was tested at three different pH conditions (pH 8.3, 9.7, and 10.3) with and without particulate iron using the dump and fill protocol previously described. The lead pipes were stored in an incubator at 4°C, 20°C, and then 30°C for two weeks at each temperature. At the start of the second week at each temperature, samples were collected and analyzed to operationally determine the relative soluble and particulate lead from each of the triplicate pipes. Soluble samples were collected after filtering a 10 mL aliquot of the sample using a 0.45 µm pore size nylon filter (Whatman) and a 10 mL BD syringe. The remaining sample was then analyzed for total metals. All samples were digested using 2% nitric acid and 1% hydroxylamine by volume and analyzed using inductively coupled plasma mass spectrometry (ICP-MS; Agilent Technologies, Santa Clara, CA) using Standard Method 3125B.⁶⁵

Field Sampling: Providence Rhode Island and Washington Aqueduct

Providence, RI. Monthly samples were collected from 8 homes (Table D2) in Providence, RI (January 2013-February 2014) as part of an assessment of water treatment process modifications. Data from this monitoring program were analyzed to characterize the effects of seasonal variations in temperature on lead and copper release at consumer taps. On-site premise plumbing surveys along with utility records were used to estimate the volume of water contained in the plumbing between the sampling tap (which was the outside garden spigot) and lead service line (LSL). After a 6-hour minimum stagnation time, a 500 mL first draw sample was collected, followed by wastage of a site specific volume, and then followed by 1 L LSL sample. After three minutes of additionally flushing, a final 1 L sample was collected to characterize the water in the distribution main. Since sample flow rate can significantly affect lead release,⁶⁷⁻⁷⁰ an effort was made to consistently collect samples at a flow rate of ~2 gpm. The pH and temperature of the first draw sample and LSL sample were measured in the field immediately after sampling

and all samples were analyzed for total and dissolved lead and copper.⁷¹ Table D3 summarizes the finished treatment plant water quality during the sampling period. In addition to field sampling, Providence Water also conducted a pipe loop study to assess potential corrosion control strategies. The pipe loops consisted of four 24-inch lead pipes harvested from the distribution system. Each rack included sampling ports, visual flow meters, throttling valves for flow adjustment, isolation valves used during sampling and upstream and downstream venting structures to allow the pipes to remain full during stagnant periods between pumping flows.⁷² Data from the control pipe loop was analyzed to determine the effect of temperature on lead release.

Washington Aqueduct. Beginning in January 2005, the Washington Aqueduct initiated a pipe loop study using harvested LSLs to simulate distribution system conditions and to better understand lead corrosion issues in the Washington DC area. The racks consisted of a single pass flow regime, with a 16-hour period of flow followed by an 8-hour stagnation period.⁷³ Data from the control pipe loop, which was exposed to finished effluent from the Aqueduct, was analyzed to determine the effects of seasonal variations in temperature on total and dissolved lead release.⁷⁴ Table D4 summarizes the water quality in the control pipe loop during the sampling period.

Statistical Analyses

A non-parametric Wilcoxon test was used to measure the difference between two groups while an analysis of variance (ANOVA) test on the log-transformed normalized data was used for multiple comparisons ($p < 0.05$). Spearman's rank correlation coefficient was used to measure the relationship between metals release and temperature while a linear regression was used to determine if the concentration tended to increase or decrease with temperature.

RESULTS AND DISCUSSION

In the following section, after describing the effects of temperature on solubility of representative lead compounds, trends in lead release to water from lead pipes are examined in the context of a bench scale study and distribution system field sampling. A final section highlights practical and regulatory implications of the results.

Lead Mineral Solubility Laboratory Experiments Compared with Theoretical Models.

Consistent with expectations, lead carbonate was the most soluble solid followed by lead oxide and lead phosphates.^{2,13-15,18,19,75} Contrary to expectations, in the case of lead carbonate and lead oxide, higher temperatures decreased lead solubility, with a slope of -1.95 and -1.36 ppb Pb/°C (Table 4-1). After 29 hours, the soluble lead concentration due to the dissolution of lead carbonate was 35% higher at 4 °C compared to 20 °C (Figure 4-1). Similarly, the soluble lead concentration in the lead oxide condition was more than 10 times higher at 4 °C compared to 3 ppb soluble lead at 20 °C. Lead oxide is very insoluble in the presence of a strong oxidant and the chlorine residual was at least 1.20 mg/L throughout the testing. Temperature did not have a detectable effect on the solubility of lead orthophosphate and chloropyromorphite.

Table 4-1: Change in soluble lead concentration with temperature

Lead Solid	Chemical Formula	Slope (ppb/°C)
Laboratory test		
Lead Carbonate	PbCO ₃	-1.95
Lead Oxide	PbO ₂	-1.36
Lead Orthophosphate	Pb ₃ (PO ₄) ₂	-0.03
Chloropyromorphite	Pb ₅ (PO ₄) ₃ Cl	-0.01
Theoretical Model		
Lead oxide carbonate	Pb ₃ O ₂ CO ₃	-3.54
Lead Oxycarbonate (Shannonite)	Pb ₂ OCO ₃	-0.61
Lead (II) hydroxide	Pb(OH) ₂	-0.02
Lead Carbonate (Cerussite)	PbCO ₃	0.00

Examination of standard, simplistic solubility models with incomplete enthalpy datasets for temperature corrections, also did not generally predict higher lead at higher temperature for representative solids. Specifically, MINEQL+ modeling predicted that there would be no discernable change in soluble lead between 4°C and 20°C (slope = 0.00 ppb/°C) for cerussite, but the soluble concentration is predicted to increase as temperature decreases for other lead carbonate solids (Pb₃O₂CO₃ and Pb₂OCO₃) as was observed in experiments (Table 4-1). In summary, the simple bench tests and solubility models did not support expectations of increased soluble lead at higher temperatures.

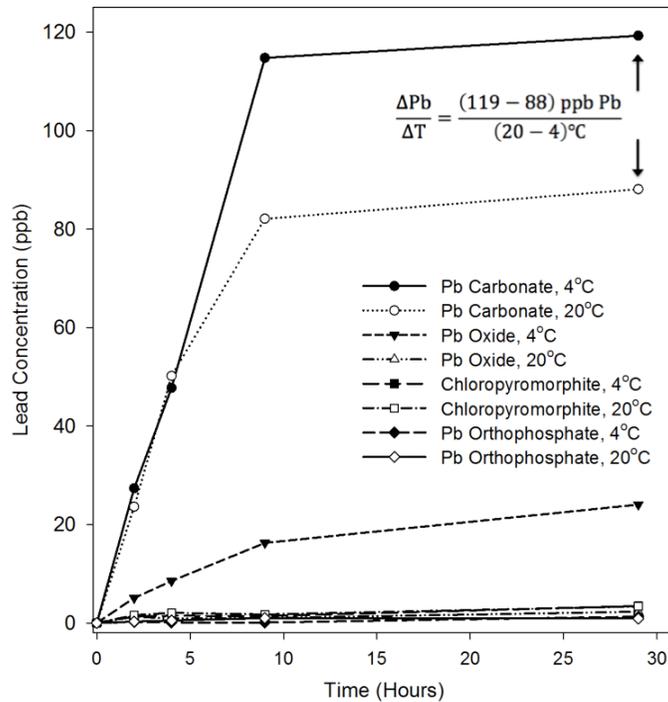


Figure 4-1: Dissolution of lead carbonate, lead oxide, chloropyromorphite and lead orthophosphate.

Practical Data: Washington Aqueduct Pipe loop Study. Data from the control condition in the Washington Aqueduct pipe loop study were analyzed to characterize the influence of seasonal variations in temperature on lead release. Total and dissolved lead release varied with seasonal changes in temperature ($\rho = 0.76$ and 0.68 respectively, $p < 0.0001$) with the highest lead level occurring during the summer months and the lowest lead release during the winter (Figure 4-2a and Figure D1 respectively). Average total lead release during the summer months was 5 times higher compared to the winter (59.2 ppb vs. 11.1 ppb, $p < 0.05$). Similarly dissolved lead was 3X higher in the summer compared to the winter (10.8 ppb vs. 3.6 ppb, $p < 0.05$). Based on a linear regression, total and dissolved lead increased at a rate of $2.76 \text{ ppb}/^\circ\text{C}$ and $0.39 \text{ ppb}/^\circ\text{C}$ respectively ($p < 0.0001$). Even though higher lead release during the summer has been speculated to be due to the higher lead solubility as discussed previously,^{10,32-46} particulate lead release increased even more dramatically in the summer months than did soluble lead (6X increase in summer vs. winter; 48.4 ppb vs. 7.6 ppb , $p < 0.05$). Thus, contrary to expectations, higher particulate lead release at higher temperature, was a bigger problem than soluble lead in terms of both magnitude and percentage increase.

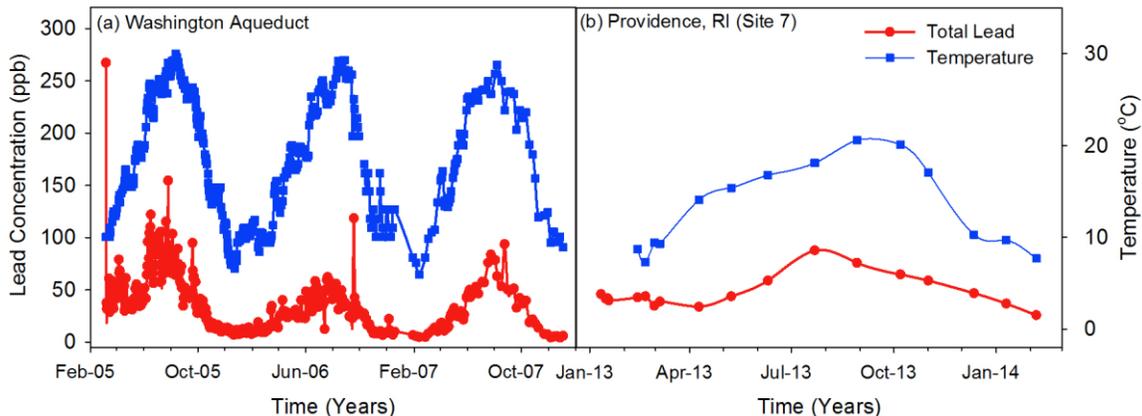


Figure 4-2: Seasonal variation in temperature and average lead in the Washington Aqueduct pipe loop study and one of the houses in the Providence, RI, field sampling.

Providence Simulated Bench Scale Testing. To further examine the temperature dependency of soluble and particulate lead release in a wide variety of waters, 18 modifications of a synthesized Providence, RI source water were constituted (Table D5). Based on a linear regression, total lead leaching increased for 50% of the conditions tested and decreased in the other 50% of conditions; however, due to the high variability in particulate lead release these differences were not statistically significant at the 95% confidence level with $n = 9$ (Table D5). Focusing on soluble lead which was less variable, of the 18 conditions tested in the laboratory, 4 conditions had a significant increase in soluble lead with higher temperature, 2 conditions saw a significant decrease in soluble lead at higher temperature ($p < 0.05$), and 12 conditions showed no significant change with temperature ($p > 0.05$). In bench scale tests best simulating the Providence, RI finished water quality (i.e. SW+NOM, $\text{pH} = \sim 10.3$) soluble lead increased with increasing temperature with a slope of $8.1 \text{ ppb}/^\circ\text{C}$ ($p = 0.01$) (Figure D2), and dissolved lead was more than 3 times higher at 30°C compared to 4°C and 20°C . The later findings were consistent with pipe loop studies conducted by Providence Water in which soluble lead levels increased at a rate of $4.3 \text{ ppb}/^\circ\text{C}$ ($p < 0.001$); moreover, there was no

significant increase in total lead with a slope of -1.2 ppb/°C ($p = 0.72$). In the presence of particulate iron (SW+NOM+Fe) in the bench scale experiments, soluble lead increased at a rate of 29.5 ppb/°C ($p = 0.004$) and there was again no significant increase in total lead ($p = 0.13$).

