CHALLENGES WITH SAMPLING AND UNDERSTANDING LEAD CORROSION ISSUES IN PUERTO RICO AFTER HURRICANE MARIA

by

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B.S. Environmental Engineering, University of Colorado, 2017

A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirement for the degree of
Master of Science
Department of Civil, Environmental, and Architectural Engineering
2019

This thesis entitled:
Challenges with Sampling and Understanding Lead Corrosion Issues in Puerto Rico After Hurricane Maria
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find that both the content and the form meet acceptable presentation standards
of scholarly work in the above mentioned discipline

ABSTRACT

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Challenges with Sampling and Understanding Lead Corrosion Issues in Puerto Rico After Hurricane Maria

Thesis directed by Assistant Professor Julie A. Korak

In January of 2018, an NSF RAPID project was launched to analyze the water quality in Puerto Rico after Hurricane Maria. More than 40 local drinking water taps were sampled over three sampling campaigns. This reconnaissance systematically included a collection of samples from publicly owned treatment systems (PRASA), privately owned systems operated by communities (non-PRASA), and unmonitored surface spring sources. The first sampling campaign was targeted towards gaining a holistic perspective of the water quality (e.g., bulk water quality parameters, nutrients, major ions, pathogens, DNA, disinfection byproducts (DBPs), and metals concentrations). However, elevated WLLs in those initial results steered the following sampling events towards a more systematic lead sampling protocol, guided by the Environmental Protection Agency (EPA) Lead and Copper Rule (LCR) compliance procedure and alternative forensic lead sampling strategies.

The results from the 2nd and 3rd sampling campaigns showed conflicting potable WLLs. Therefore, these data exemplify the challenges of rapid reconnaissance sampling when trying to implement a universal sampling approach for many different parameters. Furthermore, the variability of lead concentrations and the factors that affect corrosion contribute to this difficulty. Sampling location on the property, the volume of water collected, and reproducibility of conditions between sampling events are some of the factors that make the presence and extent of potential lead exposure difficult to interpret. This study compares aggressive water quality corrosion characteristics to the observed water quality in Puerto Rico distribution systems and presents the forensic fingerprints that may allow for the identification of lead sources.

Overall, the results of this study illustrate the difficulty in characterizing the magnitude of corrosion issues in distribution systems. Many of systems sampled show that the water quality in Puerto Rico has aggressive water characteristics that can potentially produce elevated lead concentrations in potable water distribution systems, but sampling methods have a large impact on results and interpretation.

DEDICATION

For the peoples, places, and moments in my life that made me love and appreciate water

AKNOWLEDGEMENTS

Funding for this research came from the National Science Foundation (#1812697). Southern Nevada Water Authority, Rocky Mountain Research Station Biogeochemistry Laboratory, Denver Water, and the CU Boulder Laboratory for Environmental and Geologic Studies all contributed sample analysis.

First and foremost, I would like to thank Melitza Crespo-Medina, Taína Rodriguez, Graciela Ramirez-Torro, and all of the other researchers and scientists from the Center for Environmental Education, Conservation, and Research (CECIA) at the Interamerican University of Puerto Rico for all of their efforts on this project and making it the success it was. From coordinating sampling campaigns to analyzing samples, this project was possible because of them. I would like to individually thank Melitza and Taína for also being some of the best sampling teammates I have had to date, providing good conversation and laughs, even though we were sampling in 100 °F weather with what felt like 100% humidity.

I would like to thank my thesis committee chair, advisor, and mentor Professor Julie Korak, for all of the time she spent during and outside of work on this project, from late night Skype meetings and flexibility in schedule changes to her willingness to sit down and go through the details with me in sampling campaign design sketches, Matlab code, and Excel workbooks. Without her support, patience, and encouragement the completion of my thesis would not have been possible. She will always be a source of inspiration for me throughout my career, motivating me to always think critically about my work, be meticulous in my analysis, and use meaningful words to disseminate information.

I would like to thank my second advisor and mentor throughout my graduate and undergraduate studies at CU Boulder, Professor Fernando Rosario-Ortiz, for teaching me to learn

independently, not doubt my own abilities, and being a source of vision, funny laughs, and broad guidance and scope. He always pushed me to know my own limits, gave me the reins to run project leadership, and had faith in my abilities as a professional. His support in sending me to Puerto Rico to conduct sampling allowed me grow as an engineer and as an individual.

I would like to thank my final thesis committee member, Professor Mark Hernandez, who never failed to stop short while walking past my desk throughout the year and ask me how I was doing, personally and academically, and for his guidance and feedback on my thesis writing.

I would like to thank all of the students at CU Boulder in the Rosario research group as well as in my classes, Ariel Retuta, Rosa (Yun) Yu, Frank Leresche, Garrett McKay, Kylie Couch, Tyler Kurtz, and Josh Fortenbaugh for mentoring me in the lab and in the classroom and always providing support and help when I needed it. I extend my gratitude to all of the current and previous Civil, Environmental, and Architectural Engineering Department faculty that always provided personal and professional guidance and motivated me to continue on to graduate school.

Lastly, outside of school and campus, I would like to sincerely thank my family and friends who supported me through this process. They were there through all of my ups and downs and were always available to provide a comforting shoulder to lean on. Specifically, my dad and my mom, who motivated me to go to college, always supported me in my decisions, and provided the needed logistical guidance on navigating my way through school. My aunt, Alyson, who planted the seed of curiosity for research and the graduate world and was always my best writing mentor. And finally my partner Daniel, who stood by my side from the beginning, gave me unwavering love and support, and provided the much needed outdoor adventures and mental revitalization.

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INTRODUCTION

1.1 Motivation

Hurricane Maria made landfall in Puerto Rico on September 20th, 2017 and produced heavy rains and powerful winds, resulting in extensive environmental stress across the island such as severe flooding, mudslides, and debris mobilization [1]. This high-end Category 4 hurricane significantly impacted infrastructure, compromising 80% of the island's transmissions lines and utility poles, which left nearly all residents without power for months [1]. By January 2018, 55% of the island still remained without power. The damage to the electrical infrastructure resulted in the largest blackout in the history of the United States and the second largest in the world [2].

Significant disruptions also occurred for the islands municipal water systems. The hurricane reduced access to potable water treatment systems by an estimated 70% in the days after the event [3], [4]. As of late February 2018, the Puerto Rico Aqueduct and Sewer Authority (PRASA), the main government entity responsible for providing water services, reported that 111 out of the 877 potable water pumps on the island were still inoperable due to lack of electricity [3], [4]. In addition, privately owned and operated water systems in many communities were damaged or impaired [5]. The prolonged electrical outages impacted water treatment operations and made consistent delivery of potable water nearly impossible, ultimately inducing widespread boil water notices. However, since most of island did not have reliable electricity, there were limited resources with which to boil water for human consumption [6], [7].

As a result, many residents felt compelled to consume untreated water [3] and collected water from unmonitored wells and springs, some of which were near or on toxic superfund sites [8]. In October and November of 2017, the Puerto Rico Department of Health conducted bacterial testing on public and private water systems. The results showed that 2.3 million residents used water systems that tested positive for total coliforms and *E. coli.* in at least one sample [9], [10]. These sites that tested positive were composed of systems of all sizes, from small systems serving 330 consumers (e.g., Hogares Seguros) up to large systems serving 1.1 million consumers (e.g., Metropolitano). Furthermore, by the end of October 2017, there were 76 confirmed cases and several deaths due to leptospirosis [11], a waterborne bacterium derived from rodent and animal urine, which spreads after floods through drinking water and/or open wounds [12].

These findings by the Puerto Rico Department of Health combined with the reports of illness from waterborne bacteria, widespread electrical outages, and water treatment operation disruptions raised concerns about the integrity of potable water throughout the island. Potential concerns included the occurrence of microbial pathogens and potential for elevated levels of nutrients, inorganic, and organic constituents.

1.2 Objective

Concerned about the potential public health impacts from Hurricane Maria, a National Science Foundation (NSF) Rapid Response Research (RAPID) project was launched in February 2018 to perform a comprehensive assessment of the water quality in potable water systems and spring sources used as potable supplies. The project team was a collaboration between the Environmental Engineering Program at the University of Colorado Boulder (CU Boulder) and the

Center for Environmental Education, Conservation, and Research (CECIA) at the Interamerican University of Puerto Rico. The mission of CECIA is to integrate environmental issues into disciplines taught by traditional teaching programs at the University. Overall, the center aims to develop appropriate technology as well as protection methods for the remediation and environmental conservation of Puerto Rico's natural resources. Several other laboratories and departments were critical to the deployment of the project including the Laboratory of Environmental and Geologic Studies (LEGS) at CU Boulder, Rocky Mountain Research Station (RMRS) Biogeochemistry Laboratory, Southern Nevada Water Authority (SNWA), and Denver Water (DW).

The objective of the project was to assess potential chemical and microbial constituents present in potable water systems and natural springs to better understand the hurricane impacts and the challenges associated with natural disaster humanitarian response. For a broad initial assessment, the RAPID project team collected samples from three types of sites: public water systems operated by PRASA, privately owned water supply systems operated by communities (non-PRASA), and unmonitored surface water springs actively used by communities for potable and non-potable uses (springs).

CHAPTER 2

CORROSION BACKGROUND

The corrosion of water distribution system materials is a major concern for long-term infrastructure maintenance and protection public health. Of all the trace metals that can be released due to corrosion, lead (Pb) poses the greatest public health risk. The Joint Food and Agricultural Administration (FAO) of the United Nations/World Health Organization (WHO) Expert Committee on Food Additives (JECFA) established in 1986, and confirmed in 1993, a provisional tolerable weekly intake (PTWI) of 25 µg of Pb per kg of body weight (or 3.5 µg per kg of body weight per day) for infants and children [13]. Since then, a guideline value of 10 µg/L in water was derived by assuming that 50% of the PTWI was allocated to drinking water for a 5 kg bottle-fed infant consuming 0.75 liters of water per day. However, in 2010, JECFA reevaluated lead and found that it could not establish a new PTWI due to the wide range of adverse health effects and inconclusive dose response studies, ultimately concluding that there is no safe level of lead exposure [13], [14].

2.1 Lead Corrosion Complexity

There are several challenges associated with accurately quantifying lead release in drinking water distribution systems. These challenges derive from the spatial and temporal heterogeneity of lead sources and mobilization mechanisms that can occur throughout a system. To understand lead corrosion complexity, one must understand lead sources and the subsequent lead mobilization mechanisms for those sources. This section summarizes the types of lead sources that exist in a drinking water distribution system and expands on some of the variables and factors that contribute to lead corrosion complexity and furthermore, observed water lead levels (WLL) at the tap.

2.1.1 Lead Sources

Considering drinking water on a broad scale from source to tap, lead originates from the *corrosion of plumbing materials*, rather than natural source waters or water treatment chemicals [15]. Common types of corrosion that occur in drinking water distribution systems are categorized by uniform corrosion, nonuniform corrosion, and erosion corrosion. There are several types of nonuniform corrosion including localized corrosion (pitting corrosion, concentration cell corrosion, tuberculation), galvanic corrosion, dealloying corrosion, and microbiologically influenced corrosion [16]–[18].

Uniform corrosion occurs when the anodic and cathodic sites of the corrosion cell change location constantly on the surface of the pipe material. Nonuniform corrosion occurs when either the anodic or cathodic sites cannot change and remain in the same location, however is it most commonly the anodic site [16]–[18]. The initial lead source is the physical plumbing material itself, then corrosion processes act on physical lead-bearing plumbing material, creating a new matrix of lead sources with different chemistries.

Physical Material

Differences in lead-bearing plumbing material result in inherent spatial and temporal heterogeneity of physical lead sources in a water system. These lead-bearing plumbing materials are found in drinking water distribution system transmission lines, service lines, and premise plumbing and vary spatially within households, between households within communities, and throughout drinking water distribution systems as a whole. The presence and abundance of lead in these materials depends largely on when drinking water distribution systems were installed and the contemporary regulatory framework, which is discussed in Section 2.2.

Lead Corrosion Products

Stemming from the heterogeneity of physical lead plumbing material, lead corrosion degradation products also vary throughout a drinking water distribution system and impact the chemical form of lead release. Lead is released into water in soluble or insoluble forms as either divalent (Pb (II)) or tetravalent (Pb (IV)) ions or species complexes resulting from the corrosion of these physical sources [18].

Soluble (dissolved) lead is defined as the form of lead that passes through a 0.45-micron filter. It can be a collection of free aquo ions, organic chelates, other inorganic chelates, ion pairs and complexes, bound to macromolecules, or highly dispersed colloidal material [19]. Insoluble (particulate) lead is defined as the fraction retained by a 0.45-micron filter and is derived from the pure metal material itself [20]–[22], formed from the sorption of lead to other metal particulates, such as iron [19], [20] or derived from corrosion scales [16]–[18], [23], [24]. Corrosion scales are one type of these new lead source matrices that differ from original source material.

Corrosion scales are created by passivation, a process by which the reactivity of the plumbing surface is reduced over time through the development of mineral layers on the inner wetted surface of the plumbing material. During this process, lead is leached in its Pb (II) or Pb (IV) form and reacts with different soluble ligands to create a dense layer composed of solid lead complexes. The contribution of corrosion scales to lead release is important because dissolved and particulate forms of lead both derive from their formation.

The configuration of lead corrosion scales and the lead form that is dominate is highly dependent on the site-specific water quality composition, which governs the suite of ions available for complexation [18], [25], [26]. The most common observed lead corrosion scales include lead oxides and lead carbonates, but corrosion inhibitors, such as orthophosphate, promote the formation of lead-phosphate scale layers as well. The nature of the pipe material also governs scale formation. Lead-free zinc, iron, and manganese scale complexes are known to form, onto which lead has been shown to sorb or bind [21], [27].

Understanding the potential sources and forms of lead within a distribution system are important for identifying potential mechanisms of lead release. While the current guidance on reducing lead in drinking water is targeted towards controlling Pb (II) scale solubility [16]–[18], [28]–[30], studies have shown that Pb (IV) scale solubility and the contribution of particulate lead to total observed WLLs is of equal importance, as particulate forms of lead can contribute to a greater portion of the total observed WLL at the tap [19], [28], [31]–[35].

2.1.2 Mechanisms for Lead Release

Lead is mobilized by different physical and chemical mechanisms that drive corrosion processes or destabilize corrosion byproducts. The factors that determine the extent of lead mobilization are water quality characteristics, corrosion scale properties and solubility, flow rate, pipe material, pipe size, and plumbing configuration [16]–[18], [25]. This section summarizes the different forms of lead release from a chemical and physical perspective and discusses some of the variables that influence these mechanisms.

Chemical Mechanisms

The main definition of corrosion implies that corrosion processes occur through electrochemical cells that are driven by the electrochemical potential of the metal relative to the environment to which it is exposed, in other words an oxidation-reduction (REDOX) reaction [16]–[18]. Thus, the driving forces of lead release in water distribution systems are the REDOX reactions that influence corrosion processes. These chemical reactions that corrode lead-bearing plumbing materials act on the heterogeneity of lead source materials. Solubility of corrosion degradation products or of physical lead materials is one aspect of these chemical reactions that impacts lead release [16]–[18].

Uniform Corrosion. While uniform corrosion can directly release lead in soluble form, more commonly it causes film formation on the surface of the pipe wall, or passivation layer formation [36]. The solubility limits of the film or scale product can dictate dissolved lead release in drinking water distribution systems. While passivation layers are known to prevent lead release in certain situations, destabilization of these layers can inadvertently contribute to elevated WLLs [16], [17], [32]. Factors that affect the solubility of corrosion degradation products are pH, temperature, dissolved inorganic carbon (DIC) concentrations, dissolved oxygen concentrations, concentrations of other constituents like phosphates, silicates, chlorine, chloride and sulfate, alkalinity, and the oxidation-reduction potential (ORP) of the water [16]–[18], [25]. Flow rate has also been shown to contribute to dissolved lead release by affecting mass transfer rates between scales and bulk water as a result of radial mixing in the boundary layer depending on the boundary layer thickness [31], [37].

The importance of understanding the relationship between water quality and chemical mechanisms for lead release is illustrated by the well-known lead contamination event in Washington D.C. from 2001 to 2004. For example, disinfectant residual increases the ORP of the water as more disinfectant is added. Elevated WLLs were observed in Washington, D.C. from 2001 to 2004 after the water treatment plant switched the disinfectant type from free chlorine to chloramine. Free chlorine is a stronger disinfectant that can sustain high ORP levels in the water, and as a result PbO_2 (Pb (IV) oxidation state) corrosion scales formed over time in chlorinated water (< 3 mg/L Cl_2) and over a wide range of pH values (6.65−10) [28]. PbO_2 is a rather insoluble scale and can greatly inhibit lead release if maintained. However, a change in pH or drop in ORP (as seen with the switch to chloramines) can destabilize these scales and increase lead solubility [38], [39]. While maintaining a disinfectant residual prevents microbial growth and limits the ability of microenvironments with differing oxygen and hydrogen ion concentrations to form within the biofilm, variations in the disinfectant residual can directly affect the chemical solubility of corrosion scales [17], [18].