Providence Field Study. A review of data collected in the field from single family residences was conducted in homes to confirm the validity of the bench and pilot testing. Of the 8 homes sampled, 4 were confirmed to have a significant correlation between water temperature and soluble lead in stagnant service line samples (Table 4-2) ($\rho = 0.66-0.95$, $p < 0.05$). These 4 homes also had an average of ~3 times more soluble lead release during the summer months compared to the winter (Table D6) ($p < 0.05$), which was in the range of what was observed in the bench and pilot studies. Of the 4 homes that had a correlation between soluble lead and temperature, 3 also had a correlation between water temperature and total lead release from the service line (Figure 4-2b) ($\rho = 0.62-0.76$, $p < 0.05$). However, the dissolved lead data from the other four homes showed no significant statistical relationship with temperature.

Interestingly, there was an inverse correlation between total copper release and temperature in the service line at 5 of the 8 homes (Table 4-2) ($\rho = -0.60$ to -0.84 , $p < 0.05$). On average, these homes had 2.5-15 times more total copper release during the winter compared to the summer. Similarly, there was an inverse correlation between dissolved copper and temperature in 4 homes ($\rho = -0.57$ to -0.91 , $p < 0.05$) with these homes having between 2-4.5 times more dissolved copper during the winter.

Table 4-2: Correlation (Spearman’s Rho) between temperature and lead release from the service line and copper from first draw samples

Sample Site	Lead				Copper			
	Dissolved	p-value	Total	p-value	Dissolved	p-value	Total	p-value
Site 1	0.007	0.98	-0.21	0.51	-0.16	0.58	-0.21	0.48
Site 2	0.09	0.77	-0.10	0.74	-0.27	0.37	-0.07	0.83
Site 3	0.01	0.97	-0.37	0.14	-0.40	0.11	<i>-0.61</i>	<i>0.01</i>
Site 4	<i>0.76</i>	<i>0.003</i>	<i>0.62</i>	<i>0.02</i>	<i>-0.57</i>	<i>0.03</i>	-0.49	0.08
Site 5	0.06	0.86	-0.02	0.96	<i>-0.60</i>	<i>0.03</i>	<i>-0.64</i>	<i>0.02</i>
Site 6	<i>0.69</i>	<i>0.006</i>	0.34	0.24	<i>-0.81</i>	<i>0.0005</i>	<i>-0.75</i>	<i>0.002</i>
Site 7	<i>0.95</i>	<i><0.000</i>	<i>0.76</i>	<i>0.002</i>	<i>-0.91</i>	<i><0.001</i>	<i>-0.84</i>	<i><0.001</i>
		<i>1</i>						
Site 8	<i>0.66</i>	<i>0.01</i>	<i>0.72</i>	<i>0.004</i>	-0.52	0.06	-0.75	<i>0.002</i>

*Bold and italics indicate a statistically significant difference at the 95% confidence level

Practical and Regulatory Implications. Under the current EPA LCR, water systems are required to prioritize site selection for highest risk lead leaching. However, there are currently no explicit guidelines that address seasonal variations in lead and copper measurements.⁷⁶ Several studies have attributed higher incidence of childhood lead poisoning during the summer to soil and dust,⁵⁵⁻⁶³ however, the data presented in this study adds to a growing body of evidence indicating in some cases that water may also be a significant contributing factor to elevated blood lead levels during the summer.^{8,46,77} It is also possible that a system could be in compliance during winter sampling while exceeding the lead action level during warmer months.

As a general rule, however, higher temperatures do not invariably increase lead in water. The lab studies demonstrated that in modifications of a base water using chemicals that are commonly present in a potable water supply, in a certain percentage of cases higher temperature could increase, decrease, or have no effect on lead release. Even within the same potable water system served by a single, centralized treatment plant, lead release from pure lead service lines sometimes showed a strong correlation with temperature, whereas other homes had no correlation. It is speculated that subtle changes of water throughout the distribution system, as measured by chlorine residual or iron or other factors,^{78,79} creates service line scales that are temperature dependent in some cases, and a different type of scale that is not temperature dependent in others.

On the other hand, in the majority of homes sampled in Providence, RI, copper levels increased during the winter, which confirms expectations based on anecdotal reports, bench studies and modeling data.^{80,81} Despite the fact that their corrosion chemistries are different, lead and copper are currently co-sampled from the same tap and in the same sampling pool.⁸² Thus, the fact that copper release tends to increase slightly in the winter versus summer, whereas the contrary trend is sometimes observed for lead, adds support to separate sampling programs to detect “worst case” copper and lead. The observation that highest risk copper plumbing systems tend to be newer homes^{83–88} while highest risk lead tends to be in older homes also supports this need.^{2,69,89,90}

CONCLUSIONS

Studies of lead release versus temperature were conducted in a variety of experimental settings. Clear relationships were seen in these studies between lead release and temperature; however, it was not consistent between studies or even from pipe to pipe in individual studies.

- In straight solubility experiments referencing different lead solids, it was found that in the presence of lead carbonate or lead oxide, lead solubility was negatively correlated with higher temperature, while solubilities in the presence of lead orthophosphate or chloropyromorphite showed no correlation with temperature. Theoretical calculations using the MINEQL+ model yielded results consistent with these laboratory experiments.
- Bench scale experiments with unused lead pipe using 18 variations of a synthetic water with various additions of NOM, phosphate and iron, generally showed correlations with temperature that were not statistically significant, although a four showed a significant positive correlation and two showed a significant negative.
- Two different pipe rack experiments conducted with two substantially different treatment plant waters on harvested lead pipe both showed clear seasonal trends in lead dissolved lead release, with high release in the summer.
- Intensive sampling at eight residences over the course of a year showed divergent correlations, with four residences showing strong positive correlation between dissolved lead release and temperature, and four showing no correlation.

- Generally, it is clear that the relationships observed between lead release and temperature are real, but they are not consistent, nor are they predictable based on other concurrent parameters that have been investigated.

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APPENDIX D

Supporting Information Seasonal Variations in Temperature Influence Lead Release

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KEYWORDS. Solubility; lead; copper; summer; winter

Table D1. Synthetic Providence water recipe

Target water composition	Conc. (mg/L)
Total Alkalinity, as CaCO ₃	20
TDS	113
Total Hardness, as CaCO ₃	38.5
Chloride	19.4
Sulfate	21.8
Natural Organic Matter, as C	0.3
Chemicals added	
NaHCO ₃	11.76
CaCl ₂ ·2H ₂ O	12.50
MgSO ₄ ·7H ₂ O	55.92
MgCl ₂ ·6H ₂ O	14.84
NaCl	13.44
NaNO ₃	39.95
Suwannee River Fulvic Acid (as C)	0.3
Na ₂ SiO ₃ (as SiO ₂)	4.5

Table D2. Summary of sample site characteristics

Sample Site	Service line material (public/private)	Service Line Installation	LSL length (ft)	LSL vol. (L)	LSL to spigot vol. (L)	Average Monthly Water use (ft ³)
Site 1	Cu/Pb	1998	31	2.0	1.5	31,271
Site 2	Pb/Pb	1893	21	1.4	1.5	27,174
Site 3	Pb/Pb	1929	46	2.9	1.6	150,256
Site 4	Pb/Pb	1932	53	3.3	1.1	114,184
Site 5	Pb/Pb	1888	33	2.1	3.8	30,789
Site 6	Pb/Pb	1927	44	2.8	2.1	44,153
Site 7	Pb/Pb	1931	50	3.1	1.0	199,230
Site 8	Pb/Pb	1910	78	4.7	4.4	78,733

Table D3. Providence finished water quality

Parameter	Min	Max	Average
pH	10.2	10.5	10.4
Alk. (mg/L as CaCO ₃)	13.6	16.9	15.6
Turbidity (NTU)	0.10	0.13	0.12
Total Hardness (mg/L)	38.5	43.7	41.8

Table D4. Summary of Washington Aqueduct water quality

Parameter	Average ± St. Dev.
pH	7.75±0.09
Total Chlorine (mg/L)	3.15±0.44
Alkalinity as CaCO ₃ (mg/L)	82.50±20.48
Dissolved Inorganic Carbon (mg/L)	21.43±4.89
Calcium (mg/L)	42.15±6.90
Total Dissolved Solids (mg/L)	193.84.36.19
Turbidity (NTU)	3.47±4.64
Ammonia (mg/L)	0.92±0.10
Nitrate (mg/L)	1.67±0.56
Phosphate (mg/L)	2.75±0.41

Table D5. Change in lead concentration with temperature (bold indicates statistical significance at the 95% confidence level)

Condition *	Change	Slope	p-value
Soluble Lead			
SW 8.3	Increase	10.85	0.01
SW 9.7	No change	-16.21	0.23
SW 10.3	No change	1.24	0.28
SW+Fe 8.3	Decrease	-9.41	0.04
SW+Fe 9.7	Decrease	-2.27	0.02
SW+Fe 10.3	No change	2.21	0.08
SW+NOM 8.3	No change	30.4	0.4
SW+NOM 9.7	No change	3.30	0.46
SW+NOM 10.3	Increase	8.08	0.01
SW+NOM+Fe 8.3	No change	-5.79	0.27
SW+NOM+Fe 9.7	Increase	21.86	0.004
SW+NOM+Fe 10.3	Increase	29.54	0.004
SW+NOM+P 8.3	No change	-819.9	0.21
SW+NOM+P 9.7	No change	17.96	0.24
SW+NOM+P 10.3	No change	-2.69	0.52
SW+NOM+P+Fe 8.3	No change	-8.2	0.40
SW+NOM+P+Fe 9.7	No change	-6.9	0.13
SW+NOM+P+Fe 10.3	No change	2.8	0.06
Total lead			
SW 8.3	No change	29.17	0.14
SW 9.7	No change	-15.92	0.30
SW 10.3	No change	9.01	0.22
SW+Fe 8.3	No change	-140.5	0.23
SW+Fe 9.7	No change	-40.67	0.17
SW+Fe 10.3	No change	-14.39	0.14
SW+NOM 8.3	No change	40.42	0.33
SW+NOM 9.7	No change	33.61	0.18
SW+NOM 10.3	No change	10.46	0.09
SW+NOM+Fe 8.3	No change	415	0.67
SW+NOM+Fe 9.7	No change	48.67	0.50
SW+NOM+Fe 10.3	No change	37.24	0.13
SW+NOM+P 8.3	No change	-656.3	0.41
SW+NOM+P 9.7	No change	-1.12	0.99
SW+NOM+P 10.3	No change	-22.35	0.41
SW+NOM+P+Fe 8.3	No change	-178.5	0.34
SW+NOM+P+Fe 9.7	No change	-342.1	0.17
SW+NOM+P+Fe 10.3	No change	75.16	0.73

* Condition denotes whether natural organic matter (NOM), iron (Fe) or phosphate (P) was added to the synthetic water (SW) and the pH of the tested water (8.3, 9.7 or 10.3)

Table D6. Comparison of average lead and copper at each site during the summer and winter (bold and italics indicates a statistically significant difference at the 95% confidence level)

Sample Site	First-draw winter average (ppb)	First-draw summer average (ppb)	First-draw p-value	Service line winter average (ppb)	Service line summer average (ppb)	Service line p-value
Dissolved Lead						
Site 1	5.6	15.6	0.10	9.3	8.8	0.93
Site 2	5.4	2.1	0.47	12.3	35.7	0.35
Site 3	5.5	1.0	0.36	4.2	1.5	0.67
Site 4	2.8	1.9	0.64	7.3	21	0.02
Site 5	3.6	3.6	0.37	11.6	20.9	1.0
Site 6	9.2	4.9	0.70	19.8	59.3	0.01
Site 7	3.3	3.4	0.76	19.2	59.0	0.01
Site 8	2.5	4.1	0.75	12.6	47.3	0.01
Total Lead						
Site 1	13.3	23.6	0.28	20.9	15.6	0.58
Site 2	52.3	12.1	0.37	24.2	50.8	0.44
Site 3	171.75	5.8	0.03	16.7	11.67	0.10
Site 4	17.0	15.7	0.34	32.1	43	0.24
Site 5	9.5	8.2	0.43	26.5	35.4	1.00
Site 6	31.9	33	0.88	54.3	86	0.10
Site 7	23.0	7.6	0.06	38.1	74.3	0.01
Site 8	48.1	18.0	0.59	53.3	103.0	0.02
Dissolved Copper						
Site 1	9.0	4.2	0.17	3.9	1.3	0.03
Site 2	28.1	26.6	0.74	3.2	2.5	0.57
Site 3	10.2	2.2	0.11	1.7	1.1	0.26
Site 4	6.9	3.4	0.03	1.4	1.0	0.28
Site 5	20.4	8.9	0.04	2.7	5.6	0.62
Site 6	7.8	2.9	0.02	2.0	1.5	0.24
Site 7	16.5	3.75	0.01	2.3	1.1	0.06
Site 8	18.5	10.7	0.16	3.6	1.8	0.03
Total Copper						
Site 1	14.1	5.7	0.12	5.2	1.5	0.16
Site 2	445.3	374.2	0.94	4.9	4.3	0.81
Site 3	88.59	6.0	0.02	4.1	1.6	0.01
Site 4	19.6	9.8	0.19	2.4	1.2	0.94
Site 5	37.5	15	0.04	3.1	8.2	0.62
Site 6	17.6	6.9	0.01	3.1	1.7	0.21
Site 7	34.6	5.2	0.01	3.8	1.4	0.04
Site 8	137.3	35.7	0.01	6.9	2.7	0.02

Winter (December-March)

Summer (June-September)

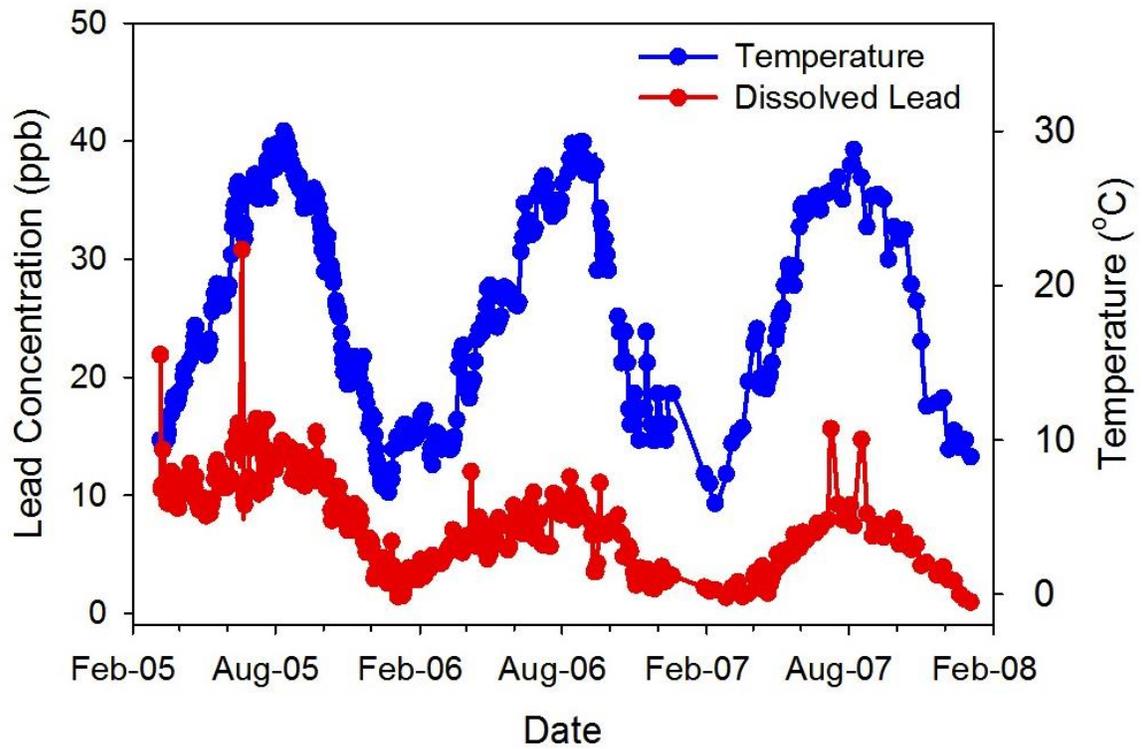


Figure D1. Seasonal variation in temperature and average dissolved lead in the Washington Aqueduct pipe loop study.

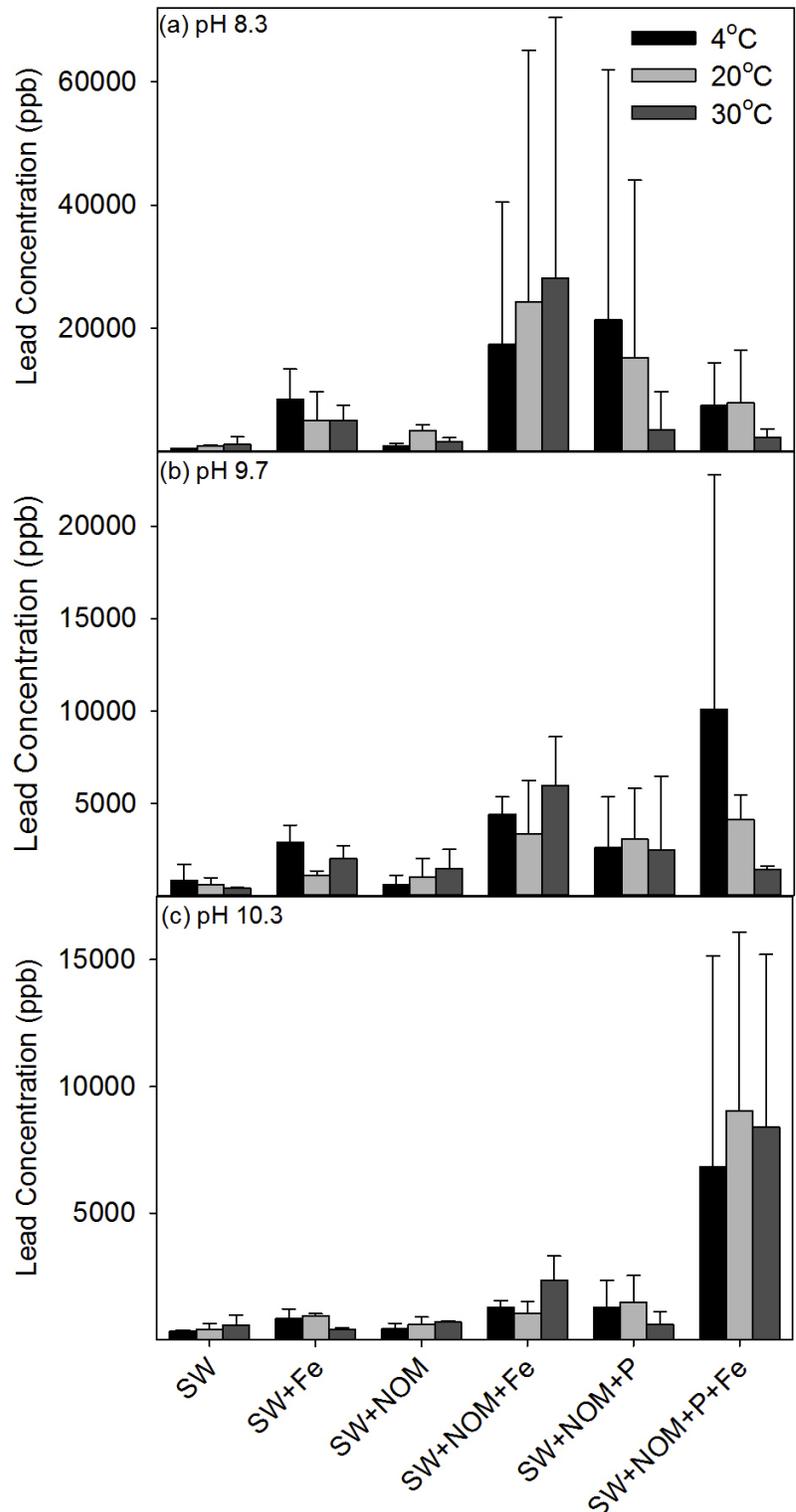


Figure D2. Average total lead release from triplicate pipes.

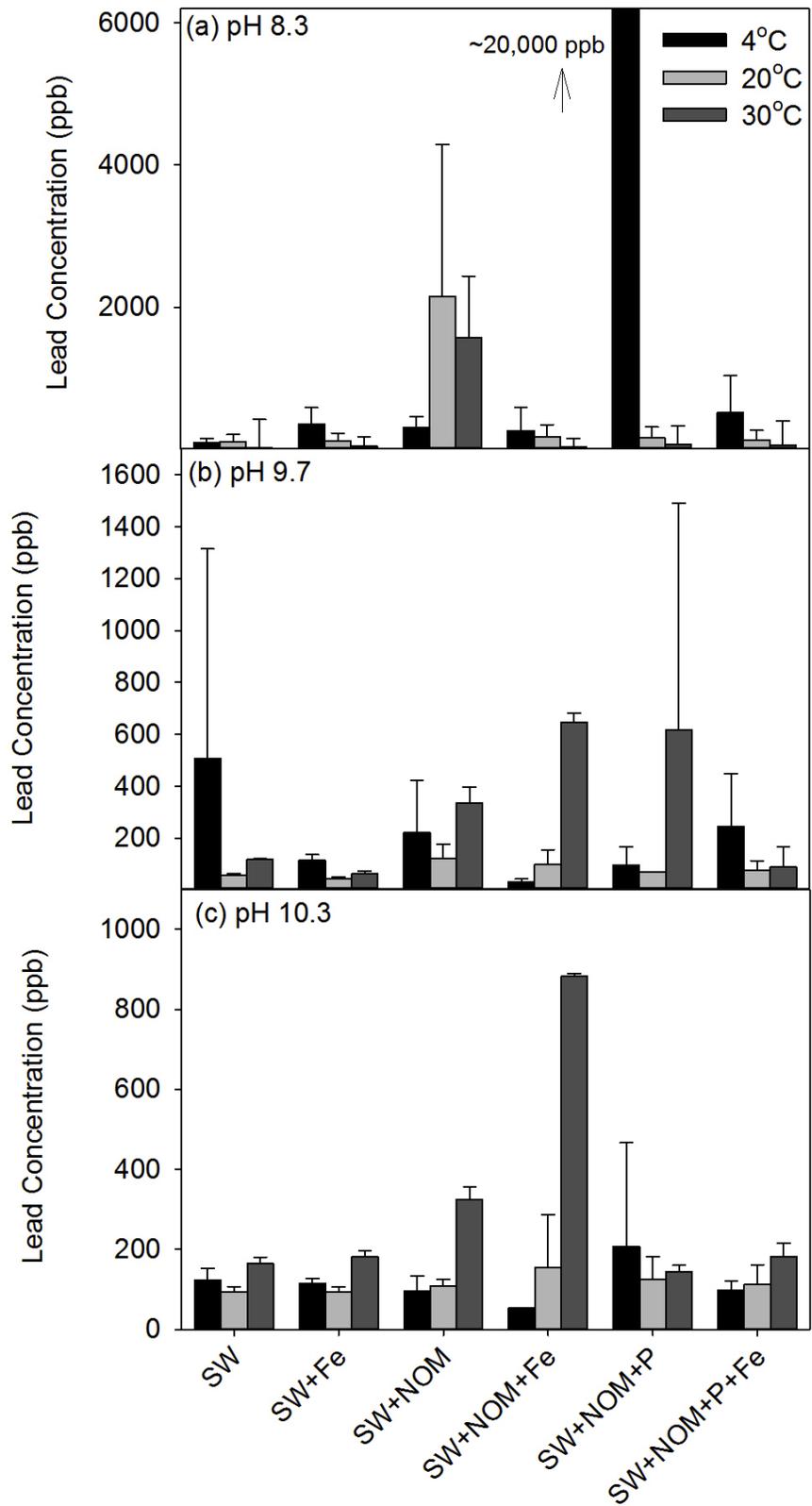


Figure D3. Average soluble lead release from triplicate pipes.