Nonuniform Corrosion. Pitting corrosion, or one type of nonuniform corrosion, results in pits or holes on the pipe surface. Tuberculation is the process resulting from pitting corrosion that creates localized corrosion debris. While the solubility of these debris can contribute to dissolved metal concentrations, it is more common to find a higher contribution of particulate lead from these processes [36]. Galvanic corrosion, a type of nonuniform corrosion, occurs when two dissimilar metals are in contact with each other and one acts as the sacrificial anode and the other the cathode. This type of corrosion can increase lead dissolution to concentrations exceeding the saturation point of some Pb (II) minerals, and subsequently precipitate secondary solids, contributing particulate lead to total WLLs in low flow conditions [31], [40]. The chloride-to-sulfate mass ratio (CSMR) has been known to affect galvanic corrosion potential and rates, which is discussed further in Section 3.7.3 [31], [41]–[44]. Dealloying corrosion is the most common form of nonuniform corrosion related to brass plumbing materials. Since brass alloys contain several different types of metals at varying ratios and distributions, different theories on the exact mechanism of lead release exist [45]. Dezincification is the most well-known type of dealloying corrosion where zinc is preferentially released into the bulk water solution. Generally, due to the nonuniformity of lead distribution in the material, it is speculated that the preferential leaching of zinc creates porous residues of copper and other various corrosion products, allowing lead to detach and diffuse more rapidly into the bulk water solution [45]. Thus, higher zinc content brasses are theorized to release more lead. However, results of other studies theorize that higher zinc content brass actually inhibit lead release, since zinc can act as a sacrificial metal in comparison to lead [46].

Physical Mechanisms

In addition to chemical processes that influence corrosion, another driving force for lead release in water distribution systems are physical mechanisms. Physical disturbances to the drinking water distribution system can mobilize lead in water, either before corrosion processes take place or after corrosion processes have formed passivation layers. In addition, physical changes of the system can take place and cause the instigation of new corrosion processes to occur, such as partially replacing a lead service line to form a galvanic connection between copper and lead pipe. Physical mechanisms for lead release include high velocity flow rates from flushing or sampling, construction or maintenance on the water system, lead service line (LSL) or partial lead service line (PLSL) replacements, the vibration, thermal expansion and contraction of pipes, and beam flexing [36]. While particulate lead is the most common form of lead release as a result of these mechanisms, soluble lead can also mobilize due to the reactions occurring in the boundary layer resulting from higher flow rates, as described previously.

With respect to particulate lead release, high velocity flow rates can cause corrosion scales to slough off from the inner surface of the pipe material or influence erosion corrosion [19], [23], [31], [37], [47]–[51]. PLSL replacement has been known to disrupt the physical stability of scales, rusts, and plumbing materials and result in higher observed WLLs after implementation [19], [31], [45], [52]–[54]. Replacing only part of a LSL can create a new electrochemical or galvanic cell, causing greater observances of particulate lead [19], [40], [55], [56]. Sampling procedures that confidently quantify particulate lead is a recurrent challenge.

2.1.3 Exposure Significance

The source and mobilization mechanism together determine which sampling techniques will identify the presence of lead. Depending on study objectives, the differentiation of dissolved and particulate lead may be informative. Regulatory approaches most often prioritize total lead concentrations, because both are important for public health. Assessing acute exposure is difficult, as particulate lead is known to significantly contribute to sporadic increases in lead concentrations [57]. When particulate lead is ingested it can be dissolved by stomach acid providing an acute source of lead or be lodged in the gastrointestinal tract and provide a long-term source of lead [19], [58]. Measuring total lead concentrations covers a basis for all lead exposure, but when the goal is to identify lead sources and release mechanisms, capturing differences in particulate and dissolved concentrations opens up an opportunity for forensic analysis.

2.2 The U.S. EPA Lead and Copper Rule

The United States (U.S.) Environmental Protection Agency (EPA) promulgated the Lead and Copper Rule (LCR) in 1991 with an effort to reduce lead and copper levels in drinking water. Since the dominate source of lead in drinking water is distribution system plumbing materials, these efforts started with the Safe Drinking Water Act (SDWA) amendments of 1986, which prohibited the use of pipes, solder, or flux that was not “lead free”. Since then, the definition of “lead free” has been redefined several times. Initially, in 1986, solder and flux were limited to less than 0.2% lead, and pipes were limited to less than 8%. In 1996, the development of the NSF International Standard/American National Standard Institute (NSF/ANSI) Standard 61, Section 9 satisfied the requirement to set a performance standard that would establish lead leaching levels in fittings used for water intended for human consumption [59]. Any plumbing material that was less than 8% and met the NSF/ANSI Standard 61, Section 9 was deemed “lead free” under the U.S. EPA SDWA.

The Reduction of Lead in Drinking Water Act (RLDWA) in 2011 (effective 2014) further reduced the maximum allowable lead content of piping and fittings to less than 0.25% of a wetted surface weighted average, but overwrote the requirement of prohibiting the use or introduction into commerce of “pipes, pipe fittings, plumbing fittings or fixtures, including backflow preventers, that are used exclusively for non-potable services such as manufacturing, industrial processing, irrigation, outdoor watering, or any other uses where the water is not anticipated to be used for human consumption” [60] and no longer mandated third party certification to the NSF/ANSI [61].

The use of lead-bearing plumbing materials has changed over time with changing regulations and the current prevalence is difficult to quantify since use has not been well documented [18]. While the implementation of lead service lines in newly constructed systems has ceased, in 2016 the American Water Works Association (AWWA) published a study concluding that there was still approximately 6.1 million LSLs in the U.S. to data [62]. Further data from a study conducted by Sandvig et. al. (2008) showed that the average distribution of plumbing material between types was 50 to 75% from lead service lines, 20 to 35% from premise plumbing (leaded solder, brass/bronze fittings, galvanized piping), and 1 to 3% from faucets [59]. Overall, the regulations have decreased the sale and distribution of lead-bearing plumbing materials, but older installations are still in service [62], [63]. Overall, it was estimated that all U.S. homes are at risk of having brass plumbing components that are between 1.5% and 8% lead by weight. It is estimated the 81 million U.S. homes at risk of brass plumbing components that exceed 8% lead by weight, 3.3 to 6.4 million U.S. homes are at risk from lead pipes, service lines, and/or goosenecks, and 81 million U.S. homes are at risk from lead solder [19].

2.2.1 LCR Sampling Specifics

The U.S. EPA LCR utilizes a *treatment technique* approach, which was developed to trigger the implementation of corrosion control based on baseline monitoring data and applies to all community water systems (CWS) and non-transient non-community water systems (NTNCWS). The regulation does not set maximum contaminant levels (MCL) or secondary MCLs under the U.S. EPA National Primary Drinking Water Regulations (NPDWR). Instead, the LCR identified a concentration based "action level" (AL) of 15 µg/L for lead and 1.3 mg/L for copper. Due to the severe health effects from lead, a maximum contaminant level goal (MCLG) of 0 µg/L was established (Table 1).

Table 1. The U.S EPA LCR lead action level, lead maximum contaminant level, maximum contaminant level goal, and secondary maximum contaminant level.

Lead (Pb)		
Action Level (AL)	15	µg/L
Maximum Contaminant Level (MCL)	NA	µg/L
Maximum Contaminant Level Goal (MCLG)	0	µg/L
Secondary Maximum Contaminant Level	NA	µg/L

If during a required monitoring event the 90th percentile concentration exceeds the AL concentration, then a *treatment technique* must be implemented, which includes starting with public education, source water monitoring, and optimization of corrosion control treatment and leading to the implementation of lead service line replacement if other measures were unsatisfactory.

Monitoring plans are developed to portray "worst-case" lead levels in water as well as to collect data most pertinent to understanding the extent and severity of corrosion in a water distribution system. Per the U.S. EPA LCR requirements, baseline monitoring data includes the contaminants of concern, lead and copper, and a few other water quality parameters (WQP): pH, alkalinity, conductivity (initial monitoring only), temperature (initial monitoring only), calcium (initial only, unless calcium carbonate stabilization is used), orthophosphate (if corrosion inhibitor is phosphate-based), and silica (if corrosion inhibitor is silicate-based).

Lead and copper are monitored at residences or locations that are identified as high risk or most susceptible to lead release based on a plumbing materials evaluation, which includes identifying sites known to have lead service lines, interior lead plumbing, copper pipes with lead solder, or other materials such as galvanized iron pipe. The number of samples collected during a monitoring period depends on the population served by the system. Sampling locations are categorized as Tier 1, Tier 2, or Tier 3 category, which varies depending on the type of plumbing material and when the material was installed. The LCR sampling protocol collects a 1-liter sample from inside a home or building as a first-draw after 6+ hours of stagnation (6+HS). The tap must be a cold-water tap from a kitchen or bathroom sink, and residents are allowed to take samples themselves. Residents are instructed to not remove or clean aerators prior to sample collection [64], however any household water treatment must be turned off or removed. Plastic or glass bottles may be used for collection but high-density polyethylene (HDPE) plastic is most common [65], [66].

In addition to lead and copper, WQPs are monitored at locations throughout the distribution system that can be *different or the same* as the taps selected for lead and copper sampling. WQP sites are at entry points to the distribution system and at representative taps throughout the distribution system. The WQP sampling method stipulates to 1) fully flush the tap and collect a sample to measure disinfectant residual, 2) collect and analyze a sample for pH and temperature, and 3) collect a sample for all other WQP to be measured in the lab. When collecting a sample for all other WQPs, two 500-milliliter samples are collected in either plastic or glass bottles.

2.2.2 LCR Sample Processing and Analytical Methods

The U.S. EPA LCR aims to measure total lead concentrations in any water sample and there are multiple approved analytical methods, either from the U.S. EPA itself or from third-party agencies. Standard preservation protocol can vary between methods. EPA Method 200.8, 200.9, 200.5, Palintest LTD Method 1001, and Hach Co. Method 1001 are the approved analytical methods for measuring lead in drinking water. Each method states that for a 1-liter sample collected, "samples are acidified with (1+1) nitric acid to $pH < 2$ (normally 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples)". Based on the definitions of "Nitric Acid" and "Nitric Acid (1+1)" defined in EPA Method 200.8, this means adding 3 mL of a 34% pure nitric acid (HNO_3) solution per liter of sample. If the concentration nitric acid is not diluted at a 1:1 ratio, then this could mean adding 1.5 mL of a 68% nitric acid solution per liter of sample. This has been further interpreted to mean adding concentrated nitric acid to a water sample to attain a 0.15% *(v/v)* HNO_3 concentration in any 1-liter water sample. After acidification there is a minimum holding time of 16 hours as required by EPA Method 200.8, but 28 hours is recommended elsewhere [66]. When samples are ready to be analyzed, turbidity is measured to determine if acid digestion is required. If the turbidity of a sample is greater than 1 NTU, then a sample aliquot must be acid digested first before lead quantification can be performed. Standard Methods for the Examination of Water and Wastewater Quality Method 3030E aims to dissolve all forms of any particulate metal into soluble form and is the method incorporated into EPA Method 200.8 and 200.9. Acid digestion is a requirement regardless of turbidity when using EPA Method 200.5, Palintest LTD Method 1001, or Hach Co. Method 1001 [67].

2.2.3 Summary of All Lead Sampling Protocols

Due to corrosion variability and the increased need to determine lead exposure in a variety of situations, various alternative sampling protocols have been developed. Each sampling protocol aims to evaluate a different aspect of WLLs and lead exposure. They are used for regulatory sampling, research studies, or both. A major driver of the type of protocol used in studies or compliance comes from the geographic location where the sampling is conducted. Table 2 summarizes common sampling methods.

Table 2. Common sampling protocols implemented in lead corrosion studies[1].

Protocol	***Pre-Flushing***	***Stagnation Time***	***Limitations***
First Draw (FD)	No	Yes	• Known to miss particulate lead release or peak lead concentrations • Exhibits the dilution effect when trying to determine a specific lead concentration from lead source
Random Daytime (RDT)	No	No	• Requires high sample number needed to achieve confidence in assessments
Stagnation (30MS)	Yes	Yes	• Does not reflect average lead concentration released from pipe • Exhibits a dilution effect when trying to determine a specific lead concentration from lead source • Confidence that samples meet compliance standard or have representative exposure is weaker
Sequential Volume Profile (SVP)	Depends	Depends	• Is time intensive • Is cost intensive
Flush Volume Profile (FVP)	Depends	Depends	• Varying flow rates from house to house based on plumbing system configurations and materials
Composite Proportional Sampling (COMP)	NA	NA	• High cost of sampling device • Longer/extra time to install and decommission device • Requires a large number of sampling events to characterize spatial and temporal lead variability • No control over quality of samples collected because requires consumer operation • Does not collect all lead consumed by consumer
Particulate Stimulation Sampling (PSS)	Depends	Depends	• Is time intensive • Is cost intensive

[1] References: [68]–[70]

First Draw

A first-draw (FD) sample is defined as a sample taken after an extended amount of stagnation time, usually in the morning or when the resident or building occupant returns for the day. The specifics of the protocol require that no other water be drawn from any fixture connected to the premise plumbing system, however this is difficult to control. A recommended minimum stagnation time is 6 hours and no more than 24 hours. For a FD sample, the 6-hour stagnation time is commonly chosen, because it represents the time closest to which maximum solubility equilibrium occurs for plumbosolvency under normal household use conditions [39], [68]. One discussed limitation of this method is the dilution effect when trying to determine specific lead release from a specific lead source. In other words, if a sampler is trying to collect a sample representative from a lead service line and the volume of water collected only captures a small portion of water from that service line, the rest of the water could be from a lead-free source, resulting in concentrations that would not be representative of the lead service line [68].

Random Daytime

Random Daytime (RDT) sampling intends to measure exposure levels typical during normal usage patterns. A sample is collected at a random time during the day without any pre-flushing or predetermined stagnation time. This method can gauge the average exposure to a population, but the method requires that enough samples are collected to get a representative sample set [70]. It is a logistically favorable sampling method due to the nature of the protocol (i.e., less requirements regarding the sample timing and sampling locations). In addition, if a selected sampling location cannot be accessed, the randomness of the sample can be preserved by sampling a location next door or within a similar vicinity [68].

Stagnation

A stagnation sample is defined as a sample taken after a predetermined period of flushing occurs followed by a prescribed stagnation time. During the stagnation time, no water should be drawn from any fixture connected to the premise plumbing system or the sample will be invalid. A common stagnation sampling approach is the 30-minute protocol (30MS), which requires the sequential collection of two (2) 1-liter samples after the stagnation period. It can be used to determine acute corrosion effects from a benchmark perspective, however the confidence that the sample is representative of normal usage conditions is lower [68].

Profile Sampling

Profile sampling is an investigative technique that has been used by researchers and utilities to measure lead concentrations at different locations in a water system [35], [49], [50], [57], [71]–[74]. The protocol samples different volumes of water from the tap to characterize water spatially within the premise plumbing based on plumbing configurations and materials. This technique can be used in combination with a first draw, random daytime, or stagnation sampling protocol. There are two ways to conduct profile sampling: sequential volume profiling (SVP) and flush volume profiling (FVP).

During SVP, a FD, RDT, or 30MS sample is collected from the chosen tap and then consecutive samples are collected one after another, discarding no water in between samples. During FVP, a FD, RDT, or 30MS sample is collected, and then other samples are collected after a designated amount of flushing time has passed. Example flush times include 45 seconds, one minute, two minutes, three minutes, five minutes, and 10 minutes of flushing time. The FVP method is also called fully flushed (FF) sampling.

Particulate Stimulation Sampling

Particulate stimulation sampling (PSS) is a method used to stimulate particulate lead detachment in the pipes. The method places a sampling bottle underneath a tap and the tap is opened and closed at maximum flow rate five (5) times and the rest of the bottle is completely filled at maximum flow rate. A second sequential liter is collected at normal flow rate, and finally a third liter is collected following the method of opening and closing of the tap five (5) times at maximum flow rate [20]. This method can be implemented following the collection of other compliance samples, such as FD or RDT, or used individually, depending on the objective of the study.