CHAPTER 5. INHERENT VARIABILITY OF LEAD AND COPPER CONCENTRATIONS COLLECTED DURING STANDARDIZED SAMPLING

Sheldon Masters, Jeffrey L. Parks, and Marc Edwards

ABSTRACT

Variability in the concentration of lead and copper sampled in consumers' homes poses challenges in assessing the effectiveness of corrosion control and identifying health threats. To explore the minimum variability achievable, standardized lead and copper containing plumbing materials (leaded brass, copper tube with lead solder, and a lead copper connection) test rigs were constructed and deployed at 5 utilities. Copper levels had a relative standard deviation (RSD) of 10-15% in replicate samples, whereas for lead the brass had the lowest variability in release (30%) followed by copper-solder (55%) and lead-copper (80%). The high lead variability is comparable to that obtained for sampling within individual homes, and is attributed to semi-random detachment of particulate lead - which has important implications for hazard identification, risk assessment and monitoring of corrosion control effectiveness.

KEYWORDS: Variability, premise plumbing, lead, copper

INTRODUCTION

The US EPA Lead and Copper Rule (LCR) was promulgated in 1991 to protect public health by minimizing lead and copper levels in drinking water. Lead and copper can be released to drinking water via corrosion of lead/copper bearing (i.e., lead pipes, brass, copper with lead solder) plumbing materials such as pipes, faucets and fittings. Since lead and copper are generally absent from water as it leaves the treatment facility, the LCR is unique in requiring utilities to collect one liter, first-draw water samples at consumers' taps after a minimum of six hours stagnation (U.S. Environmental Protection Agency 1991). If 10 percent of these samples exceed the Action Level for either lead (15 ppb) or copper (1,300 ppb), then the utility must implement an appropriate strategy to optimize their corrosion control, educate the public about lead or copper health risks and strategies to avoid their exposure.

This method of monitoring for lead and copper creates unique challenges relative to contaminant monitoring in terms of corrosion control optimization, consumer relations, reproducibility, and detection of public health problems. For instance, EPA has acknowledged that meeting the LCR does not protect consumers at individual taps, and has recommended that homeowners test their own water by collecting a single water sample after 6 hours stagnation—consumers are led to believe that the water is safe if this single sample is below 15 ppb (Triantafyllidou and Edwards 2012; US EPA 2005). But it was recently noted that in assessing water lead as a contributing factor in childhood lead poisoning and other cases, collection of a single sample during an environmental assessment can falsely indicate that a water is safe when other samples collected from the same tap can demonstrate an extreme hazard (Triantafyllidou and Edwards 2012). Likewise, there are many instances when an anomalously high lead concentration collected from a single home, triggered a lead action level exceedance even when the corrosivity of the water has not changed and the home has historically sampled for low lead concentrations.

Clearly, the variability of lead and copper concentrations in tap water measured after > 6 hours stagnation in consumers' homes creates a number of challenges (Schock and Lemieux 2010; Triantafyllidou and Edwards 2012; Triantafyllidou et al. 2015). The factors that cause variability between given homes in a distribution system are well-understood and can include the type and age of plumbing materials (Schock et al. 1996; Lagos et al. 2001; Edwards et al. 2001; Rajaratnam et al. 2002; Troesken 2006; Sandvig et al. 2008; Schock and Sandvig 2009; Turek et al. 2011; Grace et al. 2012; Triantafyllidou and Edwards 2012), chemical and biological changes throughout the distribution system or in different neighborhoods (Lu et al. 1995; American Water Works Association 2002; DiGiano et al. 2005; Al-Jasser 2007; Masters, Wang, et al. 2015), nitrification (American Water Works Association 2002; Zhang et al. 2009; Masters, Wang, et al. 2015), water main corrosion (Imran et al. 2005; Mutoti et al. 2007; Masters and Edwards 2015), biofilm formation and microbial growth (Kerneis et al. 1995; Crozes and Cushing 2000), customer error (Via 2010), sampling protocols that can miss particulate lead (Edwards and Dudi 2004; Triantafyllidou et al. 2007, 2013) and varying water use patterns between homes (Arnold and Edwards 2012; Del Toral et al. 2013) (Table 5-1).

Table 5-1 Summary of Sources of Lead and Copper Variability and How a Pipe Rig Can Minimize These With Respect to Consumer Home Sampling

Description	Consumer Home Sampling	Pipe Rig Sampling	References
Plumbing material	Can be very heterogeneous, i.e. no two houses alike	Material can be specified; all pipe rigs can be constructed identically	Schock, 1990; Schock et al., 1996; Sandvig et al., 2008; Triantafyllidou and Edwards, 2012
Plumbing age	Extremely heterogeneous throughout distribution system	All pipe rigs can be same age	Ferguson et al., 1996; Broo et al., 1997; Edwards et al., 2001; Rajaratnam et al., 2002; Schock and Sandvig, 2009; Turek et al., 2011; Grace et al., 2012
Water quality	Water age, and thus water quality, can vary throughout distribution system	Same as consumer home	Cantor et al., 2003; Renner, 2006; Stith and Raynor, 2006; Gronberg, 2007; HDR Engineering Inc, 2011; Hill and Cantor, 2011; Arnold Jr. et al., 2012; Scardina et al., 2008; Edwards, 2014; Wang et al., 2014; Masters et al., 2015
Sample collection - stagnation time	Can be highly variable since sampling protocols vary from 0 to >8 hours	Can be specified exactly for utility personnel collecting samples	Kuch and Wagner, 1983; Schock, 1990; Schock et al., 1996; Van Der Leer et al., 2002; Levin et al., 2008; Cartier et al., 2011; Triantafyllidou and Edwards, 2011, 2012; Triantafyllidou et al. 2015
Sample collection - flow rate	Can be highly variable since not specified in protocol	Can be specified for utility personnel collecting samples	Schock 1990; Reiber et al. 1997; Triantafyllidou and Edwards 2012; Cartier et al. 2012; Clark et al. 2014; Brown and Cornwell 2015
Water use	Variation in water use pattern at different homes with lower use associated with higher lead	Can be specified for utility personnel collecting samples	Arnold and Edwards 2012; Del Toral et al. 2013
Sampling protocol	Existing protocols can miss as much as 100% of the total lead which can underestimate variability	Additional acid digestion and heat treatment to recover particulate lead	Edwards and Dudi 2004; Triantafyllidou et al. 2007, 2013
Variation in temperature between homes	Lead tends to increase at warmer temperature while copper tends to decrease	All pipe rigs at the same temperature	Schaut, 1942; Moore, 1973; Karalekas et al., 1983; Gregory and Jackson, 1984; van den Hoven, 1985; Colling et al., 1987; Lee et al., 1989; Schock, 1990; Colling et al., 1992; De Rosa and Williams, 1992; Johnson et al., 1993; Rezania and Anderi, 1995; Clement et al., 2000; Fleishman, 2001; Rushing and Edwards, 2004; Tang et al., 2006; Edwards et al., 2009; Lintereur et al., 2010; Cartier et al., 2012; Deshommes et al., 2013; Del Toral et al., 2013
Inherent variability in material	Can be highly variable if mostly particulate	New lead/copper materials which are less variable than harvested samples	Pocock 1980; Matthew 1981; M. R. Schock 1990; Levin et al. 2008; Triantafyllidou and Edwards 2012

Subtle differences in sample collection protocol can lead to large differences in detection of water lead hazards at taps. For example, past research has shown that higher flow rates during sample collection can sometimes markedly increase the amount of lead or copper collected in a sample due to detachment of lead rust during high flow conditions or hydraulic disturbances (Figure 5-1) (Britton and Richards 1981; Schock 1990; De Rosa and Williams 1992; Reiber et al. 1997; Edwards et al. 2000; McNeill and Edwards 2004; Lehtola et al. 2006; Calle et al. 2007; Triantafyllidou and Edwards 2009; Vargas et al. 2010; Triantafyllidou and Edwards 2012; Cartier et al. 2012; Clark et al. 2014). This concept is particularly important since the last few decades of corrosion control have focused on reducing soluble lead (Sheiham and Jackson 1981; Schock and Gardels 1983; Schock et al. 1996; Triantafyllidou et al. 2007) and as a result the majority of lead in many distribution systems is now in a particulate form (McNeill and Edwards 2004; Triantafyllidou et al. 2007; Masters and Edwards 2015). Even though several studies have attributed some variability in lead measurements to random “spikes” in particulate lead release due to semi-random detachment of particulates from the pipe wall (Schock 1990; Triantafyllidou et al. 2007; Boyd, Pierson, Kirmeyer, and English 2008; Boyd, Pierson, Kirmeyer, Britton, et al. 2008; Triantafyllidou and Edwards 2012), the potentially important contribution of particulate lead sampling variability has never been isolated from the other factors (Table 5-1), which is important because it represents an unavoidable “inherent” variability that cannot be reasonably controlled for without running a risk of “missing” water lead hazards. That is, to reduce variability consumers have been instructed in writing to “pre-flush” plumbing lines the night before sampling, or to collect water at a very flow rate of “1 liters per minute,” which is controversial because the reduced variability comes at the direct expense of detecting taps that pose a serious public health threat when particulate lead is present (Edwards and Triantafyllidou 2007; Triantafyllidou et al. 2007; Triantafyllidou and Edwards 2012; Clark et al. 2014). Before the practice was banned in 2004, utility re-sampling of homes with high lead was often allowed, and quite frequently a low test result was then obtained which reinforced perceptions that the customer had somehow erred in collection of the original sample (Reiber et al. 1997; Grumbles 2004; Leonnig 2004).

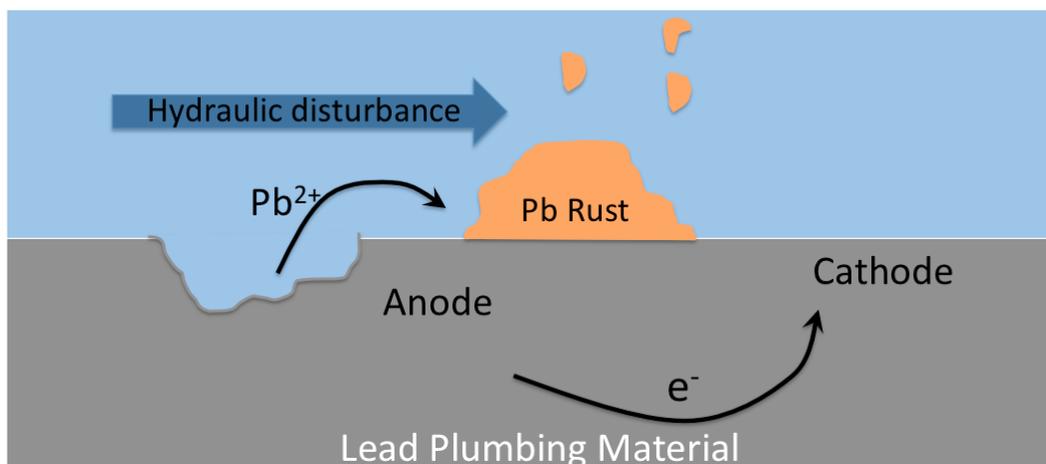


Figure 5-1 Corroded Pb^{2+} can contaminate potable water or attach to pipes, creating an accumulating rust layer which can be detached by hydraulic disturbances or high flow conditions.

In a few prior studies that have characterized the cause(s) of variability of lead and copper concentrations in premise plumbing, Schock (1990) reported a relative standard deviation (RSD) for repetitive measurements of lead concentrations at one site of 50 – 75%. Marcus et al. (1990) found the RSD for US EPA testing from individual homes in three cities averaged between 47-92% (Table 5-2) which is similar to the values obtained by Schock et al. (1990). Some of the variability in these studies can be explained by the fact that stagnation times and flow rates were not rigorously controlled at each site. In later studies using carefully constructed replicate pipe loops, which was expected to completely eliminate the nuances associated with consumer sampling and guaranteed exposure to the exact same water, the RSD was more than 60% for lead solder samples between replicates although it was speculated that this was due to workmanship issues (Economic and Engineering Services 1990).

Table 5-2 Summary of RSD Data for Homes from Selected Cities Evaluated by Marcus et al. (1990).

City	# Homes	Total # Measurements	Avg RSD	Range
New Bedford (MA)	10	137	59	0.41 - 0.80
Chicago (IL)	24	622	47	0.14 - 0.95
Newport News (VA)	37	508	92	0.49 - 1.59

The objective of this study was to conduct the first rigorous studies to characterize the inherent variability in lead and copper release from premise plumbing materials in an era when corrosion control is commonplace. Bench and field studies were designed, constructed, and operated with sufficient replication to characterize variability, while eliminating the other most commonly cited sources of variability including sample collection flow rate, different stagnation times, analytical protocols and consumer error.

MATERIALS AND METHODS

Corrosion Evaluation Rigs (CERs)

Metal Test Piece Design and Testing. Lead and copper bearing plumbing materials were constructed in a manner that minimized variability to the extent possible (e.g., using metal from the same lot, using an identical amount of flux and solder, etc.). Moreover, all samples were pre-tested before sampling, and the 25% of samples with the greatest deviation from the mean were not used in subsequent testing (Figure E1 and Table E1), further reducing variability in the lead or copper leaching propensity of the plumbing materials (Parks et al. 2014).

Leaded Brass. ½” diameter CDA360 brass bar stock (61.5% Cu nominal, 2.7% Pb minimum, 35.4% Zn nominal) was inserted into ¾” diameter PVC pipe. The brass rods were held in place by epoxy. Test pieces were 30” (76 cm) long, and rods were secured in place with a 2” (5 cm) long epoxy bead on each end.

Lead/Copper Pipe. 30” (76 cm) of ¾” diameter Type M copper tube was galvanically connected to 30” (76 cm) of 1” (2.5 cm) OD x ¾” (1.9 cm) ID new lead pipe, since

harvested lead pipe would likely increase variability (Wysock et al. 1995). A dielectric was inserted between the two dissimilar metals and the metals were electrically connected using an external jumper wire.

Leaded Solder/Copper Pipe. A 12'' (30 cm) long piece of 50:50 lead/tin solder was melted inside a 60'' (152 cm) long 3/4'' Type M copper tube. To maximize reproducibility, each solder piece was weighed (21.2 ± 0.3 g) and then melted using an 8 minute heating cycle from resistive tape wrapped around the outside of the copper tube and then covered by insulation.

Pipe Rig Design and Testing. Ten plumbing pipe rigs were constructed (Figure E2) and two pipe rigs were installed at each of five public water utilities in fall 2011. One rig was installed at the water treatment plant while the second pipe rig was installed in the distribution system (typically a water tower or administrative building). Each rig was outfitted with each type of lead and copper bearing metal pipe described above in triplicate.

The general overall design was as follows. Water entered into a common header and could flow either into a bypass line or one of three manifolds with the triplicate pipes operated in parallel. A timer was connected to all the solenoid valves to precisely control the flow duration through each manifold during normal use. A design water flow rate was always 10 L/min (water velocity 0.6 meters/second) unless stated otherwise, with an LCR minimum of 6 hour stagnation prior to sample collection, and otherwise the pipes were flushed 10 minutes every 8 hours. Thus, 300 liters of water passed through each test piece every day. The rigs were operated for a year and samples were collected from each pipe section after six hours of stagnation at least once per month by water utility personnel for each pipe rig. These samples were shipped to Virginia Tech and analyzed using ICP-MS using the same sample handling protocol and technician.

Effect of Speciation and Flow Rate on Variability. In September 2012, a 10-mL aliquot from each lead-copper sample was filtered in the field using a 0.45- μ m pore size nylon syringe filter (Whatman) and a 10-mL BD syringe to operationally determine the soluble metals concentration. A more detailed analysis was conducted at Utility A and B to examine the contribution of particulate release to variability. At Utility A, filtered measurements were taken during the last 4 months of the experiment. In the last 6 months of the field study, filtered measurements were also taken from lead-copper samples at Utility B. To further define the contribution of particulate lead to variability in concentration, samples were collected during the last month of the study at 2 flow rates. Low flow samples (i.e., 2 LPM) were collected with a water stream approximately the size of a pencil as recommended in a previous research report (Reiber et al. 1997). Twenty-four hours later (after 3 flushing and stagnation cycles) high flow samples (10 LPM) were collected for comparison. Results were interpreted qualitatively based on the premise that higher flow rate has no effect on truly soluble lead but will mobilize more particulate lead.

Data Analyses

Relative standard deviation (RSD), defined as the absolute value of the ratio of the standard deviation to the mean of the sample population expressed as a percentage, was used as one measure of variability in samples. The RSD for the 90th percentile lead and copper measurements for LCR sampling results for the years 2009 through 2012 from 5 utilities (A-E) with varying characteristics (Table E2 and Table E3) were gathered, analyzed and compared to results using test rigs described below.

RESULTS

After reviewing the variability in the LCR field data at participating cities, results from the deployed replicate pipe rigs are described for comparison. An intensive study of two utilities exhibiting extreme lead spikes and variability in the pipe rigs attempted to confirm whether trends were consistent with particulate lead detachment.

Variability in LCR Testing. Within a given LCR sampling pool, the variability in copper measurements averaged 101% (range 63-284%) within each utility from 2009-2012, during which time the cities had relatively stable corrosion control and water quality. The average inter-site variability in lead concentration of 206% (range 71-404%) was twice that of the average copper variability (Table 5-3).

Table 5-3 Summary of Lead and Copper LCR Results from Five Participating Utilities

Utility	Year	Lead					Copper					
		#Samples	90th %ile	Mean	Std Dev	RSD	#Samples	90th %ile	Mean	Std Dev	RSD	
A	2012	112	13.9	6.8	14.1	208%	102	50	30	24	79%	
	2011-2	119	21.4	11.1	25.3	228%	111	40	29	17	57%	
	2011-1	114	14.7	8.9	28.6	322%	101	60	36	21	58%	
	2010-2	107	20.4	11.8	22.6	191%	99	40	26	44	166%	
	2010-1	111	21.0	9.0	13.8	152%	99	60	40	47	118%	
B	2012	58	14.2	8.5	11.9	140%	58	165	107	304	284%	
C	2012-1	110	3.2	1.8	2.5	138%	110	41	22	14	62%	
	2011-2	107	4.4	2.2	3.4	154%	107	26	16	8	50%	
	2011-1	111	5.2	2.4	4.0	163%	111	36	22	21	97%	
	2010-2	112	5.1	3.0	5.4	180%	112	34	21	12	58%	
	2010-1	108	3.9	3.4	11.5	340%	108	39	22	23	105%	
D	2012	50	2.1	2.4	1.7	71%	50	256	128	84	66%	
	2009	51	3.0	3.5	7.9	226%	51	270	164	98	59%	
E	2011	52	7.7	7.6	30.7	404%	51	290	91	110	121%	
	2010	50	5.3	2.9	4.7	160%	50	381	114	146	128%	
	2009	53	6.5	5.3	12.0	226%	52	369	118	137	116%	
<i>Average</i>											206%	101%

Inter-site (between homes) variability is expected to be much greater than intra-site (i.e., repeated sampling at a given home) variability due to the presence of different plumbing materials and exposure histories in homes, and this was confirmed at utility A, C and E (Figure 5-2). Average intra-site lead variability ranged from 21-80% while average copper intra-site variability ranged from 30-48% RSD. The intra-site variability at utility

A was 72% for lead compared to an average of 220% for the inter-site samples. Similarly, copper variability for inter-site sampling was 2X> than repeated sampling at utility A (96% vs. 48%). A similar pattern was also observed at utility C and E where the inter-site variability was 3.3-9.3 times greater than the intra-site variability for lead and at least 2 times greater for copper.

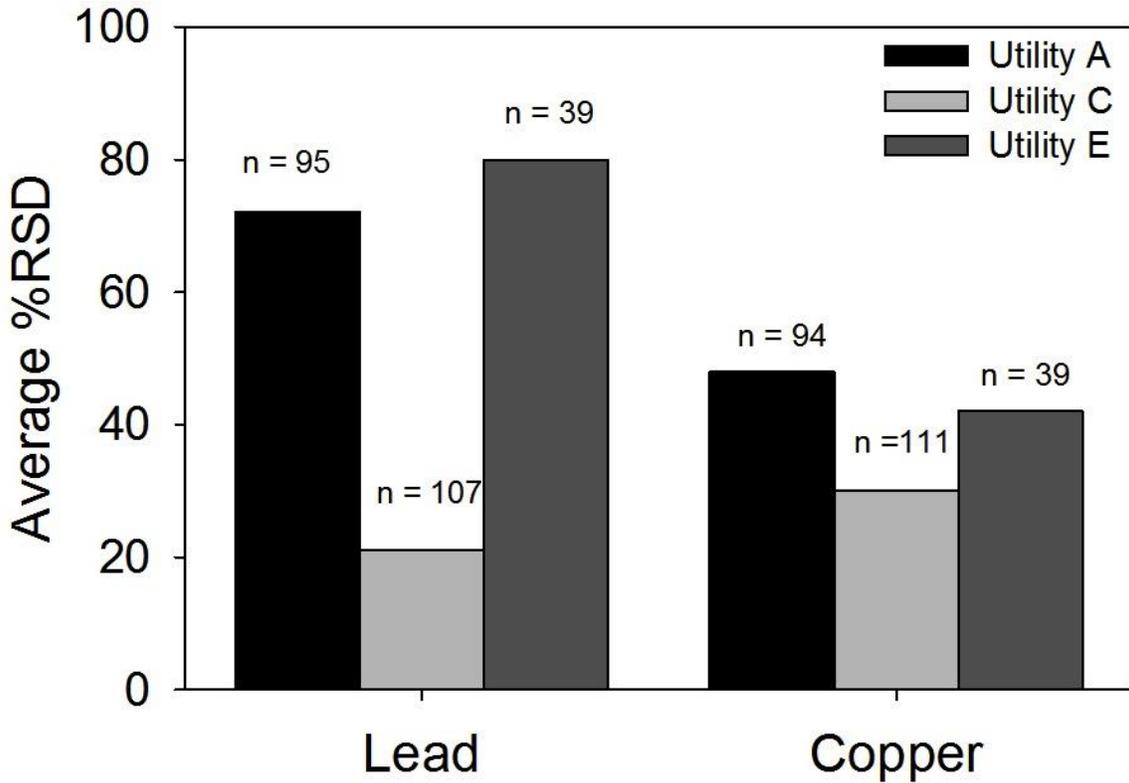


Figure 5-2 Average RSD from Individual LCR Sampling Sites at Three Participating Utilities. Only sites that were sampled three or more times are included in this analysis. ‘n’ indicates the total number of LCR sites that were sampled at least three times.

Variability in Pipe Rig Testing Replicates. For measurements of copper release, copper-solder test pieces exhibited the lowest copper variability with an RSD of 10%, compared to brass and copper-lead test pieces with an average RSD of 15% and 13%, respectively (Figure 5-3a). For lead release the brass test pieces exhibited the lowest lead variability (30%) followed by copper-solder (55%) and brass (80%). These results from the rigorously controlled replicate standardized pipe rigs, are well within the range of RSDs exhibited by the repetitive measurements at a given site. That is, replicate lead samples from individual homes at utilities had a variability of 21-81% compared to pipe rig results of 30-80%, suggesting that much of the variability observed in customer sampling has less to do with variation in their sampling method and errors, and more to do with inherent variability for sampling lead materials.