Composite Proportional Sampling

Composite Proportional Sampling (COMP) is used for lead exposure assessment and collected during normal water usage patterns. A device is installed on the tap for one week and collects 5% of every draw. It provides an estimation of the average lead levels at consumers taps and approximates the amount of lead ingested [68]. Of all the methods, COMP is considered to be best representative of the average weekly lead intake in consumers drinking water from that tap because it captures all variations within one week [69]. However, this method is costly and time consuming, among other limitations outlined in Table 2.

2.3 U.S. EPA LCR Limitations

Since its promulgation, numerous studies have found that the U.S. EPA LCR has limitations with regards to accurately determining and characterizing lead corrosion issues in drinking water distribution systems [19], [30], [48], [50], [58], [59], [67], [72], [75]–[84]. It can identify taps where high levels of lead may be found, but it cannot adequately quantify the extent of lead exposure [58]. More specifically, the type of sampling protocol used can have a large impact on observed WLLs at the tap and contribute to difficulties interpreting sampling data.

Overall, the rule has limitations with regards to the sampling method and the sample processing procedure. Some of the sampling method limitations relate to the requirement of a first draw sample, as this type of sample does not always capture lead release from a lead service line [17], [76]. There are also unspecified rules for other household tap use during the designated stagnation time, no specifications for pre-stagnation flushing or the sampling flow rate, and no specific requirements of the sampling location in the distribution system. In response some of these identified limitations, the U.S. EPA issued a memorandum in February of 2016 to Regional Water Division Directors [64] that included updated sampling instructions, specifically eliminating pre-stagnation flushing, clarifying that faucet aerators should not be removed prior to sampling, and encouraging the use of wide-mouth bottles to prevent water loss. For sample processing, many factors can contribute to discrepancies in observed lead concentrations as discussed in Section 2.1.2, including making sure aliquots are representative of composite samples, sample filtration for measuring dissolved and particulate lead, and the sample preservation and digestion techniques [19], [58], [67].

2.4 U.S. EPA LCR Future Changes

In August of 2015, the Lead and Copper Rule Working Group (LCRWG) of the National Drinking Water Advisory Council (NDWAC) completed a report outlining recommendations for proposed long-term revisions to the U.S. EPA LCR [85]. One of the recommendations proposed modifying the monitoring requirements of the rule in order to reach a more robust geographic sample set by allowing consumers to request analysis of their specific tap samples. Under the current rule requirements, many consumers do not understand lead prevalence in their specific premise plumbing system. This data would be used to educate the consumer of associated lead exposure risks specific to themselves, overall empowering the consumer. In addition, they recommended modifying the monitoring requirements to tailor water quality parameters to the specific CWS corrosion control treatment program, since each system is unique with regards to water quality. For example, the rule only requires pH and alkalinity along with various corrosion inhibitor indicator constituents, if applicable. However, these water quality parameters are not the only chemical factors to influence lead release, as discussed in Section 2.1.2.

To address the concerns of the effectiveness of the U.S. EPA LCR, in October of 2016 the U.S. EPA Office of Water published a white paper titled *Lead and Copper Revisions,* incorporating recommendations from the NDWAC and other stakeholders such as the Flint Water Interagency Coordinating Committee and local citizens impacted by lead contamination events. The five key principles in this document include focusing on minimizing exposure to lead in drinking water, clear and enforceable requirements, transparency, environmental justice and children's health, and integrating drinking water with cross-media lead reduction efforts.

Ultimately, there is a proposal from the U.S. EPA to update the LCR federal regulations in early 2019 [86], [87]. These proposed regulatory revisions will consider the revisions outlined in the white paper as well as input from other associations, such as the Association of Metropolitan Water Agencies [88].

2.5 History of Water Quality Concerns in Puerto Rico

Water quality issues in Puerto Rico did not start after Hurricane Maria. A National Resources Defense Council (NRDC) Report stated that in 2015, 99.5% of the population in Puerto Rico was served by community water systems that were in violation of the U.S. EPA SDWA and 69.4% of residents were served by water that did not comply with health-based standards defined by SDWA maximum contaminant levels [89]. The NRDC reported violations including, but not limited to, 607 violations of the LCR, 739 violations of the Total Coliform Rule, 248 violations of the Surface Water Treatment Rule, and 19 violations of the Inorganic Contaminants Rule. Other noncompliance data for Puerto Rico goes back as far as 2005, reporting violations of health-based standards, monitoring requirements, and reporting requirements under the SDWA.

With regards to the U.S. EPA LCR, in 2015 97.2% of the population was served by 158 water systems in violation of the rule. The violations of the U.S. EPA LCR affected the largest population in comparison to other rule violations (e.g., Combined Disinfectants and Disinfection Byproducts Rule, the Stage 2 Disinfectants and Disinfection Byproducts Rule, Combined Surface, Groundwater, and Filter Backwash Rules, etc.). All of the 607 violations except for one violation were failure to test for lead or report problems to health authorities or the public. The one other case was a violation of the treatment requirements under the rule. In some cases, the water system exceeded the lead AL, but the report did not specify the name of the communities or the population affected. The reported violations include large systems and small systems. Twenty-four (24) of Puerto Rico's 316 small water systems had Tier 1 (worst-case with immediate 24-hour notice) violations in October of 2011. In 2015, 23 of those systems still had not come into compliance.

Overall, the report recommends that the citizens, the government, and the financial agencies must work together to identify and immediately address sources of lead release, but it does not state the current status of potential lead corrosion problems. The following systems were the top 10 identified by the report and ranked by the population served with health-based violations that were also in violation of the U.S. EPA LCR (Table 3). Seven of these systems relate to systems sampled during the initial sampling events of this study. However, due to the complexities of the

Puerto Rican water network (e.g., several different CWSs can serve one town), it cannot be confirmed that the sites sampled in this study directly correspond to the system listed in Table 3.

Table 3. Top 10 systems in Puerto Rico ranked by population served that had health-based violations as well as U.S. EPA LCR violations in 2015.

System Name	***Population Served***
Metropolitano	1,064,730
Mayaguez	181,972
Aguadilla	132,716
Isabela	59,196
Vega Baja Urbano	49,853
Manati East	47,519
Lajas	47,310
Guayama Urbano	45,959
Regional Villalba Toa Vaca	45,080
Caguas Norte	41,971

CHAPTER 3

MATERIALS AND METHODS

Four sampling campaigns were conducted: February 2018 (SC 1), March to April 2018 (SC 2), July 2018 (SC 3), and December 2018 to January 2019 (SC 4). This methods section is organized by sampling campaign, because each campaign had a different objective. The project started with the intent of conducting only two, broad water quality sampling campaigns. Sampling methodology prioritized a universal sampling approach to evaluate as many water quality parameters as possible to meet the objective of the rapid reconnaissance research. By doing this, it was impossible to adopt unique sampling protocols for individual parameters. There was little previous knowledge about the baseline water quality conditions, and no indication that lead would become a focal point of the study after the initial results were reviewed. Therefore, it is important to note that sample site selection and collection methods for early campaigns did not adhere to the U.S. EPA LCR protocol. As the study objective narrowed to understanding lead corrosion issues, the sampling protocols shifted to align with the U.S. EPA LCR.

3.1 Site and Tap Selection

3.1.1 Sampling Campaign 1

During the first sampling campaign (SC 1), 40 samples were collected from 40 unique sites including community water systems and spring sources identified as public water collection sites. Community water system sampling sites were chosen on a volunteer basis from Puerto Rican residents who are community contacts engaged with CECIA at the Interamerican University of Puerto Rico. Sites were distributed across the island between 24 PRASA systems, nine (9) non-PRASA systems, and seven (7) spring sources. Sampling locations included hose bibs from PRASA or non-PRASA distribution systems located on the outside of a home or building or from open pipe flows from spring sources. One site from a PRASA system was sampled from a bathroom tap located inside a school (Site 5 – Appendix A). Figure 1 shows the sampling sites and system types across Puerto Rico.

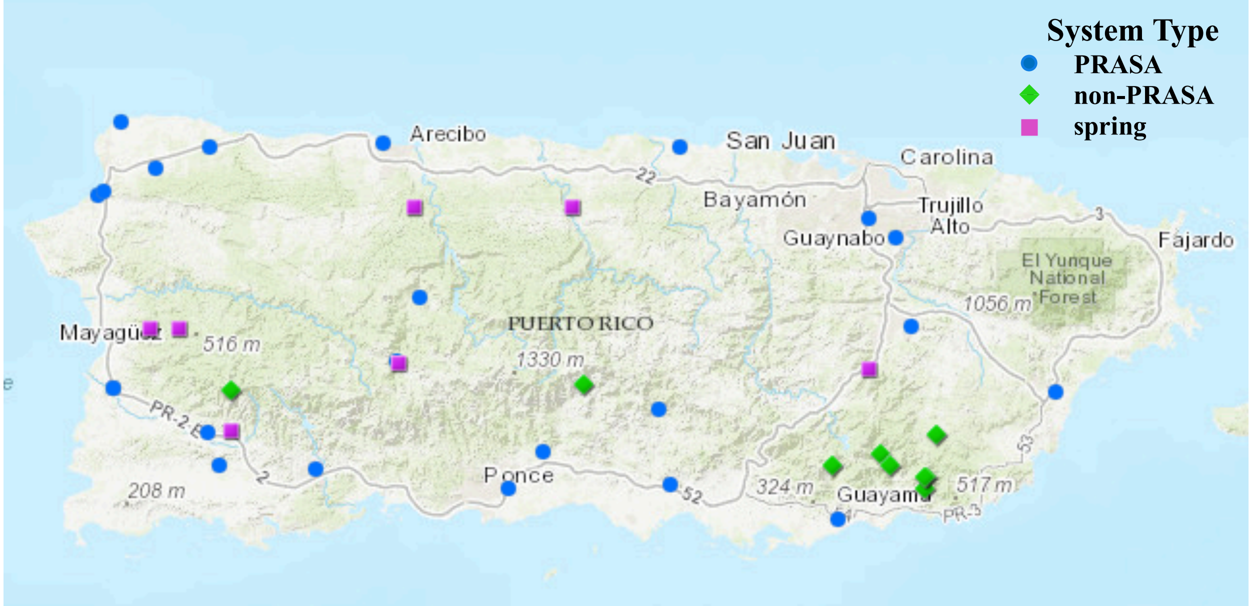


Figure 1. Sampling Campaign 1: Sampling site locations by system throughout Puerto Rico. Some of the icons are overlapping. Map was created using ERSI arcGIS online mapping tool.

3.1.2 Sampling Campaign 2

The second sampling campaign (SC 2) collected 11 samples from a subset of eight (8) sites revisited from SC 1 to confirm elevated lead levels observed in SC 1. All of these sites were supplied water from either a PRASA or non-PRASA system. Eight (8) samples from the SC 2 were temporal replicates revisiting the same outside hose bib taps from SC 1, and three (3) samples were collected from new locations within the community with the highest observed WLLs, Patillas-Mulas (Site 33 Appendix A), to expand the dataset and confirm trends. For the new locations, one site was from a point-of-use community sampling tap, and the other two sites were raw water sources taken from the river and the raw water intake to the community treatment system. While plumbing materials are known to be the primary sources of lead in finished water, these sites were chosen to confirm that no raw water lead sources exist since there was no pre-known information about the CWS construction materials.

3.1.3 Sampling Campaign 3

Based on the initial results from SC 1 and SC 2, it was decided that a more comprehensive lead study needed to be conducted in order to confirm if observed concentrations from outside hose bib taps were representative of point-of-use locations inside the home or building. Therefore, a systematic lead sampling campaign was developed using a protocol that better aligned with the U.S. EPA LCR. During the third sampling campaign (SC 3), two community systems were chosen, Lajas (Site 2 Appendix A) and Patillas-Mulas (Site 33 Appendix A) that each had a home with elevated WLLs in both SC 1 and SC 2. Six (6) homes were chosen from each community with one of those homes being the same site where high WLLs were observed in SC 1 and SC 2. No information was available to assess the sampling sites against the U.S. EPA LCR tiering system.

3.1.4 Sampling Campaign 4

For the fourth sampling campaign (SC 4), a broader assessment of multiple communities was conducted to evaluate interior WLLs. The primary goal was not to only resample homes from SC 1 and SC 2, but to sample multiple homes within those same systems to better assess water quality spatially. SC 4 was conducted utilizing a citizen science sampling approach that implemented protocols aligning with the U.S. EPA LCR except for the LCR tiering system. However, sampling sites were specifically chosen if the house was known to be old or built before

1950 based on anecdotal information from homeowner or observed building materials. This work is ongoing, and the results are not presented in this thesis.

3.2 Sampling Protocol

Sampling methods followed protocols published by the U.S. EPA, the United States Geological Survey (USGS), HACH Incorporated, and/or Standard Methods for the Examination of Water and Wastewater Quality [65], [90], [91, p. 6]. Sampled taps for all sampling campaigns contained no point-of-use filters, water softeners, or other point-of-use treatment. Aerators, if present, remained installed at the time of sampling. However, Site 5, which was a bathroom tap located inside a school, contained an integrated faucet filter that could not be removed (Appendix A).

3.2.1 Sampling Campaign 1 and 2

As mentioned, initial sampling campaigns were designed around a universal sampling approach that considered the constraints of conducting rapid reconnaissance research. These constraints included minimizing sample volume for shipping, selecting tap locations to reduce homeowner disturbance, and reducing in-field water quality measurements to accomplish sampling a large number of sites in a short amount of time. Therefore, samples from SC 1 and SC 2 did not strictly adhere to the requirements of any single SDWA rule or analyte. However, the research was able to reach a large number of residents from different communities served by government and privately operated systems, presenting a robust initial sample set.

SC 1 was conducted in the entire month of February of 2018 and SC 2 was conducted in the last week of March and first week of April of 2018. Samples from SC 1 were analyzed on-site for bulk water quality parameters (i.e., pH, temperature, turbidity, total and free chlorine) and in the laboratory for alkalinity, dissolved organic carbon (DOC), ultraviolet-visible absorbance at wavelength 254 nanometers (UV_{254}), and select ions, nutrients, disinfection byproducts (DBP), and trace elements. Samples and sites for SC 2 were only analyzed on-site for select bulk water quality parameters (i.e., pH, turbidity, temperature, total and free chlorine) and in the laboratory for select trace elements.

The sampling method collected a first draw (FD) 6-plus hour stagnation (6+HS) 125 mL sample (termed SC1–B1) in a wide-mouth HDPE bottle for trace elements. The tap was left open allowing the water to flush. pH, temperature, and total and free chlorine were measured from a free-flowing stream after readings were stable. Following, a flushed 500 mL sample (termed SC1–B2) was collected in either a narrow mouth amber glass or wide-mouth brown opaque HDPE bottle for laboratory measurements of select bulk water quality parameters. SC1−B2 was rinsed three times prior to collection and samples were collected avoiding headspace as much as feasible. Total trihalomethane (TTHM) samples were collected in triplicate in vials with a volume of 40 mL prefilled with ascorbic acid ($C_6H_8O_6$) for dechlorination. Haloacetic acid (HAA5) samples were collected in singlet vials with a volume of 60 mL prefilled with ammonium chloride (NH_4Cl) for dechlorination. After samples were collected, 15 drops of 1:1 $HCl:H_2O$ was added to the TTHM vials only. Samples were capped headspace free. Flow rate for all samples (SC1–B1, SC1–B2, and DBP vials) was adjusted to prevent spilling or splashing.

3.2.2 Sampling Campaign 3

SC 3 was conducted over the time span of two (2) days, July 30th and 31st, where each community was sampled on separate days. Samples and sites from SC 3 were analyzed on-site for bulk water quality parameters (i.e., pH, temperature, turbidity, total and free chlorine, and alkalinity) and in the lab for conductivity, DOC, UV_{254}, and select ions, nutrients, and trace elements. The sampling method better aligned with standard U.S. EPA LCR sampling protocol by collecting a 1-liter first draw sample, but also employed an abbreviated sequential volume profiling (SVP) approach.

A FD 6+HS 1-liter sample was collected in a wide-mouth HDPE bottle for lead, copper, and other trace elements (termed SC3–B1) (Figure 2). Following, two (2) sequential 1-liter samples (termed SC3–B2 and SC3–B3) were also collected, bringing the total of the SVP to three (3) liters. As SC3–B2 was being filled, a 30 mL aliquot was collected from a free-flowing stream, and free chlorine was measured. The tap was left open for 10 to 20 seconds, allowing the water to flush, and one 500 mL sample (termed SC3–B4) was collected in a wide-mouth HDPE bottle for bulk water quality parameters. Flow rate was estimated by determining the amount of time to fill SC3–B4. SC3–B4 was rinsed three times prior to collection and samples were collected avoiding headspace as much as feasible. With the tap still open, two (2) 1-liter bottles were collected headspace free (termed SC3–B5 and SC3–B6). pH, temperature, and total and free chlorine were measured from a free-flowing stream after the SVP samples were collected and value was recorded after readings were stable. Alkalinity was measured on-site from SC3–B5 and SC3–B6, the value was averaged (relative difference 4.5%), and the samples were discarded. Each SVP sample was measured on-site for turbidity and inspected for signs of particulate material or discoloration compared to other samples. SC3–B2 was discarded after turbidity and physical characteristics were recorded. A final, 1-liter sample (SC3–B7) was collected from the exterior hose bib after all interior collections were finished. SC3–B1, SC3–3, SC3–B4, and SC3–B7 were shipped back to Colorado for analysis.

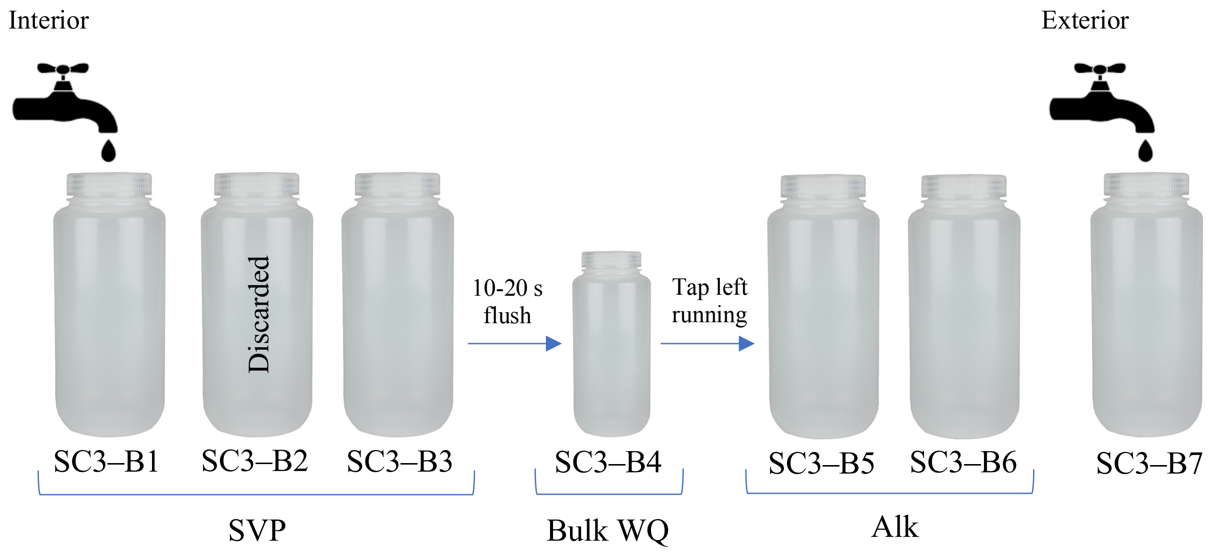


Figure 2. Sampling Campaign 3: Graphic depicting the sampling approach.

3.2.3 Sampling Campaign 4

SC 4 utilized sampling kits that were distributed to homeowners to collect samples. Sampling kits contained one 1-liter sampling bottle, one 500 mL sampling bottle, a sampling instruction sheet translated into Spanish, and a pen. Each sampling instruction sheet had written steps, a pictographic schematic, and blank lines for voluntarily provided demographic information and feedback on water quality perceptions and experiences after Hurricane Maria (Appendix B). This work is ongoing.

3.3 Analytical Methods

For a detailed list and description of all analytical methods and laboratories for each parameter, see Appendix C. *All trace element concentrations (lead, copper, etc.) were measured as a total recoverable concentration for all four (4) sampling campaigns* as there was no differentiation between dissolved and particulate forms of lead. Field blanks were collected for SC

1 (n=4), SC 2 (n=1), and SC 3 (n=2) for quality assurance and quality control (QA/QC) purposes. All blanks were processed and analyzed following the same procedures as a bulk sample.

3.3.1 Sampling Campaign 1 and 2

All sample bottles were stored in the dark at 4 °C in Puerto Rico until shipped with artificial ice packs overnight to the CU Boulder within 14 days of collection. DBP vials were shipped directly to SNWA from Puerto Rico. SC1–B1 was used to measure trace elements. SC1–B2 was used to measure alkalinity, DOC, UV_{254}, select ions and nutrients.

At CU Boulder, all samples were also stored in the dark at 4 °C. SC1–B2 for each sampling site was filtered through a rinsed 0.7 µm nominal pore size glass fiber filter (GF/F) (Whatman™ GE Healthcare Life Sciences). DOC, UV_{254}, and alkalinity were analyzed post-filtration. A ~50 mL aliquot was partitioned from SC1–B2 and sent to RMRS laboratory to be analyzed for select ions and nutrients by ion-chromatography (IC). SC1–B1 was acidified with concentrated (68%) Trace Metal Grade (TMG) nitric acid (HNO_3) (Fisher Scientific Lot #1116100) to $pH < 2$ within 14 days of collection. Sample pH was re-checked after a minimum of 24 hours holding time to make sure sample was properly acidified. An aliquot (10 to 20 mL) was partitioned out of the trace element sample bottle and sent to LEGS Lab at CU Boulder to be analyzed for a full-suite of metals. Samples were analyzed by EPA Method 200.8 through Inductively Couple Plasma-Mass Spectrometry (ICP–MS) using a PerkinElmer SCIEX Model Elan® DRC-e ICP–MS. Indium was used as an internal standard. Four standards (blank, 100, 500, and 1000 µg/L) were used for calibration for each element. Higher concentration standards were added during the run to extend the calibrations of select elements as needed. TTHMs were analyzed at SNWA by EPA Method 524.2 using Capillary Column Gas Chromatography/Mass Spectrometry. HAA5s were analyzed by EPA Method 552.2 using Liquid-Liquid Extraction, Derivatization, and Gas Chromatography with electron capture detection.

3.3.2 Sampling Campaign 3

All SVP samples (SC3–B1 and SC3–B3) and each hose bib sample (SC3–B7) were stored at room temperature, and each bulk water quality sample (SC3–B4) was stored in the dark at 4 °C in Puerto Rico until shipping. Samples were shipped with artificial ice packs overnight to CU Boulder within 14 days of collection. SVP samples and SC3–B7 were used to measure trace elements. SC3–B4 was used to measure conductivity, DOC, UV_{254}, and select ions and nutrients.

At CU Boulder, all samples were then stored in the dark at 4 °C. SC3–B4 samples were first analyzed for conductivity and then filtered through a rinsed, 47 mm 0.45 µm pore size Metricel® membrane filter (Pall Cooperation Life Sciences). DOC and UV_{254} were analyzed at CU Boulder post-filtration. A ~50 mL aliquot was partitioned from SC3–B4 and sent to RMRS to be analyzed for major ions and nutrients by IC. SVP samples were acidified with concentrated (68%) TMG nitric acid (HNO_3) (Fisher Scientific Lot #1116100) to $pH < 2$ within 14 days of collection. For the Lajas samples, 3 mL of acid was added for each sample. For the Patillas-Mulas samples, 6 mL of acid was added for each sample. Sample pH was re-checked after a minimum of 24 hours holding time to make sure the sample was properly acidified. A 250 mL aliquot was partitioned and sent to the Water Quality Laboratory at Denver Water for lead and copper analysis. Samples were analyzed by EPA Method 200.8 through Inductively Couple Plasma-Mass Spectrometry (ICP–MS) using an Agilent Technologies 7900 series ICP–MS. Bismuth was used as an internal standard. Seven standards (blank, 1, 5, 10, 40, 80, and 100 µg/L) were used for calibration for each element.

3.3.3 Sampling Campaign 4

All sample bottles were stored in Puerto Rico in their original sampling kits at room temperature and then shipped at room temperature overnight to CU Boulder within 14 days of collection. At CU Boulder, all samples were then stored in the dark at 4 °C. pH, conductivity, turbidity, and alkalinity were measured from SC4–B2 upon arrival. SC4–B1 was measured for turbidity and then acidified with concentrated (69%) TMG nitric acid (HNO_3) to pH < 2 (Fisher Scientific Lot #1118040) within 14 days of collection. For each FD 6+HS sample, 3 mL of nitric acid was added for preservation. A 125 mL aliquot was partitioned from SC4–B2 for analysis by IC and the rest of SC4–B2 was acidified following the same acidification procedure, however only 1.5 mL of acid was added per bottle due to the smaller sample volume. Sample pH was re-checked after a minimum of 24 hours holding time to make sure sample was properly acidified. Turbidity was re-measured after acidification to ensure that no sample digestion was required per EPA Method 200.8. This work is ongoing, and samples are properly preserved waiting analysis.

3.4 Statistical Analysis

Since several different laboratories were used to analyze samples, consistency had to be developed between the data sets. For all raw data provided in Tables 4, 6, 7, 8, and 11, a value that was reported as "<MDL" means that the value was less than the lab specific method detection limit (MDL) provided with the data. Moving forward, a project practical quantification limit (PQL) was developed for each analyte and used to provide uniformity in reporting values close to the MDL when performing statistical calculations across and between the data sets. Any value that was reported as < project PQL was reported as ½ the project PQL for statistical calculations to prevent bias in the calculations depending on analysis lab. The 90th percentile concentration was taken as a linear interpolation using the built-in Excel function PERCENTILE. See Appendix D for a full list of parameters, reporting limits, and analytical laboratory identification. Significance and hypothesis tests were conducted in MATLAB R2017a. Since lead concentrations were not normally distributed (Kolmogorov-Smirnov test $p < 0.001$), the Kruskal-Wallis nonparametric alternative of a one-way ANOVA ($\alpha = 0.05$ significance level) was used to compare the occurrence of other trace metals, variations in bulk water quality parameters, and corrosion indices with the observation of high or low WLLs. If the data in each category come from the same distribution, the test compares median concentrations and if the data do not come from the same distribution, the test compares mean ranks.

3.5 Conductivity, Total Dissolved Solids, and Ionic Strength

Major ions in fresh waters include sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), sulfate (SO_4^{2-}), chloride (Cl^-), and bicarbonate (HCO_3^-) with smaller contributions from fluoride (F^-), bromide (Br^-), and carbonate (CO_3^{2-}) [92]. The ionic strength of a solution, which is an indicator of the quantity of free ions in solution, is an important parameter for understanding corrosion chemistry. It can be calculated using Equation 3.1, where m is the molality of the ith ion and Z_i is an integer representing the charge on the ith ion.

$$I = \frac{1}{2}\sum_i m_i {Z_i}^2 \qquad \text{Equation 3.1}$$

Even though this calculated method is most accurate, due to analytical limitations of accurately measuring the complete ionic composition of natural waters, using this equation can be merely an estimation. Thus, ionic strength is related to two other measurements, total dissolved solids (TDS) and specific conductance (SC), through Equation 3.2 and Equation 3.3 [92].

$$I = 2.5 \times 10^{-5} \times TDS \qquad \text{Equation 3.2}$$

$$I = 1.6 \times 10^{-5} \times \mathrm{SC} \; \mathit{for}\ I < 0.06 \qquad \text{Equation 3.3}$$

TDS is given in units of mg/L and assumes that the composition of natural waters is relatively constant. Specific conductance is given in units of μS/cm. Ionic strength was calculated using Equation 3.1, since it provided consistency across the data sets since specific conductance was not measured for SC 1 or SC 2 and only for SC 3. TDS was estimated using Equation 3.2 for SC 1 and SC 2 using ionic strength calculated from Equation 3.1, but then TDS was calculated for SC 3 with the estimated ionic strength from Equation 3.3 using the field-measured specific conductance. The ions used in this calculation were Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, Cl^-, Br^-, HCO_3^-, CO_3^{2-}, F^-, nitrate (NO_3^-), phosphate (PO_4^-), and ammonium (NH_4^+). Every ion was measured by RMRS (See Appendix D) using IC except for HCO_3^- and CO_3^{2-}, which were estimated using geochemical alkalinity calculations as discussed in the next section.

3.6 Geochemical Alkalinity

Alkalinity is the acid-neutralizing capacity (ANC) of a water, or the ability of the water to resist changes in pH, and is defined as the sum of all titratable bases to endpoints based on the carbonate system [92]. The geochemical or charge-balance definition of alkalinity, which is based on the principle of electroneutrality, is the difference between the sum of all conservative cations and the sum of all conservative anions on a charge equivalent basis. These two definitions of alkalinity are essentially the same but emphasize a different aspect of the property: how the parameter is measured through titration compared to the charge imbalance between strong base cations or strong acid anions [92].

Conservative ions are those unaffected by changes in pH and primarily include Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, Cl^-, and NO_3^{2-}. Since alkalinity was not measured by titration (HACH Method

8203 Appendix C) for all samples from SC 1, geochemical alkalinity in mg/L as $CaCO_3$ was calculated based on the observed concentrations of conservative ions in solution using Equation 3.4.

$$Alkalinity = \sum_i [SBC] - [SAA] \qquad \text{Equation 3.4}$$

[SBC] is the concentration strong base cations and [SAA] is the concentration of strong acid anions in units of eq/L. After alkalinity was estimated using Equation 3.4 in units of eq/L, alkalinity was converted to units of mg/L as $CaCO_3$ and defined as total alkalinity and all attributed to bicarbonate (HCO_3^-) since no samples had an observed pH above 8.3.

3.7 Calculation of Corrosion Indices

There are several indices developed to understand the corrosivity of the water with respect to water quality characteristics. Several of these indices are not specific to corrosion of lead-bearing plumbing material, and thus the use of these indices to predict lead release should be highly cautious. Furthermore, the conditions for which the metrics were developed were model systems with specific corrosion mechanisms. Despite the criticisms, corrosion indices were calculated to compare the results from this study to other values reported in literature.

3.7.1 Langelier Saturation Index

The Langelier Saturation Index (LSI) determines the degree to which calcium carbonate will precipitate on pipe walls as a function of pH, ionic strength, calcium concentration, and bicarbonate concentration. However, while this index is widely used across corrosion studies, it has been shown to not be a good predictor of water corrosivity towards cast iron pipes [18]. Even with this knowledge, the LSI can provide valuable information that can be used in conjunction with other analyses to make corrosion control treatment decisions. A slightly positive value indicates scale layer formation due to supersaturation of calcium carbonate and a negative value indicates scale layer dissolution. LSI was calculated using Equation 3.5 under APHE, AWWA, WEF Standard Method 2330 B and included the recently published correction [93].

$$LSI = pH - pH_S \qquad \text{Equation 3.5}$$

$$pH_s = pK_2 - pK_s + p[Ca^{2+}] + p[HCO_3{}^{-}] + 5pf_m \qquad \text{Equation 3.6}$$

$$pf_m = A\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right] \qquad \text{Equation 3.7}$$

$$I = \frac{1}{2}\sum_{i=1}^{n} m_i Z_i^2 \qquad \text{Equation 3.8}$$

$$A = 1.86 \times 10^6\ (E\ T)^{-1.5} \qquad \text{Equation 3.9}$$

$$E = \frac{60\,954}{T + 116} - 68.937 \qquad \text{Equation 3.10}$$

An average temperature was calculated for each sampling campaign and converted to degrees Kelvin (°K) and used in the estimation of the dielectric constant (*E*) in Equation 3.10 and the constant *A* in Equation 3.9. Ionic strength (*I*) was calculated using Equation 3.8, which has the same units as Equation 3.1. K_s is the solubility product for calcite, K_2 is the second dissociation constant for carbonic acid, f_m is the activity coefficient for a monovalent species at the specified temperature, and pH_s is the pH of the water if it were in equilibrium with $CaCO_3$ at the existing Ca^{2+} and HCO_3^- concentrations.

3.7.2 Larson-Skold Ratio

The Larson-Skold Ratio (LSR) was developed to predict the corrosion of cast iron pipes and mild steel towards water quality conditions of the Great Lakes. The general theory behind the ratio considered the concentrations of corrosive agents, chloride and sulfate, relative to inhibitive agents, such as calcium and carbonate constituents [94]. The relative effectiveness of each is not constant as each factor can influence each other through different mechanisms [94].