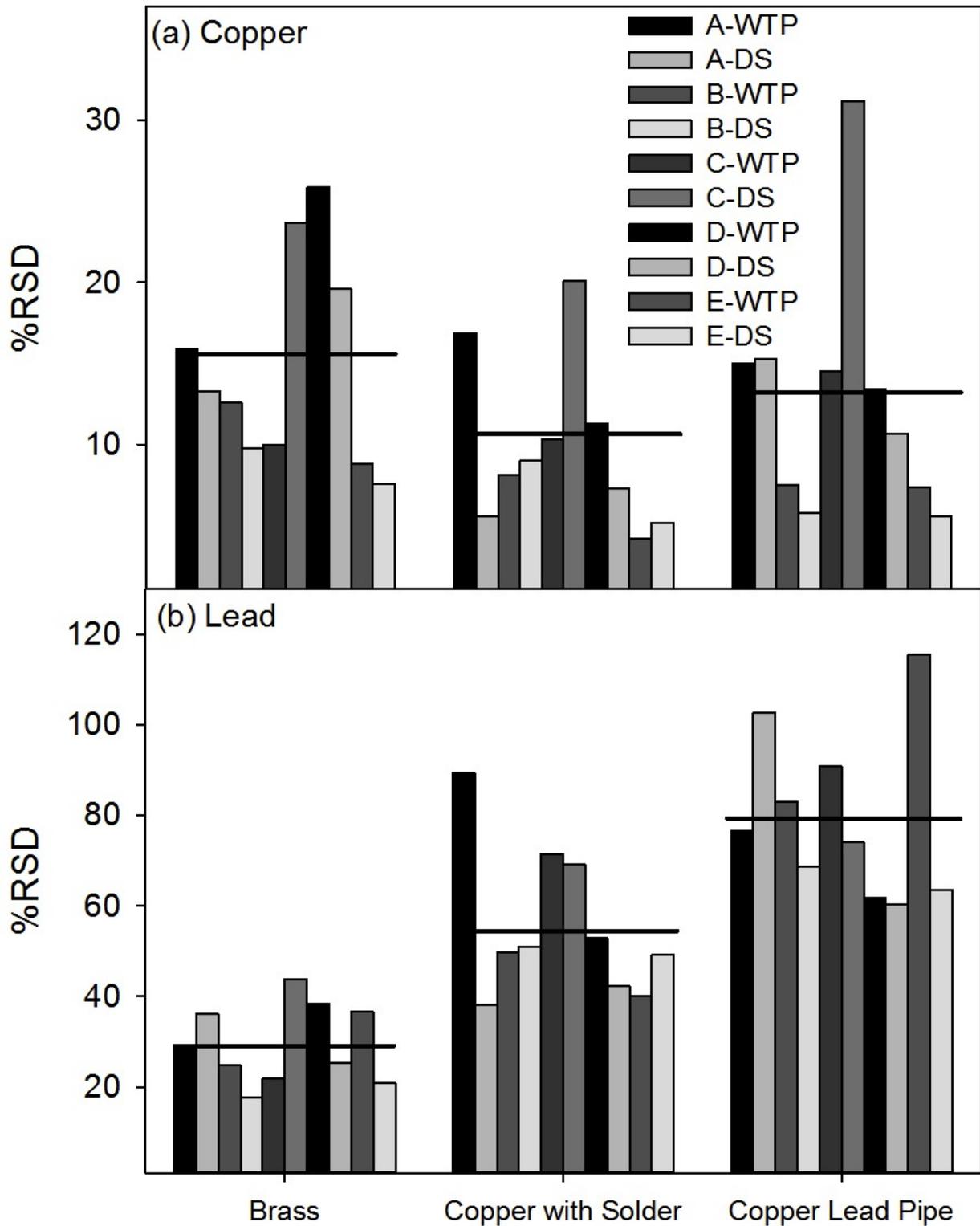


Figure 5-3 Average monthly RSD for (a) copper and (b) lead for Corrosion Evaluation Rigs. Horizontal black bar indicates average RSD for all utilities (WTP = water treatment plant; DS = distribution system).

Variability in Pipe Rig Testing. One city compared to another. Since all test rigs were confirmed to have the same starting point, water exposure history, flow volumes, exposure times and sample flow rates, it was possible to compare the impact of the utilities different water chemistry and treatment processes on variability for replicate samples (Table E4). Variability in lead leaching from brass was very consistent across all utilities (29-33%) even though the average lead release ranged from 3-118 ppb. The highest variability in lead occurred for lead-copper pipe at utilities A and E (both 90%), compared to utilities B-D which had 61-83%. Utility C and D shared the same source water but had slightly different treatment processes. This resulted in a higher variability at utility C for both lead-copper (83% vs. 61%) and copper-solder (70% vs. 48%) compared to D. The highest lead variability for copper-solder was at C (70%) while the lowest was at E (45%). The copper variability was relatively low with an RSD between 5% and 23%.

Contribution of Particulate Lead to Variability

To test the hypothesis that the major source of variability in lead measurements was due to semi-random sloughing during sampling (Figure 5-1), a series of tests were conducted during special sampling events at all utilities and more intensive sampling at two utilities. Utility A was selected for special study because it has exceeded the lead action level since 2006, whereas utility B was selected for further analysis because it had the highest average lead release during the field study (Masters, Parks, et al. 2015).

All Utilities. Of the 30 lead-copper pipe samples collected from the 5 utilities in September 2012, 10 measurements were less than 100 ppb, 12 were 100-1,000 ppb and 8 measurements were more than 1,000 ppb. Samples that were less than 100 ppb were on average 51% particulate as defined by filtration through a 0.45- μ m pore size filter, while samples more than 1,000 ppb were on average 99% particulate (Figure 5-3a). The higher level of particulates also contributed to higher RSD (samples < 100 ppb with RSD of 44% versus 69% for samples > 1,000 ppb).

Focus on Utility A. During the last 4 months of the study, filtered measurements were collected at Utility A for all materials. The lead release from the copper-solder and brass test pieces were very low with an average release of 1.2-2.5 ppb. Thus, in this water at least, significant spikes never occurred from these materials that could seriously affect consumer health or LCR compliance. But in the same water with the lead-copper material, the average lead concentration was 5361 ppb and ranged from 90-94, 220 ppb (Figure 5-4). For the samples < 100 ppb the variability was low with an RSD of 3%, but samples between 100-1,000 ppb had an average RSD of 89% while sample above 1,000 ppb had an RSD of more than 260%. This further demonstrates the dangers of failing to collect LCR samples that do not characterize lead release from the service line, since the highest levels of lead and the greatest variability and greatest health risk are sometimes derived from this source (Edwards and Dudi 2004; Del Toral et al. 2013; Clark et al. 2014).

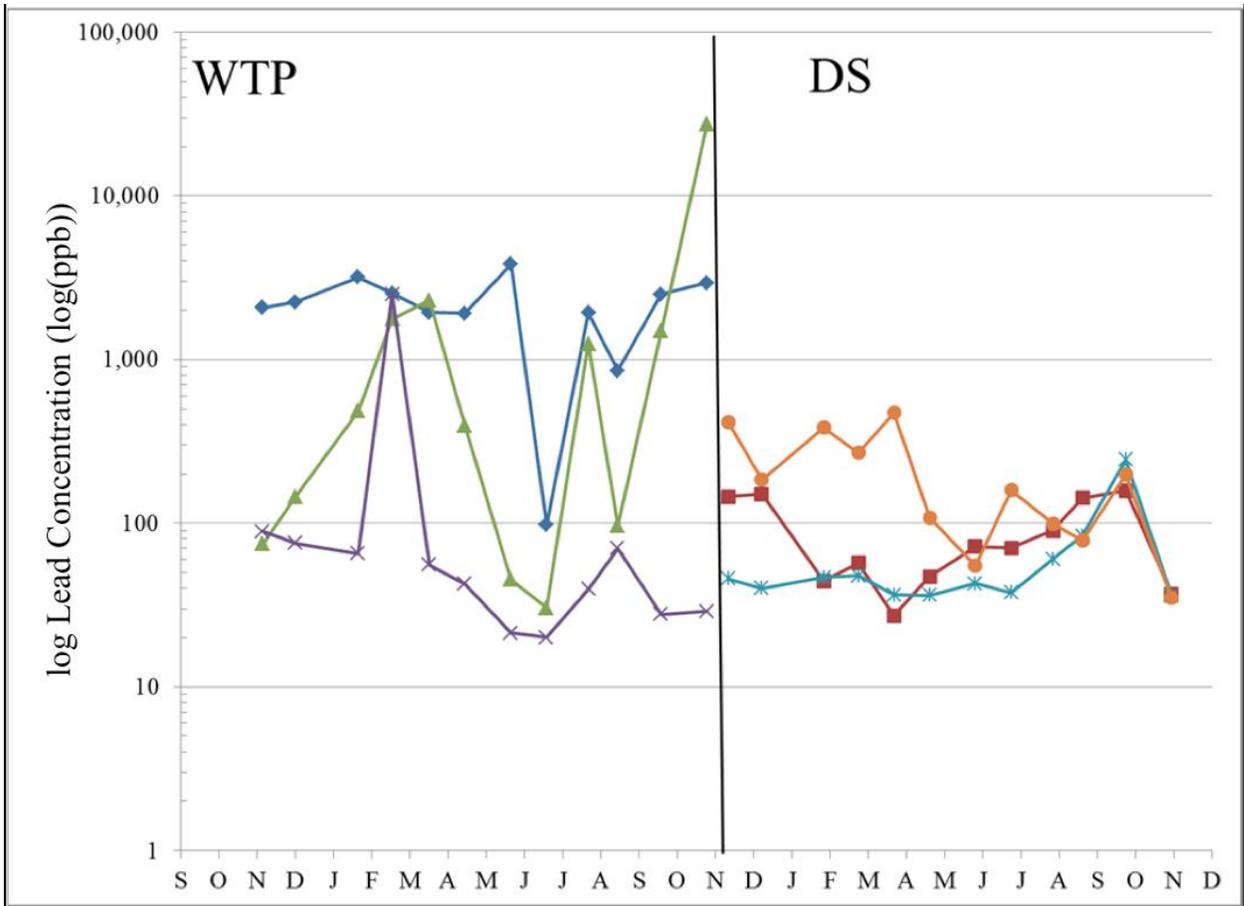


Figure 5-4 Lead data for lead-copper test pieces at the WTP and DS for utility A (modified from Parks et al. (2014)).

Focus on Utility B. These samples frequently had large, visible, white sand-like lead bearing particles present. As such, during the last six months of the field study, the lead-copper test pieces were sampled 9 times and filtered measurements were collected in order to assess the contribution of particulates to the lead levels. The average lead concentration during this period was 6,273 ppb and ranged between 48 ppb to 81,720 ppb. Samples that were < 100 ppb and 100-1,000 ppb were ~70% particulate while samples > 1,000 ppb were 97% particulate, consistent with expectations of a relatively stable soluble lead concentration and a highly variability particulate fraction. Consistent with the previous findings (Figure 5-5a and Figure 5-5b), variability increased at higher concentrations of lead and in samples with a greater fraction of particles. For example, the RSD for measurements < 100 ppb was 26% compared to 155% for samples > 1,000 ppb.