Overall, the ratio was defined as the concentration of chloride and/or sulfate to system alkalinity. Depending on the total alkalinity speciation and the units of the input parameters, there are different equations used to calculate this index. Equation 3.11 is used when expressing concentrations in mol/L [16], [18] and assumes that the system alkalinity is all attributed to bicarbonate. It is important to consider that the ratio was developed around the conditions of the Great Lakes waters, so extrapolating the ratio to extreme conditions of alkalinity is not recommended [95].

$$LSR = \frac{[Cl^{-}] + 2\left[{SO_4}^{2-}\right]}{[{HCO_3}^{-}]} \qquad \text{Equation 3.11}$$

The original work by Larson and Skold suggests a ratio of less than 0.2 to 0.3 to reduce corrosion rates [16], [18], [94], but other work has suggested that ratios less than 0.6 to 0.8 are sufficient to mitigate iron corrosion [18], [96]. Interpretations of the guidelines and research suggest that LSR ratios between 0.8 and 1.2 are conducive to higher than desired corrosion rates and ratios greater than 1.2 are indicative of highly corrosive conditions [95], [97].

3.7.3 Chloride-to-Sulfate Mass Ratio

Chloride and sulfate are two parameters important in corrosion chemistry because they influence uniform corrosion due to their high ionic strength capability. Thus, a ratio was developed using these two parameters, the Chloride-to-Sulfate Mass Ratio (CSMR). The CSMR has been linked to increased galvanic corrosion between lead pipe-to-copper and lead solder-to-copper [41], [43], [44], [76]. Lead-chloride complexes are more soluble than lead-sulfate complexes, hence, a lower CSMR ratio may be indicative of lower lead release due to the promotion of insoluble lead-sulfate complexes, and a higher ratio may be indicative of soluble lead-chloride complexes [43], [76], [98]. The CSMR and the correlation to observed WLLs is dependent on other water quality parameters, such as pH, alkalinity, and ion speciation, among others [41]. A high CSMR (> 0.5) combined with alkalinity less than 50 mg/L as $CaCO_3$ poses the most serious risk to lead leaching [44]. The ratio is calculated using Equation 3.12, where each concentration is in mg/L.

$$CSMR = \frac{[Cl^-]}{[SO_4{}^{2-}]} \qquad \text{Equation 3.12}$$

An increase in the ratio from 0.1 to 1 has been linked to the most severe increase in lead release due to galvanic corrosion of lead solder connected to copper pipe [44]. The original recommended ratio varied between less than 0.2 as ideal and less than 0.5 as tolerable [43], [76], but further fundamental research on the mechanistic basis of the ratio indicates a critical threshold ratio of less than 0.77 [41].

3.7.4 Ryznar Index

The Ryznar Index (RI) is another metric used to predict calcium carbonate precipitation and is similar to the LSI but was developed differently to emphasize the importance of calcium and alkalinity on scale formation. The RI is calculated using Equation 3.13, where the pH_s is calculated using Equation 3.6.

$$RI = 2pH_S - pH \qquad \text{Equation 3.13}$$

The proposed threshold values for this index vary, but overall it was observed that scale formation increased as the index decreased less than six (6) [99]. In general, it is proposed that regions < 5 and > 7 are regions of most interest, where values < 5 indicate scale formation potential, values > 7 indicate scale dissolution, and values greater than 8.5 are said to be very aggressive

[100]. When determining these thresholds, the classification for aggressive water was based on the premise that $CaCO_3$ scale formation was protective, however that is no longer the conventional wisdom.

3.7.5 Buffer Intensity

Buffer intensity is the capacity of a water to resist changes in pH and is often confused with alkalinity. In order to understand the difference between buffer intensity and alkalinity, it is important to understand the DIC concentration and the relationship of DIC and buffer intensity to pH. DIC is defined as the total concentration of inorganic carbon from the carbonate system (H_2CO_3, HCO_3^-, CO_3^{2-}) as well as dissolved carbon dioxide ($CO_{2\,(aq)}$). In contrast, alkalinity is a measurement of all titratable bases in solution, which in most cases can be attributed to HCO_3^- and CO_3^{2-}. pH controls the speciation of the carbonate constituents in the water and thus controls DIC and further controls buffer intensity. At varying pH levels, several waters with identical alkalinity can have different buffering capacities. Buffer intensity is lowest at the pK_a's of H_2CO_3 and HCO_3^- and highest around neutral pH levels [16].

Buffer intensity is calculated using Equation 3.14 [16], where TALK is the total alkalinity expressed in eq/L, $[H^+]$ is the hydrogen ion concentration expressed in mol/L, K_w is the acid dissociation constant of water, and K_1 and K_2 are the first and second dissociation constants of carbonic acid, respectively.

$$\beta = 2.303\left[\left(\frac{[H^+]TALK}{[H^+]+K_2}\right)\times\left(\frac{[H^+]}{[H^+]+K_1}+\frac{K_2}{[H^+]+K_2}\right)+[H^+]-\frac{K_W}{[H^+]}\right] \qquad \text{Equation 3.14}$$

With regards to corrosion, buffer intensity influences the pH shift that occurs at the anodic and cathodic sites of an electrochemical cell [18]. The benefit of buffer intensity is to prevent localized sites of high pH to provide better pH distribution and even scale formation across the pipe material [16].When implementing corrosion control, achieving an alkalinity that can maintain a buffer intensity of at least 0.1 meq/L is recommended [17].

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Sampling Campaign 1 & 2

4.1.1 General Water Quality Conditions

The general water quality results exhibited a range of characteristics across sampling sites and water system types as summarized in Table 4. pH values ranged from 6.5 to 8.1 for SC 1 and SC 2 combined, with an average value of 7.2. Turbidity was generally low for SC 1 and SC 2 combined, with 80% of samples less than 1 NTU. While the average turbidity was 2.2 NTU, the median value was 0.3 NTU and the maximum value was 65 NTU. Six (6) samples had turbidities between 1 NTU and 10 NTU, and two (2) samples from PRASA systems had turbidities that were greater than 10 NTU. Three (3) out of the eight (8) samples that had a turbidity > 1 NTU were from spring sites. Hardness varied considerably for SC 1 and SC 2 combined, with a minimum value of 20 mg/L, a maximum value of 393 mg/L, and an average value of 130 mg/L. Geochemical alkalinity also had a wide range of values for SC 1, with a minimum value of 16 mg/L as $CaCO_3$ (Site 7) and a maximum value of 356 mg/L as $CaCO_3$ (Site 2). Using the Safe Drinking Water Information System (SDWIS) database, the primary source water for both systems, Lajas (Site 2) and Humacao (Site 7), is surface water. The source of the surface water is unknown. The sample with the highest turbidity of 65 NTU was from a non-PRASA system (Site 26) that also had low alkalinity (36 mg/L $CaCO_3$) and low hardness (34 mg/L as $CaCO_3$).

Table 4. Sampling Campaign 1 & Sampling Campaign 2: Bulk water quality results. The results from Sampling Campaign 2 are indented and shaded in grey.

System Type	***Site #***	***Community***	***pH***	***Turbidity*** *(NTU)*	***Alkalinity*** *(mg/L as $CaCO_3$)*	***Hardness*** *(mg/L as $CaCO_3$)*	***Buffer Intensity*** *(mol/L per pH unit)*
PRASA	1	Sabana Grande	7.4	0.2	139	145	0.55
		Sabana Grande 2	6.9	0.0	-	123	-
	2	Lajas	7.0	0.1	356	325	3.18
		Lajas 2	6.8	0.0	-	374	-
	3	Hormigueros	7.5	0.3	92.0	93	0.27
	4	Arecibo	7.1	0.2	121	140	0.79
	5	Utuado	7.0	3.0	84.0	106	0.63
	6	Vega Alta	6.8	0.4	35.1	67	0.40
	7	Humacao	6.8	0.2	16.0	20	0.17
	8	Gurabo	7.2	0.7	74.9	81	0.45
	9	Trujillo Alto	7.1	1.3	103	100	0.64
	10	San Juan	7.2	0.5	107	107	0.65
		San Juan 2	6.5	0.6	-	112	-
	11	Adjuntas	7.3	0.1	63.3	67	0.30
	12	Coamo	7.5	0.1	104	116	0.30
	13	Santa Isabel	7.2	0.1	310	340	1.74
	14	Juana Díaz	7.0	0.2	245	276	1.88
	15	Yauco	7.6	0.1	138	143	0.31
	16	San Germán	7.5	0.3	130	146	0.39
		San Germán 2	7.0	0.1	-	144	-
	17	Mayagüez	7.2	0.2	121	120	0.72
	18	Aguada	7.2	0.3	125	125	0.73
	19	Aguadilla-Pueblo	7.2	0.3	121	127	0.74
	20	Isabela	7.0	0.2	121	131	1.04
	21	Moca	7.3	0.5	120	126	0.59
		Moca 2	6.9	0.3	-	113	-
	22	Aguadilla-Base Ramey	7.3	0.5	94.8	101	0.41
	23	Ponce	7.0	0.1	294	393	2.53
	24	Guayama	7.3	0.2	46.6	53	0.21
		Guayama 2	7.2	0.2	-	55	-
NON-PRASA	25	San German	7.5	0.7	113	123	0.35
	26	Yabucoa	7.1	65	36.3	34	0.23
	27	Villalba	8.1	0.4	119	130	0.11
	28	Guayama	8.1	0.2	151	162	0.15
	29	Patillas-Don Conde	7.2	0.2	240	248	1.27
	30	Patillas-Tanque 2	7.4	0.8	76.1	72	0.27
	31	Patillas-Tanque 1	7.8	0.2	74.1	62	0.12
		Patillas-Tanque 1 2	7.5	-	-	64	-
	32	Patillas-El Real	7.3	3.1	28.8	29	0.13
	33	Patillas-Mulas	7.2	10.6	16.1	29	0.09
		Patillas-Mulas 2	7.0	0.6	-	33	-
	33a	Community Tap	6.6	2.2	-	34	-
	33b	Raw Water Intake	7.2	1.0	-	31	-
	33c	River Source Water	7.4	2.5	-	33	-
SPRING	34	Maricao/Sabana	7.5	6.2	147	154	0.44
	35	Utuado	7.1	1.4	159	172	1.13
	36	Manatí	6.7	0.1	292	318	3.77
	37	Caguas	6.7	0.0	103	85	1.40
	38	Adjuntas	7.1	2.1	179	162	1.28
	39	Mayagüez-Quemado	6.8	0.3	154	153	1.77
	40	Mayagüez-Río Cañas	7.1	0.5	112	120	0.70

Microbiology

While microbial analysis was performed in this study for SC 1, analytical methods were not included in Chapter 3 due to the ultimate scope of the project focusing on corrosion issues. However, the microbial results are significant when evaluating the general water quality of the first sampling campaign. Two methods were used to quantify *Escherichia coli (E. coli)*: the Aquagenx Compartment Bag Test (CBT) and the Most Probable Number Method using Multiple Tube Fermentation in lauryl tryptose broth (LTB)-methylumbelliferyl-β-glucuronide (MUG). Total coliforms were analyzed using a presence/absence (PA) method followed by confirmation phase in brilliant green lactose bile (BGLB). All samples positive for microbiological constituents came from either non-PRASA or spring sampling sites, as summarized in Table 5.

Table 5. Sampling Campaign 1: Microbial results. Turbidities are restated for easy reference.

System Type	***Site #***	***Community***	***Turbidity*** *(NTU)*	***Total Coliform*** *(Presence/Absence w/ Confirmation Phase)*	***E. coli*** *(Aquagenx)*	***E. coli*** *(LTB-MUG)*
NON-PRASA	26	Yabucoa	65	+[1]		+
	28	Guayama	0.2	+	+	+
	30	Patillas-Tanque 2	0.8	+	+	+
	33	Patillas-Mulas	10.6	+		
SPRING	34	Maricao/Sabana	6.2	+		
	35	Utuado	1.4	+	+	+
	36	Manatí	0.1	+		
	37	Caguas	0.0	+		
	38	Adjuntas	2.1	+	+	
	39	Mayagüez-Quemado	0.3	+	+	
	40	Mayagüez-Río Cañas	0.5	+	+	

[1] A positive (+) sign indicates positive detection. All other cells were left blank for non-detection.

SC 1 had 11 samples positive for total coliforms, of which four (4) came from non-PRASA systems and seven (7) came from spring sites. Using the Aquagenx CBT method, six (6) samples were positive for *E. coli*, four (4) from spring sites and two (2) non-PRASA systems. Using Multiple Tube Fermentation, only four (4) samples were positive, three (3) from non-PRASA systems and one (1) from a spring site. Overall, all seven (7) of the spring sites were positive for total coliforms and four (4) of those spring sites were positive for *E. coli.* Community water systems Maricao/Sabana (Site 34), Utuado (Site 35), and Adjuntas (Site 38) all had turbidities greater than 1 NTU. The presence of microbial contamination combined with higher turbidities suggests that all of these spring sites were under the influence of surface water.

Nitrate

A report released in December 2018 using unpublished data by the University of New Hampshire (UNH) studied watershed water quality in Puerto Rico in the year after Hurricanes Maria and Irma and found "unprecedentedly high levels" of nitrate in many of the streams. Typically, nitrate levels are expected to increase within the first four months post-storm and then decrease. In the nine months following the hurricane, the levels had still not returned to baseline levels [101]. Based on the UNH study, there are indications that a new baseline nitrate level will be established. Nitrate is an important nutrient for plant growth but can have adverse health impacts when ingested, and thus the U.S. EPA set an MCL of 10 mg/L as N. No sampling sites from SC 1 had nitrate levels above the MCL. The long-term impacts of elevated nitrate levels on watershed water quality is still uncertain, however theories suggest that if these levels continue it could disrupt forest productivity and coastal ecosystems in Puerto Rico [101].

Furthermore, elevated nitrate levels could disrupt water treatment operations by promoting algae growth and accelerating lake or source water eutrophication, with levels higher than 5 mg/L as N (22.1 mg/L as NO_3^-) seen to exacerbate this condition [102]. Only one sample had a nitrate level greater than 22.1 mg/L as NO_3^- (Table 6), and that was from a PRASA system (Site 2), which had a nitrate level of 22.4 mg/L as NO_3^-. In addition, two samples from PRASA systems (Site 13 and Site 14) had levels greater than 4 mg/L as N (17.7 mg/L as NO_3^-), but both of these had non-detect levels of phosphate (discussed in future sections).

Table 6. Sampling Campaign 1 & Sampling Campaign 2: Select ion water quality results. The results from Sampling Campaign 2 are indented and shaded in grey.

System Type	***Site #***	***Community***	***Ca^{2+} (mg/L)***	***Mg^{2+} (mg/L)***	***Na^{+} (mg/L)***	***K^{+} (mg/L)***	***NO_3^- (mg/L as NO_3^-)***	***Cl^- (mg/L)***	***SO_4^{2-} (mg/L)***
PRASA	1	Sabana Grande	26	20	7.7	2.2	1.8	14	3.0
		Sabana Grande 2	24	16	8.2	1.5	-	-	-
	2	Lajas	90	24	77	3.4	22	48	52
		Lajas 2	107	26	85	1.8	-	-	-
	3	Hormigueros	25	7.3	8.2	2.1	0.5	9.3	7.8
	4	Arecibo	48	4.8	9.0	2.1	3.5	14	19
	5	Utuado	29	8.5	16	3.5	4.9	21	28
	6	Vega Alta	19	4.5	6.7	2.5	1.9	11	32
	7	Humacao	5.3	1.8	8.2	1.6	0.1	14	3.8
	8	Gurabo	22	6.3	16	2.2	1.4	18	17
	9	Trujillo Alto	26	8.4	19	2.9	3.8	25	2.9
	10	San Juan	28	8.9	21	2.8	3.7	24	12
		San Juan 2	29	10	25	2.6	-	-	-
	11	Adjuntas	18	5.5	6.9	2.1	1.7	10	5.6
	12	Coamo	28	11	12	1.4	2.1	21	8.3
	13	Santa Isabel	92	26	45	1.8	19	40	55
	14	Juana Díaz	79	19	24	1.8	19	26	32
	15	Yauco	39	11	12	2.1	2.1	13	12
	16	San Germán	3.3	33	3.1	0.4	2.1	11	5.2
		San Germán 2	3.4	33	3.2	0.8	-	-	-
	17	Mayagüez	33	8.8	10	1.7	1.2	10	8.4
	18	Aguada	41	5.4	13	2.2	1.4	15	7.8
	19	Aguadilla-Pueblo	43	4.9	9.4	2.2	1.2	15	7.3
	20	Isabela	47	3.5	5.1	2.3	0.5	12	6.3
	21	Moca	43	4.7	9.0	2.3	1.2	14	7.3
		Moca 2	38	4.4	9.0	2.3	-	-	-
	22	Aguadilla-Base Ramey	33	4.6	8.8	2.7	1.2	14	7.4
	23	Ponce	124	20	36	2.4	9.8	50	98
	24	Guayama	13	5.0	14	1.1	2.6	19	7.0
		Guayama 2	13	5.4	16	0.9	-	-	-
NON-PRASA	25	San German	1.4	29	2.6	1.2	4.4	6.3	5.1
	26	Yabucoa	7.1	3.9	12	1.3	1.1	14	4.7
	27	Villalba	40	7.0	11	0.9	2.9	8.6	21
	28	Guayama	38	16	31	0.9	2.2	28	38
	29	Patillas-Don Conde	60	24	64	0.9	0.7	51	73
	30	Patillas-Tanque 2	16	7.5	17	0.8	0.8	20	4.3
	31	Patillas-Tanque 1	14	6.5	17	0.9	0.9	15	3.6
		Patillas-Tanque 1 2	15	6.7	18	1.6	-	-	-
	32	Patillas-El Real	7.2	2.7	11	0.8	2.4	14	3.3
	33	Patillas-Mulas	7.1	2.7	10	0.9	5.5	18	6.2
		Patillas-Mulas 2	8.2	3.1	11	0.8	-	-	-
	33a	Community Tap	8.3	3.2	11	0.9	-	-	-
	33b	Raw Water Intake	7.6	3.0	11	0.9	-	-	-
	33c	River Source Water	7.9	3.2	12	0.8	-	-	-
SPRING	34	Maricao/Sabana	4.0	35	3.0	1.0	0.8	6.6	4.8
	35	Utuado	66	2.0	4.2	0.7	5.8	8.5	6.6
	36	Manatí	119	5.3	16	0.2	14	24	16
	37	Caguas	20	8.7	20	0.6	0.6	14	5.1
	38	Adjuntas	42	14	13	0.9	0.2	4.8	5.0
	39	Mayagüez-Quemado	51	6.2	8.5	1.2	3.1	8.4	4.4
	40	Mayagüez-Río Cañas	27	13	9.1	1.6	3.9	16	3.0

DOC concentrations ranged from 0.1 to 5.3 mg_C/L across sampling sites for SC 1, with an average of 1.10 and the 1st and 3rd quartiles at 0.56 to 1.26 mg_C/L, respectively (Table 7). The DOC concentrations from all spring sites were below 0.6 mg_C/L. Free chlorine residual was not measured for spring sites since spring sources implemented no water treatment. Free chlorine residual ranged from non-detect in a non-PRASA system to a max of 3 mg/L in a PRASA system. Three (3) sites exceeded the TTHM MCL of 80 μg/L (Sites 9, 10, and 19). Each of these sites had DOC concentrations at 2.4, 2.4, and 1.6 mg_C/L, respectively. While no site exceeded the HAA5 MCL of 60 μg/L, two sites approached the MCL at 57 (Site 19) and 54 μg/L (Site 26).

Dissolved organic matter (DOM), and subsequently DOC, in source waters is affected by precipitation, runoff, and seasonal changes in the watershed. Hurricanes, which cause severe flooding and sediment mobilization, exacerbate these conditions and impact water treatment operations. After Hurricane Irene, Esopus Creek, NY saw a four-fold increase in DOC concentration in just five days, which exported 43% of its average annual concentration [103], [104]. In Maryland, Hurricane Irene resulted in a ten-fold increase in DOC concentrations, which contributed to 19% of the annual 2011 exported DOC concentrations in a 12-ha watershed during the period of the event [103], [105].

Overall, the impacts of Hurricane Maria on finished water quality conditions in this study were hard to implicate due to not having baseline data for reference. Furthermore, the long-term impacts of hurricanes on DOC concentrations in watersheds is not certain. However, the low DOC concentrations and turbidity values in the finished waters suggest that water treatment operations, in general, were operating normally, with exceptions as mentioned.

Table 7. Sampling Campaign 1 & Sampling Campaign 2: Dissolved organic carbon, free chlorine, and disinfection byproduct results. The results from Sampling Campaign 2 are indented and shaded in grey.

System Type	***Site #***	***Community***	***DOC*** ***(mg_C/L)***	***Free Chlorine*** ***(mg/L as Cl_2)***	***TTHM*** ***(µg/L)***	***HAA5*** ***(µg/L)***
PRASA	1	Sabana Grande	1.0	2.3	48.1	27.9
		Sabana Grande 2	-	1.6	-	-
	2	Lajas	0.6	2.3	4.2	1.7
		Lajas 2	-	1.8	-	-
	3	Hormigueros	0.8	1.8	32.8	12.9
	4	Arecibo	0.8	0.4	43.1	27.8
	5	Utuado	0.9	1.7	21.4	15.0
	6	Vega Alta	1.3	1.5	40.8	50.7
	7	Humacao	1.2	1.1	37.4	20.3
	8	Gurabo	1.2	0.6	53.3	19.2
	9	Trujillo Alto	2.4	0.7	79.9	-
	10	San Juan	2.4	0.9	85.9	43.5
		San Juan 2	-	0.7	-	-
	11	Adjuntas	1.0	1.6	19.7	15.6
	12	Coamo	0.9	1.8	37.8	18.7
	13	Santa Isabel	0.4	1.8	4.1	1.3
	14	Juana Díaz	0.5	0.9	12.5	2.6
	15	Yauco	1.2	1.3	40.7	21.6
	16	San Germán	0.6	1.7	18.6	18.5
		San Germán 2	-	0.7	-	-
	17	Mayagüez	0.6	1.5	25.9	13.3
	18	Aguada	1.3	2.0	57.9	34.3
	19	Aguadilla-Pueblo	1.6	1.0	80.7	57.1
	20	Isabela	1.8	2.0	56.4	31.8
	21	Moca	1.6	1.5	63.3	45.9
		Moca 2	-	1.4	-	-
	22	Aguadilla-Base Ramey	1.7	1.8	68.9	45.2
	23	Ponce	0.3	3.0	3.7	-
	24	Guayama	1.1	0.4	83	-
		Guayama 2	-	0.7	-	-
NON-PRASA	25	San German	1.1	1.6	12.7	14.3
	26	Yabucoa	5.3	0.1	43.3	54.1
	27	Villalba	0.8	1.0	23.8	13.7
	28	Guayama	1.0	0.0	< DL	-
	29	Patillas Don Conde	0.7	3.0	44.5	-
	30	Patillas-Tanque 2	1.2	0.0	< DL	-
	31	Patillas-Tanque 1	0.4	0.5	29.2	-
		Patillas-Tanque 1 2	-	1.5	-	-
	32	Patillas-El Real	2.3	1.5	-	-
	33	Patillas-Mulas	2.0	0.0	5.7	-
		Patillas-Mulas 2	-	-	-	-
	33a	Community Tap	-	-	-	-
	33b	Raw Water Intake	-	-	-	-
	33c	River Source Water	-	-	-	-
SPRING	34	Maricao/Sabana	0.4	-	-	-
	35	Utuado	0.6	-	-	-
	36	Manatí	0.3	-	-	-
	37	Caguas	0.1	-	-	-
	38	Adjuntas	0.4	-	-	-
	39	Mayagüez-Quemado	0.2	-	-	-
	40	Mayagüez-Río Cañas	0.2	-	-	-

4.1.2 Observed Water Lead Levels

The results from SC 1 and SC 2 indicated that elevated lead levels were a potential concern (and are still a concern moving forward with this project). Table 8 shows that detectable levels of lead were measured in 75% (38 of 51) of samples from SC 1 and SC 2, including spring sources. No lead was detected in samples collected from spring sources (Sites 34-40) or raw water samples (Sites 33b, 33c). To further investigate the occurrence and trends in water lead levels, only a subset of the original sample set is included in statistical analyses. Since the primary source of lead in drinking water is distribution system and premise plumbing materials, only samples collected from distribution systems are included, which means all spring sources and Sites 33b and 33c are excluded.

Table 8. Sampling Campaign 1 & Sampling Campaign 2: Lead, copper, and phosphate results. The results from Sampling Campaign 2 are indented and shaded in grey.

System Type	***Site #***	***Community***	***Cd*** ***(µg/L)***	***Pb*** ***(µg/L)***	***Cu*** ***(µg/L)***	***PO_4^{2-}*** ***(mg/L)***
PRASA	1	Sabana Grande	0.099	35.6	401	<MDL
		Sabana Grande 2	0.034	13.3	139	-
	2	Lajas	0.436	33.0	268	<MDL
		Lajas 2	0.020	13.5	202	-
	3	Hormigueros	<MDL	0.59	70.8	<MDL
	4	Arecibo	<MDL	16.3	669	<MDL
	5	Utuado	<MDL	0.13	21.2	<MDL
	6	Vega Alta	<MDL	2.4	198	<MDL
	7	Humacao	<MDL	4.7	565	<MDL
	8	Gurabo	<MDL	4.3	89.9	<MDL
	9	Trujillo Alto	<MDL	3.1	652	<MDL
	10	San Juan	0.008	24.0	396	<MDL
		San Juan 2	<MDL	8.6	161	-
	11	Adjuntas	0.038	2.2	20.5	<MDL
	12	Coamo	<MDL	6.1	216	<MDL
	13	Santa Isabel	0.015	2.8	99.7	<MDL
	14	Juana Díaz	0.021	8.7	228	<MDL
	15	Yauco	<MDL	3.0	2.77	<MDL
	16	San Germán	<MDL	14.2	772	0.98
		San Germán 2	<MDL	18.7	1119	-
	17	Mayagüez	<MDL	2.9	86.5	<MDL
	18	Aguada	<MDL	0.15	43.5	<MDL
	19	Aguadilla-Pueblo	<MDL	2.4	316	<MDL
	20	Isabela	<MDL	5.8	147	<MDL
	21	Moca	<MDL	62.0	718	<MDL
		Moca 2	0.514	19.8	913	-
	22	Aguadilla-Base Ramey	<MDL	2.4	94.7	<MDL
	23	Ponce	0.088	8.0	865	<MDL
	24	Guayama	0.507	37.4	299	<MDL
		Guayama 2	0.717	23.4	688	-
NON-PRASA	25	San German	<MDL	0.63	20.3	0.65
	26	Yabucoa	<MDL	2.8	46.9	<MDL
	27	Villalba	0.141	1.2	72.0	<MDL
	28	Guayama	<MDL	1.1	29.5	<MDL
	29	Patillas-Don Conde	0.078	2.1	100	<MDL
	30	Patillas-Tanque 2	<MDL	3.0	81.5	<MDL
	31	Patillas-Tanque 1	0.049	12.2	155	<MDL
		Patillas-Tanque 1 2	<MDL	3.2	63.3	-
	32	Patillas-El Real	0.030	5.7	217	<MDL
	33	Patillas-Mulas	<MDL	615	87.4	<MDL
		Mulas 2	<MDL	170	164	-
	33a	Community Tap	0.065	11.3	84.9	-
	33b	Raw Water Intake	<MDL	<MDL	2.67	-
	33c	River Source Water	<MDL	<MDL	1.28	-
SPRING	34	Maricao/Sabana	<MDL	0.03	0.64	1.3
	35	Utuado	<MDL	<MDL	0.12	<MDL
	36	Manatí	<MDL	<MDL	0.42	<MDL
	37	Caguas	<MDL	<MDL	0.57	<MDL
	38	Adjuntas	<MDL	<MDL	0.55	<MDL
	39	Mayagüez-Quemado	<MDL	<MDL	0.24	<MDL
	40	Mayagüez-Río Cañas	<MDL	<MDL	0.25	<MDL

In samples collected from distribution samples (PRASA and non-PRASA systems) for SC 1 and SC 2 combined, lead concentrations ranged from non-detect (< 1 µg/L) to 615 µg/L, with an average value of 29 µg/L, as shown in Table 9. Overall, non-PRASA systems exhibited higher lead concentrations, with an average of 69 µg/L between both sampling campaigns. Samples from PRASA systems had an average concentration of 13 µg/L. However, when doing a 2-sample t-test with unequal variance, there was not a statistically significant difference in the average lead concentration between non-PRASA and PRASA systems ($p_{one\text{-}tail} = 0.149$, $p_{two\text{-}tail} = 0.298$). The maximum observed concentration in PRASA systems was 62 µg/L (Site 21 Moca), and in non-PRASA systems was 615 µg/L (Site 33 Patillas-Mulas) (Table 8 and Table 9).

Table 9. Sampling Campaign 1 & Sampling Campaign 2: Descriptive statistics of lead concentrations in µg/L organized by sampling campaign and system type. Spring systems excluded.

Parameter	***SC 1***			***SC 2[1]***			***SC 1 & 2[1]***		
System Type	PRASA	non-PRASA	All	PRASA	non-PRASA	All	PRASA	non-PRASA	All
# of Samples	n = 24	n = 9	n = 33	n = 6	n = 3	n = 9	n = 30	n = 12	n = 42
# of CWS[2]	n = 24	n = 9	n = 33	n = 6	n = 2	n = 8	n = 24	n = 9	n = 33
Above PQL[3]	88%	89%	88%	100%	100%	100%	90%	92%	90%
Pb (µg/L)									
Average	11.8	71.5	28.1	16.2	61.3	31.3	12.7	69.0	28.8
Median	4.5	2.8	3.1	16.1	11.3	13.5	7.1	3.1	5.8
Maximum	62.0	615	615	23.4	169	169	62.0	615	615
Minimum	< 1	< 1	< 1	8.6	< 1	< 1	< 1	< 1	< 1
90th Percentile	34.8	133	35.1	21.6	139	52.6	33.3	153.8	35.3

[1] The two new locations in the Patillas-Mulas system from raw water sources (Site 33b and Site 33c) are excluded in these statistics [3] Project Practical Quantification Limit (PQL)=1 µg/L

To assess the overall distribution of lead concentrations, Figure 3 plots the rank order percentile for samples collected from distribution systems in SC 1 and SC 2. As previously mentioned, the locations for SC 1 were randomly selected with no adherence to the U.S. EPA LCR tiering system, and the nine (9) samples for SC 2 were re-sampled sites that had elevated WLLs above the U.S. EPA LCR AL in SC 1. Sample volumes were 125 mL for both SC 1 and SC 2. For both sampling campaigns, the combined the 90th percentile concentration was 35 µg/L. While this comparison to the AL is out of context, since the sampling protocol did not adhere to the U.S. EPA LCR requirements, it still raises a concern, since the concentration is more than twice the U.S. EPA AL of 15 µg/L.

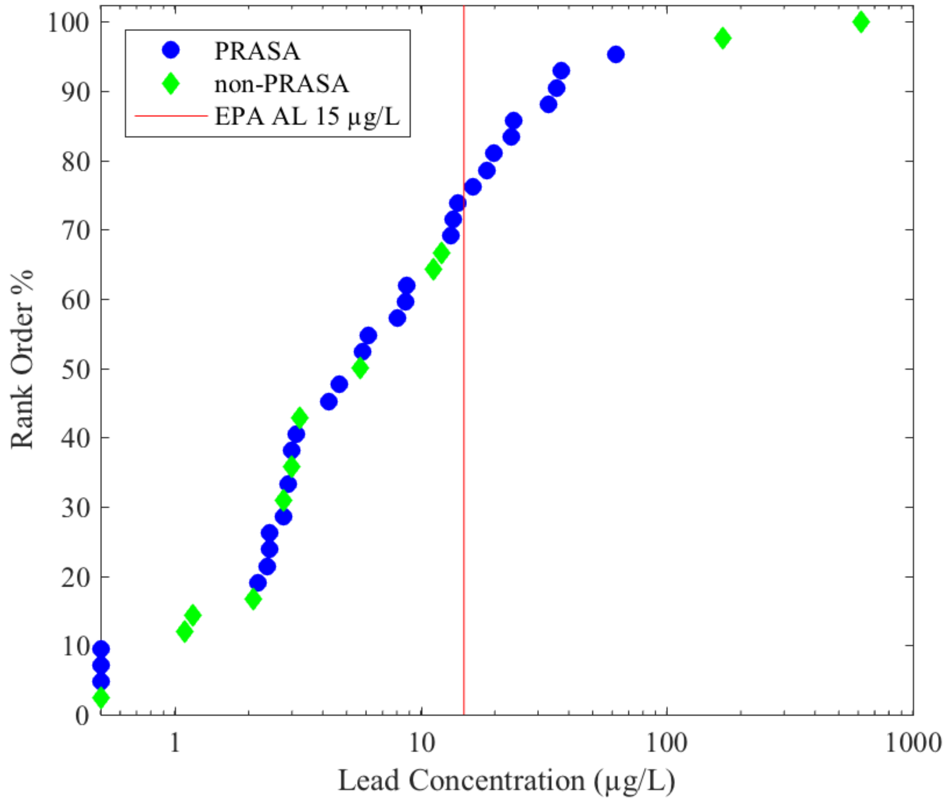


Figure 3. Rank order versus lead concentration of all samples across all locations for PRASA and non-PRASA systems from Sampling Campaign 1 & Sampling Campaign 2. This graph includes data points for the new sampling location in the Patillas-Mulas system, Site 33a, but excludes Sites 33b and 33c.