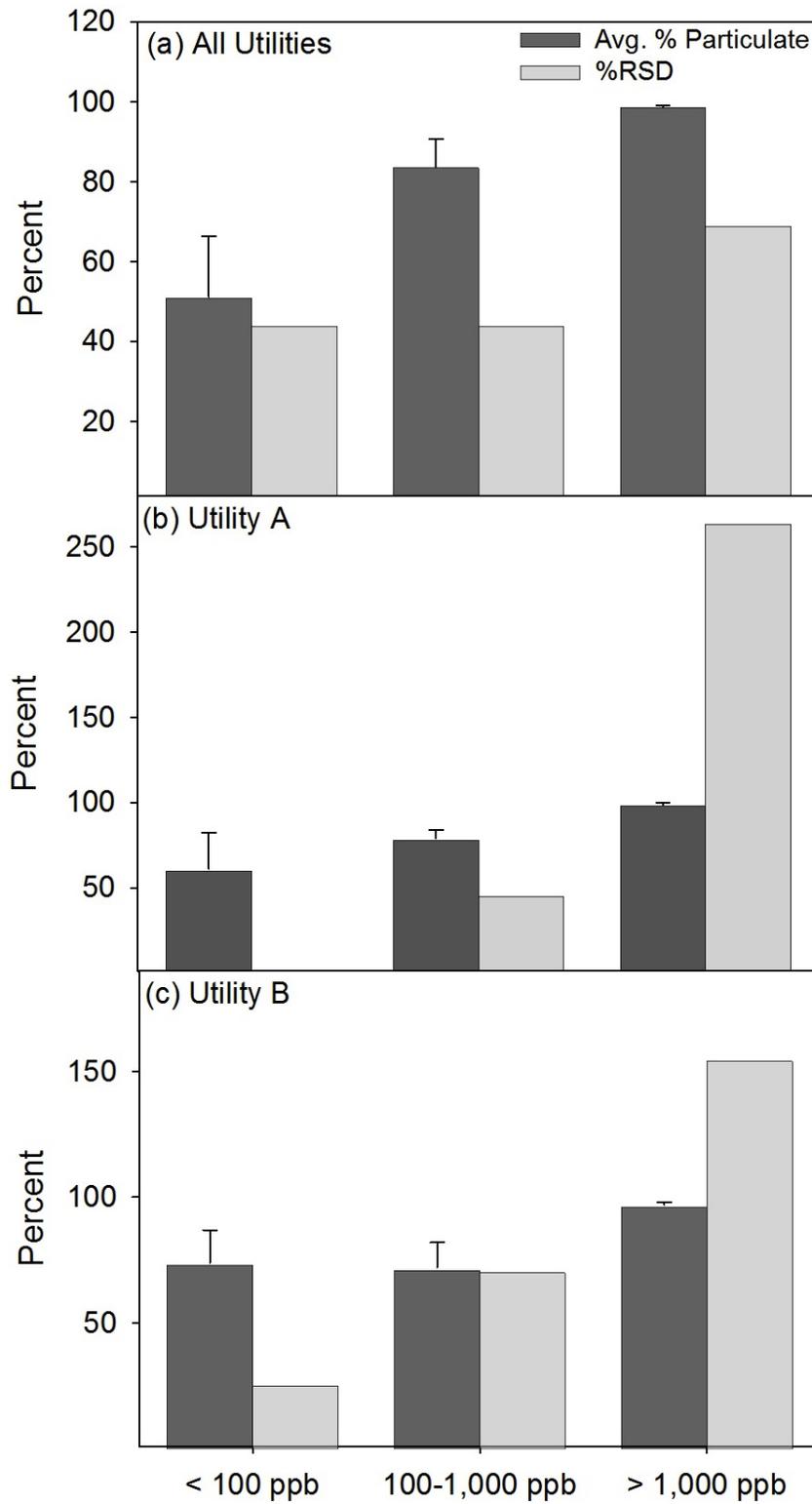


Figure 5-5 Average percent particulate lead and RSD from lead-copper samples for three threshold ranges at (a) all utilities, (b) Utility A and (c) Utility B.

Effect of Sampling Flow Rate. The effect of sampling flow rate on lead release was examined in order to more carefully define the contribution of particulates to variability. In all cases where lead was > 15 ppb, higher flow (10 LMP) caused more lead release compared to low flow conditions (2 LMP). At high flow, lead was higher by as much as 290X for brass, 3X for solder and 220X for lead (Figure 5-6). For example, at utility C WTP, average lead release from brass was 114 ppb at high flow (150% RSD) versus 0.4 ppb at low flow (57% RSD). The highest average lead release from copper-lead test pieces was 10,136 ppb (149% RSD) compared to 47 ppb (87% RSD) at low flow (E WTP), reinforcing the hypothesis that hydraulic disturbances increases particulate lead release and variability.

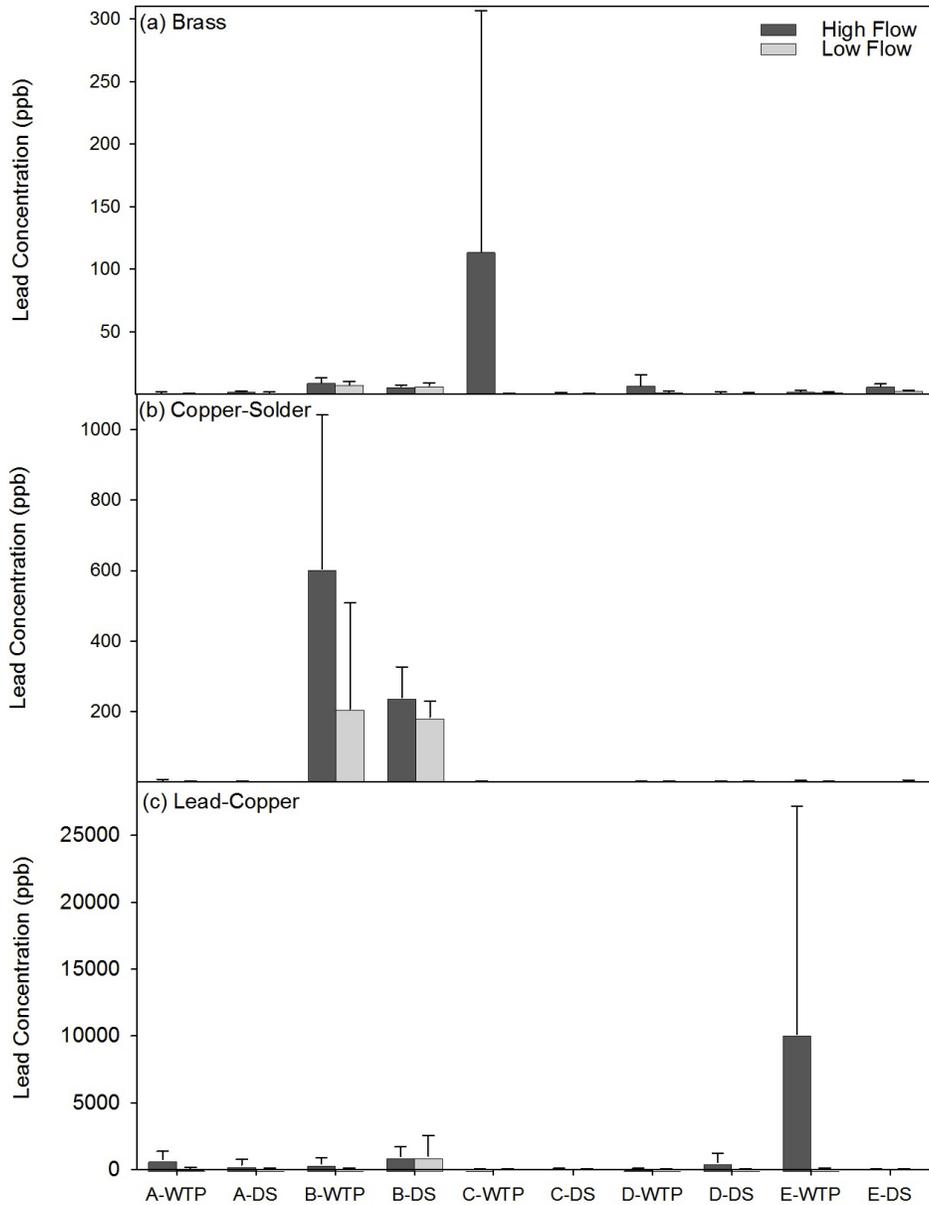


Figure 5-6 Impact of sample flow rate on lead release from (a) brass, (b) copper-solder, and (c) lead copper test pieces.

DISCUSSION

The majority of the variability in lead measurements between test rig replicate samples on a given day, is consistent with hypothesized semi-random/random detachment of lead particles, since virtually all other sources of variability were eliminated or reduced in the experimental design. It is possible and even likely, that the sampling variability and fraction of particulate lead has risen in the last few decades, since corrosion control strategies have focused on reducing soluble lead (Sheiham and Jackson 1981; Schock and Gardels 1983; Schock et al. 1996; Triantafyllidou et al. 2007) resulting in a greater fraction of particulate lead (McNeill and Edwards 2004; Triantafyllidou et al. 2007). Regardless, the high lead variability due to particulate release clearly has important practical and regulatory implications, including the need to explicitly consider the durability and adherence of lead scales when designing monitoring programs, sampling protocols and corrosion control strategies. Variability in water lead concentrations are inherent to sampling of premise plumbing, and the levels of variability based on consumer sampling are well within the range of that obtained herein from replicate rigs with computer control of flow and other factors to minimize variability.

A comparison of the effect of flow rate on metals release confirmed previous findings (Britton and Richards 1981; M. R. Schock 1990; De Rosa and Williams 1992; Reiber et al. 1997; McNeill and Edwards 2004; Lehtola et al. 2006; Calle et al. 2007; Triantafyllidou and Edwards 2009; Vargas et al. 2010; Triantafyllidou and Edwards 2012; Cartier et al. 2012; Clark et al. 2014) that hydraulic disturbances and higher flow rates sometimes play an important role in consumer exposure to lead and copper. For example, in this study lead was as much as 99.9% lower at the lower flow conditions. Thus, previous suggestions that samples be collected at very low flow (Reiber et al. 1997) would indeed decrease variability, but also quantify health risks to consumers from particulate lead hazards.

Utility C and D shared the same source water but had slightly different treatment processes which resulted in different levels of variability. Variability was slightly higher at utility C for both lead-copper (83% vs. 61%) and copper-solder (70% vs. 48%) compared to D. The most obvious water quality differences were that utility C had a pH which was more than 1 unit higher than D and 40% less total phosphate (~130 mg/L vs. 230 ~mg/L). Higher pH and higher phosphate may be more associated with particulate lead, which can potentially explain the higher variability at Utility C.

Practical and Regulatory Implications of Variability and Particulate Lead Release.

Sampling Protocols. Previous studies have shown that lead levels can vary significantly within a distribution system even when the LCR is met (Gronberg 2007; Renner 2006a; Stith and Raynor 2006; HDR Engineering Inc 2011; Edwards 2014; Wang et al. 2014). Particulate lead from lead solder has been implicated in several cases of childhood lead poisoning while the utilities were in compliance with the LCR (Copeland 2004; Bachelor 2005; Allegood 2005; Renner 2006b; Gronberg 2007). In these cases, current regulations and analytical methods were shown to “miss” particulate lead (Triantafyllidou et al.

2007). Due to the fact that conditions in the human stomach (chloride, low pH, and warm temperature) are more aggressive than the acid employed for metals analysis, a significant portion of particulate lead that is “missed” by these protocols can become bioavailable when consumed (Triantafyllidou et al. 2007, 2013). Since existing sampling and analytical protocols can miss as much as 100% of the total lead that is present (Edwards and Dudi 2004; Triantafyllidou et al. 2007, 2013), health-risks can be underestimated.

Number of Samples. The LCR requires utilities to sample homes with the highest propensity to leach lead. The number of sites varies depending on the size of the system and the monitoring frequency with 5-100 samples under standard monitoring and 5-50 under reduced monitoring (U.S. Environmental Protection Agency 1991, 2014). Ideally, the number of sites sampled should be large enough to estimate the mean (and also 90%ile) lead and copper concentration within a certain accuracy and confidence level. However, the larger the variability in sampling, the more samples that are needed to define the mean and 90%ile values with statistical confidence. A power analysis (power = 0.9 and $\alpha = 0.05$) was used to estimate the number of samples needed to determine the mean concentration within 20% of the true mean. In order to characterize the mean lead concentration for intra-site variability 134-4289 samples would have to be collected. The number of samples required tended to increase with the standard deviation. Even in the well-controlled test rigs, 25-8375 lead samples would be needed depending on the material.

Environmental Assessment and Characterizing Risks at Individual Taps. In assessing water lead as a contributing factor in childhood lead poisoning and other cases, collection of a single sample during an environmental assessment that happens to measure below 15 ppb, can falsely indicate to consumers that a water is safe while repeated measurements from the same tap can demonstrate an extreme lead hazard (Triantafyllidou and Edwards 2012). In one sampling event, 8 of the 10 samples collected from a single tap was less than 15 ppb while the other two samples measured 16,030 and 28,985 ppb and had an RSD of 221% (Triantafyllidou and Edwards 2009). Clearly, guidance from US EPA imply that testing of taps can verify a water is safe, can be misleading as long as lead bearing plumbing materials are present (US EPA 2005). Ultimately, the only way to truly have confidence in the water’s safety is to install inexpensive filters (\$30-100) that can remove the majority of the particulate lead spikes from the water or to completely remove the lead sources. However, even after complete removal of the lead sources, it can take months before accumulated particulate lead risks are cleaned from a plumbing system (Schock et al. 2014). New public education materials directed at consumers should reflect this reality.

CONCLUSIONS

- Variability in lead and copper measurements poses challenges in assessing corrosion controls strategies and can sometimes lead to underestimated public health risks. The average inter-site variability for copper and lead measurements in distribution systems was 101% and 206% respectively. As would be expected, intra-site variability was less than inter-site. However, hundreds of samples would

still have to be collected to accurately characterize the lead concentration at a single tap.