When implementing corrosion control, phosphate base inhibitors are commonly used. Phosphate (PO_4^{3-}) levels in drinking water distribution systems can be used as an indicator of implemented corrosion control treatment. Its presence can also indicate other non-point pollution sources if observed in source waters, such as agricultural runoff, atmospheric deposition, stream bank erosion, stormwater runoff, wastewaters, and fertilizers [106].

Orthophosphate-P (in mg/L as PO_4^{3-}) was only measured in samples from SC 1, as shown in Table 8. Out of the 33 samples from PRASA and non-PRASA systems, only two (2) were above the project PQL of 0.06 mg/L as PO_4^{3-} with high concentrations of 0.65 mg/L as PO_4^{3-} (Site 25) and 0.98 mg/L as PO_4^{3-} (Site 16). This non-observance of residual phosphate in a majority of the systems suggest no use of phosphate-based corrosion inhibitors. When specifically using orthophosphate as a corrosion inhibitor, typical residual phosphate concentrations should be between 1.0 to 3.0 mg/L as PO_4^{3-} at the tap for a pH range of 7.2 to 7.8, however this treatment can be effective as high as pH 9 [98]. For the two, distribution system derived samples, it is possible that the treatment plants for these systems were adding phosphate-based corrosion inhibitors since both concentrations were close to the 1.0 mg/L as PO_4^{3-} minimum targeted residual concentration. However, due to the lack of treatment process information for these systems, use could not be confirmed.

Furthermore, phosphorus is an essential nutrient for all biological activity, but at excess levels can disrupt aquatic ecosystems by promoting excess algal growth [107]–[110]. Reference levels for total phosphorus in source waters have been reported in the range of 0.03 to 0.2 mg/L as PO_4^{3-} [108]. One spring source had a concentration of 1.3 mg/L as PO_4^{3-} (Site 34), which is high for a source water [108], [110].

Lead Spatial Distribution Across Puerto Rico. The distribution of lead above the AL was evaluated for spatial trends corresponding to specific watersheds. Figure 4 depicts this distribution. Puerto Rico is of USGS Caribbean HUC-2 Region 21 and HUC-4 subregion 2101. It has five (5) HUC-8 cataloging unit regions on the mainland including 21010001 Interior Puerto Rico, 21010002 Cibuco-Guajataca, 21010003 Culebrina-Guanajibo, 21010004 Southern Puerto Rico, and 21010005 Eastern Puerto Rico. Four (4) out of the five (5) main watersheds each had an elevated lead concentration at a sampling site, and no patterns could be identified. Therefore, the occurrence of lead does not appear to be associated with any specific watershed.

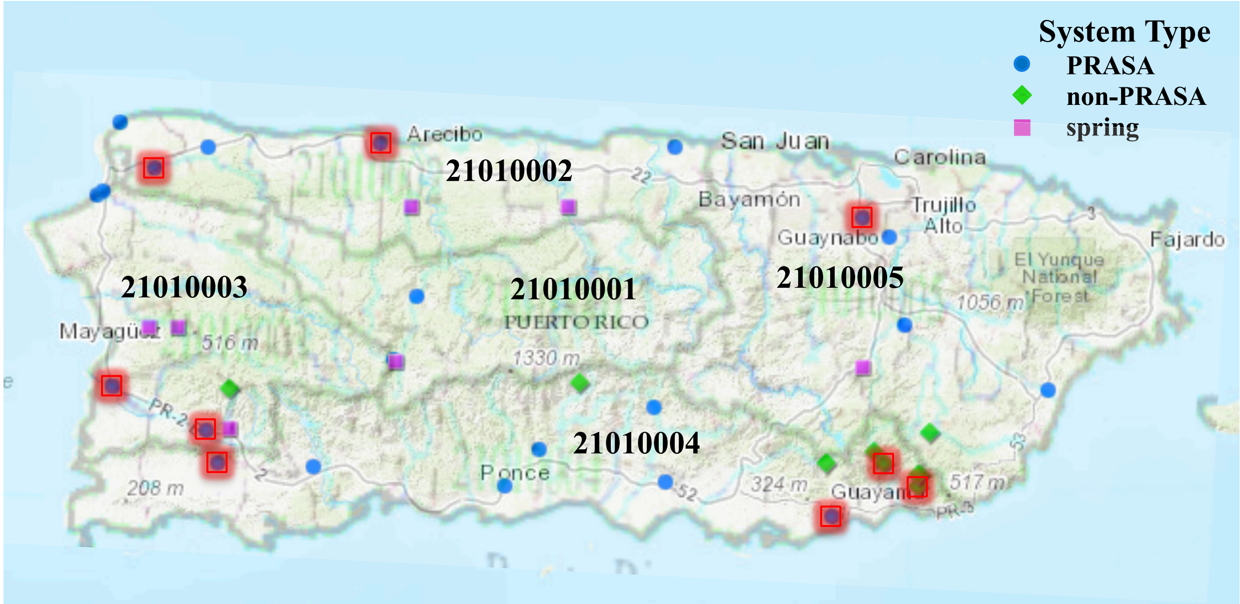
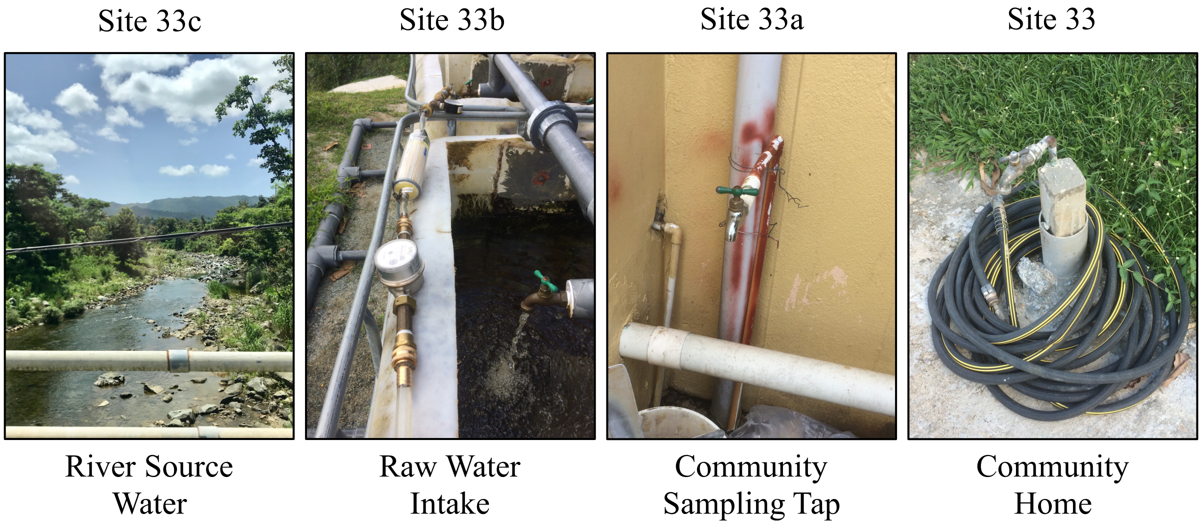


Figure 4. Sampling Campaign 1 & Sampling Campaign 2: High WLLs and their distribution relative to Puerto Rico. The red highlighted sites are the ones that exhibited high WLLs, close to or above 15 µg/L. The five (5) major watershed basins across the island are delineated by a dark green line with the 8-digit hydrologic unit code.

Tracing Lead Through A Distribution System. During SC 2, three (3) other samples were collected at different locations in the Mulas community of Patillas (Sites 33a, 33b, and 33c). While it is known that lead primarily comes from plumbing materials [16]–[18], [25], additional samples were collected profiling from source water to point-of-use taps to rule out the possibility of lead in the source water. The first sampling location was from the river (Site 33c) serving as the source water for the community system. The second sampling location was from the raw water intake to the roughing filter (Site 33b) of the treatment system. The third sampling location (Site 33a) was at a point-of-use community sampling tap. The river water (Site 33c) and raw water (Site 33b) samples were both below the lead detection level and the community sampling tap had a WLL of 11.3 μg/L, supporting that lead was indeed coming from the distribution system in that community. This community had the highest WLL of 615 μg/L in SC 1, and the WLL was 169 μg/L from the same tap in SC 2. Anecdotal information from a homeowner in SC3 suggests that that the home hose bib tap for Site 33 was installed with lead solder.


Site 33c River Source Water

Site 33b Raw Water Intake

Site 33a Community Sampling Tap

Site 33 Community Home

Figure 5. Sampling Campaign 2: Sampling locations for Site 33, Site 33a, Site 33b, and Site 33c.

4.1.3 Relationship of Water Quality and Lead

Corrosion research, specifically for lead, has focused on understanding the water quality conditions that affect lead release and the factors that contribute to elevated WLLs. To relate WLLs to other water quality characteristics, Kruskal-Wallis nonparametric comparison tests were used to determine if there are significant differences in water quality observations for samples with and without observed lead. Specifically, the Kruskal-Wallis test will inform at a 95% confidence level whether the median or mean ranks of each categorical bin are from different populations. The null hypothesis states that the observed median or mean ranks are from the same population and the alternative hypothesis states that they are, in fact, different. For this study, the data were divided into categorical bins based on the U.S. EPA AL (15 μg/L) (only applies to pH), the recommended drinking water level threshold by WHO (10 μg/L). Box plots are also provided for a third cutoff concentration of 1 μg/L, which is the project PQL for lead, but since the number of samples in each bin were very unequal, Kruskal-Wallis tests were not performed for these data and thus no p-value is reported. The plots are used to evaluate trends and observances. Again, only samples from PRASA or non-PRASA distribution systems are analyzed, which means that all spring sources and Sites 33b and 33c are excluded from the Kruskal-Wallis analysis.

Hypothesis testing is prone to two types of error: Type I (false positives) and Type II (false negatives). More important to this study is the probability of Type II error occurrence, where there are indeed statistically significant differences in water quality between categorical lead bins, however the test fails to recognize that those differences are there. For the Kruskal-Wallis test itself, the Type II error rate depends on the number of samples collected. Furthermore, in this study, the initial study design is prone to Type II error. To have observed lead release at the tap there needs to be the intersection of three things: a lead-bearing plumbing material, a mechanism for lead release, and a sampling approach that captures lead. The Type II error that exists for this study stems from either the nonexistence of a lead-bearing plumbing material at a sampling site or a sampling approach was used that did not capture lead release. For example, a water quality characteristic of a specific system could be corrosive, however, if a sampling site from that system was chosen that did not contain lead plumbing, then the sample would be binned with other low-lead samples from non-corrosive environments. In addition, there could be a LSL upstream of the sampling tap, but the sampling approach volume did not capture water that was sitting stagnant in that LSL, and thus missed lead release.

pH

The pH is one of the most important variables for corrosion evaluations. At acidic pH values the solubility of many metals increase, leading to increased dissolution and dissociation of complexes [16]–[18]. It is also important for determining speciation and characteristics of other elemental components in water important for corrosion [16]–[18], [25]. A 1993 AWWA survey showed that 50% of water systems with a pH lower than 7.0 units had U.S. EPA LCR AL exceedances with the percentage decreasing consistently as pH increased [18].

As presented in Section 4.1.1, the pH values ranged from 6.5 to 8.1 across sampling locations for SC 1 and SC 2 combined, with an average of 7.2. For the sites that were resampled in Sampling Campaign 2, the pH of the second sample was 0.1 to 0.6 units lower than the first sample. Based on the Kruskal-Wallis test, there was no statistically significant difference (p = 0.191) in pH values between samples with high WLLs (> 10 μg/L) and samples with low WLLs (< 10 μg/L) (Figure 6b).

However, while the population medians are similar, the range of pH values between sample subsets were notably different if binned high and low WLLs with a cutoff concentration of 15 μg/L or when binned into detect and non-detect WLLs with a cutoff concentration of 1 μg/L. For samples with lead levels less than 15 μg/L, pH ranged from 6.6 to 8.1, whereas pH only ranged from 6.9 to 7.4 for samples with lead levels greater than 15 μg/L (Figure 6a). On the contrary, for samples that had detectable WLLs pH values had a much wider range, whereas for samples with non-detect lead levels, or less than 1 μg/L, the pH range was notably smaller (Figure 6c).

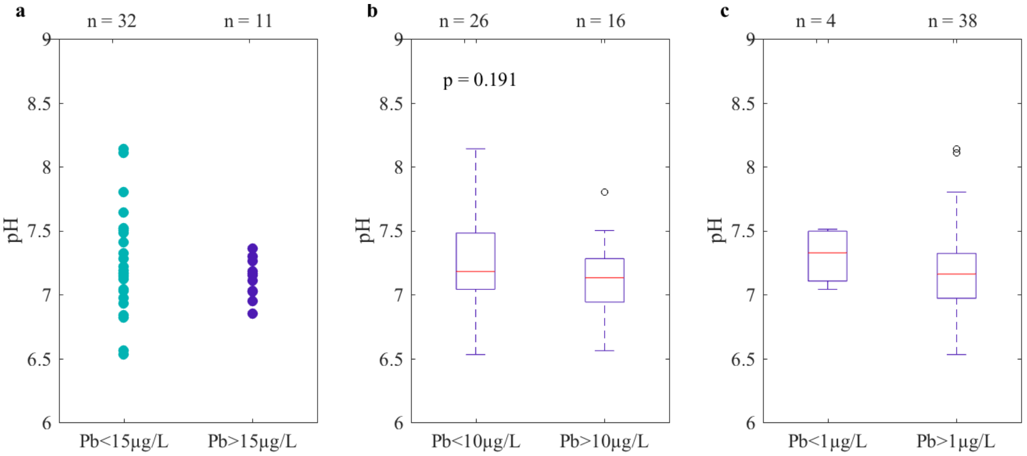


Figure 6. Sampling Campaign 1 & Sampling Campaign 2: pH distributions and comparisons for samples from PRASA and non-PRASA systems. (a) Binning cutoff concentration of 15 µg/L. (b) Binning cutoff concentrations of 10 µg/L. The p-value for the Kruskal-Wallis test is reported. (c) Binning cutoff concentration of 1 µg/L.

Since each sample is from a different system in Puerto Rico, it is difficult to draw conclusions about trends of lead release with varying pH when comparing each sample against each other. This apparent lack of relationship with pH appears to conflict with fundamental relationships between pH and lead release, but it may also be an artifact of the sampling design limitations. Sampling sites were selected randomly without any prior knowledge of construction materials. All water samples with pH less than 7 may be extremely corrosive. If the sampling location did not have lead-bearing plumbing materials or a sampling approach that captured lead, then measuring lead concentrations would be a poor indicator of corrosivity resulting in Type II error.

Alkalinity

Alkalinity is an important factor for corrosion science, because the carbonate complexes that contribute to alkalinity also form common metal-carbonate passivation layers. In addition, waters with higher alkalinities also have a higher buffering capacity and stronger ability to resist changes in pH, which ultimately lowers general corrosion potential [17]. There was also no statistically significant difference (p = 0.872) in SC 1 alkalinity values between samples with high WLLs (>10 µg/L) and samples with low WLLs (<10 µg/L) (Figure 7a).