- Lead variability in well-controlled pipe rigs with brass, copper-solder, and copper-lead test pieces was within the range of the RSD for the repeated measurements from consumer taps. Variability in measurements which were once attributed to nuances in consumer sampling, might be dominated by the inherent variability in lead release from the plumbing system itself.
- In the test rigs, variability increased at higher concentrations of lead and in samples with a greater fraction of particles. Since existing protocols can miss the majority of particulate lead in samples, health-risks as well as variability are likely to be underestimated especially in highly contaminated water.
- To adequately characterize whether water in a given home with lead plumbing is truly safe, an unreasonable number of samples would have to be collected under a range of flow conditions. It would simply be more cost effective to assume that as long as lead bearing plumbing is present, there is a significant possibility of high, semi-random concentrations of lead in water samples, that can only be avoided by installing filters or ultimately by removing the lead plumbing.

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APPENDIX E

Supporting Information for Chapter 5

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KEYWORDS. Variability, premise plumbing, lead, copper

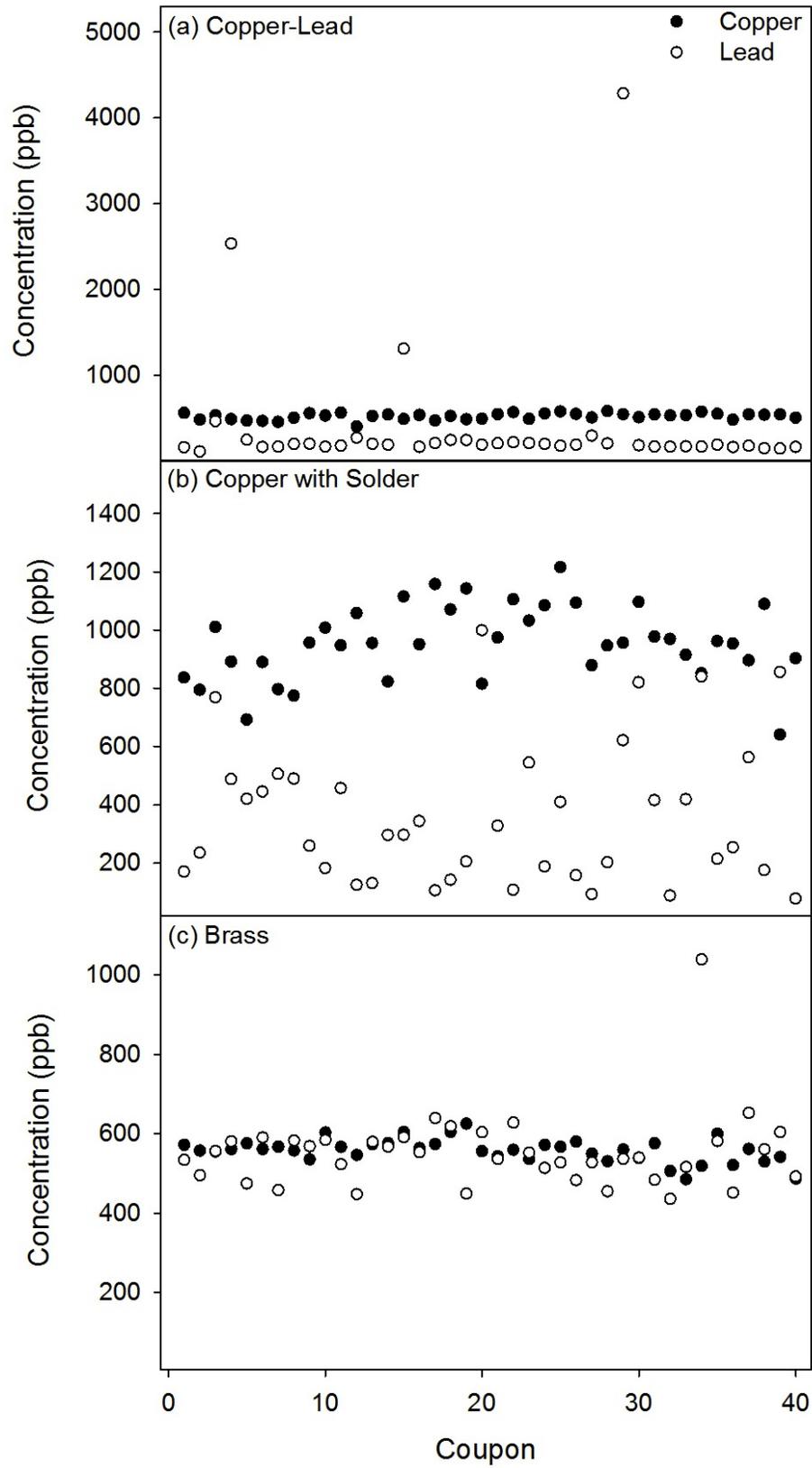


Fig E1 Lead and copper concentration for (a) brass, (b) copper with solder and (c) copper-lead pipe pretest coupons.



Fig E2 Corrosion evaluation rig.

Table E1 Summary of Lead and Copper Statistics for the Carefully Constructed Test Pieces

	CDA360 Brass in PVC Pipe		Copper Tube with 50:50 Lead/Tin Solder		Copper Tube Galvanically Connected to Lead Pipe	
	Lead (ppb)	Copper (ppb)	Lead (ppb)	Copper (ppb)	Lead (ppb)	Copper (ppb)
<i>All coupons (n = 40)</i>						
Range	435 - 1,039	485 - 625	78 - 1,000	641 - 1,216	112 - 4,286	402 - 583
Mean	552	557	361	956	387	522
Std Dev	97	30	242	128	753	39
% RSD	17.6	5.4	67.0	13.4	194.6	7.5
<i>Selected coupons (n = 30)</i>						
Range	474 - 619	485 - 604	106 - 545	692 - 1,216	147 - 220	456 - 583
Mean	548	559	291	974	182	531
Std Dev	40	28	137	126	19	34
% RSD	7.3	5.0	47.1	12.9	10.4	6.4

Table E2 Summary of characteristics of drinking water utilities.#

Utility	Treatment Process	LCR Compliance History	Utility Interest in Project
A	Conventional treatment with chlorine disinfection/Lime and CO ₂ for water stability/no corrosion inhibitor	Out of compliance: 2006-2011; part of 2012	Lead compliance problems; large fraction of unlined iron distribution system
B	Conventional treatment/UV and chloramine disinfection/no corrosion inhibitor	In compliance	Multi-source water with large distribution system; some nitrification and copper corrosion issues
C	Conventional treatment plus GAC contactors/Chlorine disinfection and corrosion inhibitor	In compliance	Use of testing technique to evaluate corrosion issues in distribution system
D	Three treatment plants with conventional treatment/Chlorine disinfection and corrosion inhibitor	In compliance	Difficult to find LCR volunteers. Variable water quality.
E	Conventional treatment plus ultra-filtration membranes/Chlorine disinfection and corrosion inhibitor	Out of compliance: 2004-2007	Past lead corrosion problems; old distribution system

#Adapted from Masters et al. (2015)

Table E3 Comparison of water quality parameters of drinking water utilities (\pm standard deviation). #

Parameter	Utility A			Utility B			Utility C			Utility D			Utility E		
	WTP	DS	p-val.	WTP	DS	p-val.	WTP	DS	p-val.	WTP	DS	p-val.	WTP	DS	p-val.
pH	9.9 \pm 0.13	9.7 \pm 0.1	0.001	7.60 \pm 0.11	7.6 \pm 0.1	0.64	8.6 \pm 0.1	8.6 \pm 0.1	0.69	7.4 \pm 0.1	7.3 \pm 0.1	0.06	8.01 \pm 0.1	8.07 \pm 0.1	0.08
Alkalinity (mg/L as CaCO ₃)	19.0 \pm 1.7	17.3 \pm 1.4	0.026	218.3 \pm 27.0	206.5 \pm 25.9	0.39	79*	N/M	-	54.3 \pm 24.7	53.2 \pm 24.4	0.77	106.5 \pm 1.8	106.9 \pm 2.3	0.57
Total Chlorine (mg/L as Cl ₂)	1.1 \pm 0.3	0.6 \pm 0.1	<0.0001	1.8 \pm 0.3	1.0 \pm 0.3	0.0001	1.1 \pm 0.1	0.9 \pm 0.1	0.001	1.7 \pm 0.2	1.7 \pm 0.2	0.74	1.3 \pm 0.2	1.1 \pm 0.1	0.003
Total Phosphate (μ g/L)	-	-	-	-	-	-	131.9 \pm 23.7	137.5 \pm 20.3	0.51	228.5 \pm 40.9	223.8 \pm 38.1	0.67	281.0 \pm 19.6	276.1 \pm 27.5	0.80
Iron (μ g/L)	12.8 \pm 12.6	64.6 \pm 63.1	<0.0001	4.8 \pm 3.7	22.4 \pm 11.0	<0.0001	-	-	-	-	-	-	-	-	-
Aluminum (μ g/L)	2.3 \pm 1.4	3.0 \pm 2.2	0.10	74.7 \pm 40.6	54.2 \pm 28.0	0.11	63.6 \pm 34.9	61.8 \pm 36.6	0.64	17.3 \pm 15.5	17.6 \pm 15.6	0.93	5.0 \pm 2.8	3.3 \pm 1.30	0.10
Nitrate (mg/L as N)	0.09 \pm 0.16	0.11 \pm 0.15	0.93	1.98 \pm 1.00	0.84 \pm 0.51	0.004	0.66 \pm 0.26	0.70 \pm 0.41	0.84	0.59 \pm 0.27	0.55 \pm 0.31	0.89	0.36 \pm 0.18	0.36 \pm 0.18	1
Chloride (mg/L)	22.0 \pm 2.7	21.9 \pm 2.8	0.66	105.7 \pm 23.5	67.5 \pm 10.5	0.002	30.6 \pm 16.9	31.1 \pm 17.0	0.98	32.8 \pm 13.7	32.7 \pm 13.1	0.86	18.21 \pm 3.3	18.5 \pm 3.5	0.88
Sulfate (mg/L)	33.2 \pm 7.6	33.4 \pm 7.4	0.98	116.2 \pm 62.1	97.6 \pm 60.0	0.02	104.8 \pm 47.2	105.4 \pm 49.2	1	111.9 \pm 42.6	112.1 \pm 44.7	0.89	25.0 \pm 3.0	25.0 \pm 2.8	0.95
CSMR	0.68 \pm 0.10	0.67 \pm 0.9	0.98	0.99 \pm 0.27	0.83 \pm 28	0.17	0.29 \pm 0.05	0.29 \pm 0.05	0.80	0.29 \pm 0.10	0.29 \pm 0.10	0.93	0.73 \pm 0.13	0.75 \pm 0.14	0.74
TOC (mg/L as C)	2.0 \pm 0.7	1.6 \pm 0.7	0.04	2.2 \pm 0.7	2.3 \pm 0.8	0.61	1.2 \pm 0.9	1.0 \pm 0.7	0.45	1.5 \pm 0.7	1.6 \pm 0.5	0.77	1.61 \pm 0.48	1.62 \pm 0.47	0.77
Pb-Cu Pipe Galvanic Current (μ A)	24.8 \pm 4.5	19.7 \pm 3.7	<0.0001	36.3 \pm 13.9	51.3 \pm 14.7	0.0003	36.0 \pm 3.0	35.3 \pm 6.6	0.60	31.9 \pm 6.9	33.1 \pm 6.7	0.44	23.1 \pm 10.1	42.5 \pm 10.8	<0.0001
Water Age (Days)	0	0.75	-	<1	3	-	0	4-5	-	0	<1	-	0	0.5-0.75	-

*Average of 2010 data

#Adapted from Masters et al. (2015)

Table E4 Summary of Average RSD at each Utility

	Lead		
Utility	Copper Solder	Pb-Cu	Brass
A	64%	90%	33%
B	50%	76%	21%
C	70%	83%	33%
D	48%	61%	32%
E	45%	90%	29%
	Copper		
	Copper Solder	Pb-Cu	Brass
A	11%	15%	15%
B	9%	7%	11%
C	15%	23%	17%
D	9%	12%	23%
E	5%	7%	8%