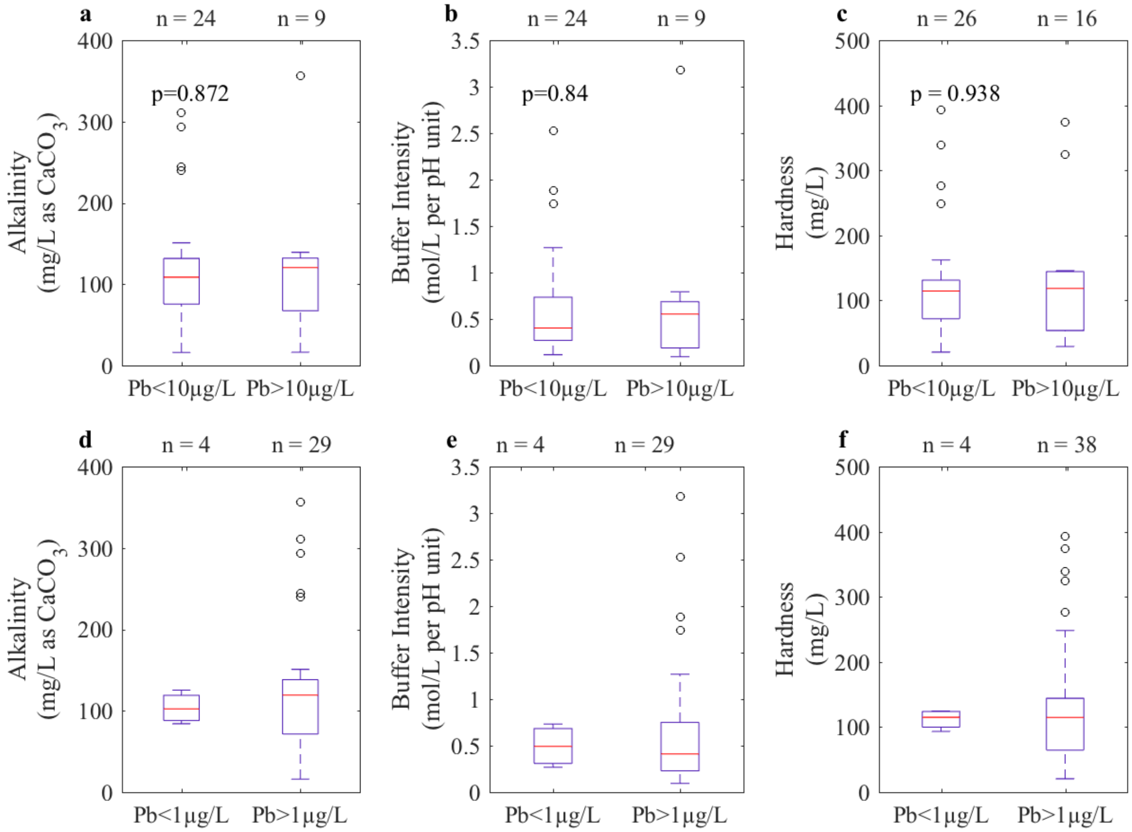


Figure 7. Sampling Campaign 1 & Sampling Campaign 2: Alkalinity (SC 1 only), buffer intensity (SC 1 only), and hardness (SC 1 and SC 2) distributions and comparisons for samples from PRASA and non-PRASA systems. (a-c) Binning cutoff concentration of 10 µg/L. The p-value for the Kruskal-Wallis test is reported. (d-f) Binning cutoff concentration of 1 µg/L.

In the same survey of water utilities by AWWA in 1993 that looked at pH and lead release trends, 23.8% of water systems with corrosion inhibitors and 15.6% of water systems without corrosion inhibitors and with alkalinity <50 mg/L as $CaCO_3$ were found to have WLLs above the U.S. EPA LCR AL. This percentage increased to 40% and 45%, respectively, when the alkalinity dropped below 25 mg/L as $CaCO_3$ [18]. When alkalinity was greater than 150 mg/L as $CaCO_3$ there were no U.S. EPA LCR AL exceedances.

Few samples (n=2) from SC 1 had alkalinities less than 25 mg/L as $CaCO_3$, but 10 samples had an alkalinity greater than or equal to 150 mg/L as $CaCO_3$. The median alkalinity of samples with WLLs greater than 10 µg/L or greater than 1 µg/L was higher than the median alkalinity of samples with WLLs in the lower bin. In addition, a sample with alkalinity equal to 356 mg/L as $CaCO_3$ had a WLL greater than 30 µg/L. These results suggest that either differences in alkalinity is not a common factor for lead release between systems, or the analysis is impacted again by Type II error, where some systems with low alkalinities are susceptible to lead release, but the sampling location perhaps did not have lead-bearing materials or a sampling approach that captured lead.

Buffer Intensity

Buffer intensity also showed no statistically significant difference ($p = 0.840$) in SC 1 values between samples with high WLLs (>10 µg/L) and samples with low WLLs (<10 µg/L) (Figure 7b). For samples with WLLs greater than 10 µg/L, the median buffer intensity was higher than samples with WLLs less than 10 µg/L. All else equal, waters with lower buffer intensity are more susceptible to corrosion [98]. The lack of relationship indicates that either buffer intensity is not an important factor for lead release or that the sampling design has a high Type II error rate due to sampling sites without lead bearing materials or a sampling approach that captured lead release.

Hardness

Hardness cannot be used as a standalone indicator of corrosion potential, but is an important parameter to consider when implementing corrosion control treatment as the levels of calcium and magnesium in the water can affect the formation of passivation layers [17]. Hardness had no statistically significant difference ($p = 0.938$) in SC 1 and SC 2 values between samples with high WLLs (>10 µg/L) and samples with low WLLs (< 10 µg/L) (Figure 7c).

Free Chlorine

Free chlorine ranged from non-detect to a max of 3 mg/L for all PRASA and non-PRASA system from SC 1 and SC 2 (excluding Sites 33b and 33c since they were raw water sources and therefore free chlorine was not measured). As discussed in Chapter 2, disinfectant residual affects the ORP of the water as well as the overall water biostability, which is the condition of the water to support microbial growth. Higher ORP favors the formation of PbO_2, which is a rather insoluble scale and can greatly inhibit lead release if maintained [28]. While the exact role that microbes contribute to corrosion is uncertain, it has been inferred that the factors influencing microbial induced corrosion (MIC) are biofilm formation and distribution along the inner surfaces of pipes and the role microbes play as a catalyst in REDOX reactions [18].

There was no statistically significant difference ($p = 0.161$) in free chlorine concentrations between samples with high WLLs (>10 µg/L) and samples with low WLLs (<10 µg/L) (Figure 8a) at a 95% confidence level. When looking at median concentrations for both lead cutoff bins, the concentration was substantially lower in samples from the higher lead bin (>10 µg/L and >1 µg/L). For example, the median free chlorine concentration for samples with WLLs greater than 10 µg/L is 0.8 mg/L as Cl_2, whereas the median for samples with WLLs less than 10 µg/L is 1.5 mg/L. When samples are binned based on detect or non-detect WLLs, the free chlorine 25th percentile for samples in the detectable lead category is much lower (0.6 mg/L as Cl_2) compared to samples without detectable lead (1.7 mg/L as Cl_2). While the Kruskal-Wallis test did not identify a statistical difference in free chlorine at a 95% confidence level, the central tendency and distribution of data suggest there may be a meaningful relationship that warrants further investigation. Similar to other relationships, the lack of a significant relationship may be due to Type II error.

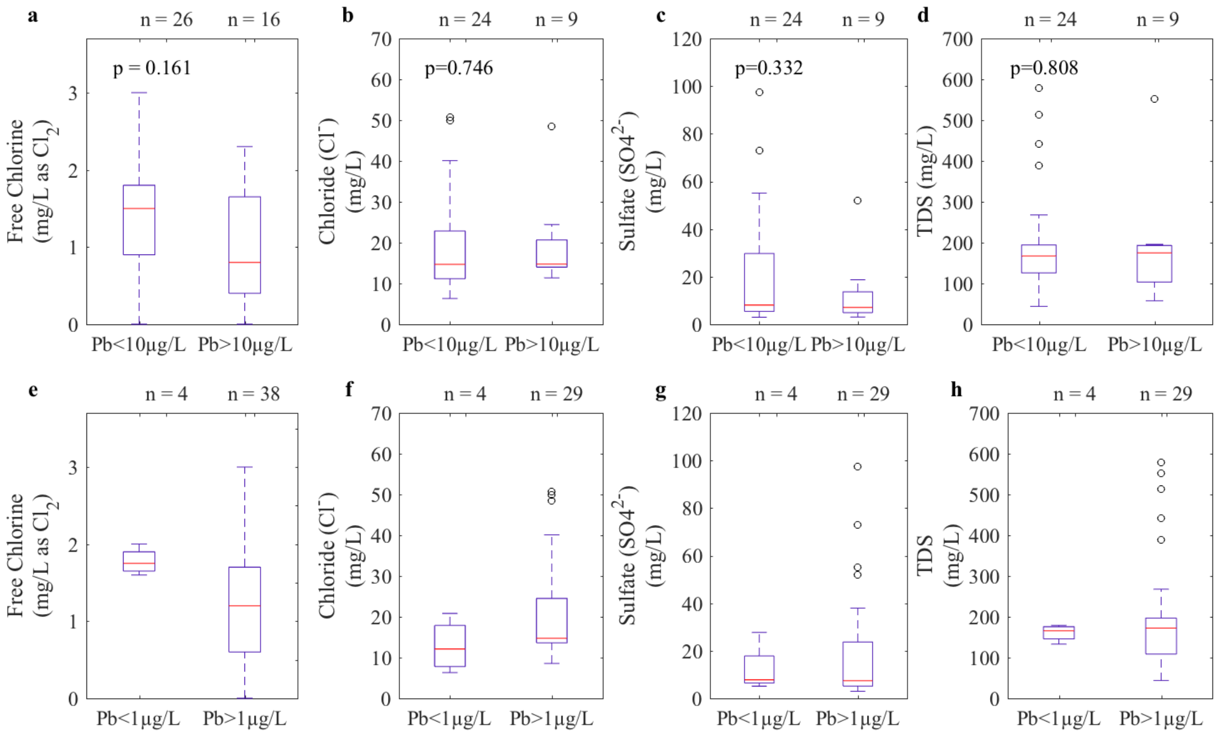


Figure 8. Sampling Campaign 1 & Sampling Campaign 2: Free chlorine (SC 1 & SC 2), chloride (SC 1 only), sulfate (SC 1 only), and total dissolved solids (SC 1 only) distributions and comparisons for samples from PRASA and non-PRASA systems. (a-d) Binning cutoff concentration of 10 μg/L. The p-value for the Kruskal-Wallis test is reported. (e-h) Binning cutoff concentration of 1 μg/L.

Chloride and Sulfate

Chloride and sulfate are two ions that are known to impact corrosion rates in water distribution systems. As discussed in Chapter 3, chloride has the capacity to increase corrosion by creating soluble lead-chloride complexes and sulfate has the capacity to reduce corrosion by forming insoluble lead-sulfate complexes. The ratio of chloride to sulfate has also been identified as an important metric and is discussed in future sections. Individually, neither chloride or sulfate concentrations exhibited statistically significant differences (p_{Cl} = 0.746, p_{SO4} = 0.332) in concentrations between samples with high WLLs (>10 μg/L) and samples with low WLLs (<10 μg/L) (Figure 8b, c). However, in the median concentration of chloride was higher in waters with detectable lead concentrations (> 1 μg/L), indicating that while not statistically significant in this sample set, the observance is important for future studies. Again, the failure to find statistically significant differences could be attributed to Type II error as an artifact of sampling design.

Total Dissolved Solids

TDS ranged from a minimum value of 43 mg/L to a maximum value of 579 mg/L, with an average value of 199 mg/L across sampling locations for SC 1. Higher ion concentrations result in higher conductivity and increases the ability of the water to conduct a current and further increases corrosion potential unless passivating layers are produced on the pipe surface [17], [23]. Although, higher-level observations observed an increase in corrosion in low TDS water as well through scale dissolution and corrosion of pipe surface [17]. The location with the highest TDS value also had higher concentrations of copper and lead, at 865 µg/L and 8 µg/L, respectively. There was no significant difference ($p = 0.808$) in TDS concentrations between samples with high WLLs (> 10 µg/L) and samples with low WLLs (< 10 µg/L) (Figure 8d). These results show that TDS is not a primary factor to differentiate waters based on observed WLLs, which could be due to either differences in chemistry or experimental design.

Corrosion Indices

Corrosion indices have been proposed for evaluating the potential corrosivity of water, and in some cases, have been shown to correlate with observed lead concentrations. However, caution should always be used when using these indicators as a prediction tool that lead will be present. Table 10 shows the results of each corrosion index evaluated in this study for each sampling site. Since bulk water quality samples were not collected in SC 2, corrosion indices could not be calculated for that sampling campaign. Thus, this analysis is representative of samples from SC 1 only. As stated in Section 3.7, there are guideline values for each index, which are further discussed in this section.

Chloride-to-Sulfate Mass Ratio. Waters with CSMRs above 0.2, 0.5, and further above 0.77 are said to be potentially corrosive, with the most lead release observed from an increase of 0.1 to 1 [41], [44]. In SC 1, 100% of PRASA and non-PRASA sampling sites combined had a CSMR above 0.2, 94% had a CSMR above 0.5, and 76% of samples had a CSMR above 0.77. For the 5% of samples (n = 2 at Site 6 and Site 27) that had a CSMR less than 0.5, the corresponding WLLs were 2.4 µg/L and 1.2 µg/L, consistent with theoretical predictions that a lower CSMR results in lower lead release. The high CSMRs for many of the systems in Puerto Rico indicates the high susceptibility of the systems to galvanic corrosion. If a system exhibits plumbing characteristics conducive to this corrosion mechanism (e.g., lead solder connected to copper pipe), then there presents a higher risk for lead exposure.

Table 10. Sampling Campaign 1 and Sampling Campaign 2: Common corrosion index values. The results from Sampling Campaign 2 are indented and shaded in grey.

System Type	***Site #***	***Community***	***CSMR***	***LSR***	***LSI***	***RI***
PRASA	1	Sabana Grande	4.84	0.17	-0.62	8.6
		Sabana Grande 2	-	-	-	-
	2	Lajas	0.93	0.35	-0.38	7.7
		Lajas 2	-	-	-	-
	3	Hormigueros	1.18	0.23	-0.55	8.6
	4	Arecibo	0.74	0.33	-0.67	8.5
	5	Utuado	0.75	0.70	-0.90	8.8
	6	Vega Alta	0.33	1.38	-1.73	10.3
	7	Humacao	3.84	1.55	-2.47	11.8
	8	Gurabo	1.06	0.58	-1.00	9.2
	9	Trujillo Alto	8.41	0.38	-0.74	8.6
	10	San Juan	2.05	0.45	-0.92	9.0
		San Juan 2	-	-	-	-
	11	Adjuntas	1.86	0.33	-0.95	9.2
	12	Coamo	2.54	0.37	-0.32	8.2
	13	Santa Isabel	0.73	0.37	-0.22	7.6
	14	Juana Díaz	0.83	0.29	-0.07	7.2
	15	Yauco	1.05	0.23	-0.11	7.9
	16	San Germán	2.18	0.17	-1.37	10.2
		San Germán 2	-	-	-	-
	17	Mayagüez	1.15	0.19	-0.55	8.3
	18	Aguada	1.93	0.24	-0.51	8.2
	19	Aguadilla-Pueblo	2.05	0.24	-0.50	8.1
	20	Isabela	1.86	0.20	-0.85	8.7
	21	Moca	1.92	0.23	-0.52	8.3
		Moca 2	-	-	-	-
	22	Aguadilla-Base Ramey	1.87	0.29	-0.49	8.3
	23	Ponce	0.51	0.59	-0.19	7.4
	24	Guayama	2.75	0.76	-1.31	9.9
		Guayama 2	-	-	-	-
NON-PRASA	25	San German	1.25	0.13	-1.73	10.9
	26	Yabucoa	3.0	0.71	-1.73	10.6
	27	Villalba	0.41	0.29	0.50	7.1
	28	Guayama	0.73	0.53	0.28	7.5
	29	Patillas-Don Conde	0.70	0.63	-0.18	7.6
	30	Patillas-Tanque 2	4.62	0.44	-0.81	9.0
	31	Patillas-Tanque 1	4.05	0.34	-0.56	8.9
		Patillas-Tanque 1 2	-	-	-	-
	32	Patillas-El Real	4.34	0.85	-1.68	10.6
	33	Patillas-Mulas	2.87	2.01	-2.02	11.2
		Patillas-Mulas 2	-	-	-	-
	33a	Community Tap	-	-	-	-
	33b	Raw Water Intake	-	-	-	-
	33c	River Source Water	-	-	-	-
SPRING	34	Maricao/Sabana	1.37	0.10	-1.06	9.6
	35	Utuado	1.30	0.12	-0.25	7.6
	36	Manati	1.50	0.18	-0.12	7.0
	37	Caguas	2.81	0.25	-1.47	9.6
	38	Adjuntas	0.94	0.07	-0.58	8.2
	39	Mayagüez-Quemado	1.88	0.11	-0.89	8.6
	40	Mayagüez-Río Cañas	5.45	0.24	-0.69	8.5

Overall across all sampling sites, there were no statistically significant difference ($p = 0.106$) at a 95% confidence level in CSMR values between samples with high WLLs (>10 µg/L) and samples with low WLLs (< 10 µg/L) (Figure 9a). However, at a 90% confidence level, there could be a statistically significant difference based on the p-value. This non-observance of statistically significant differences but the high percentage of CSMRs greater than the critical threshold indicates that Type II error potentially exists of not choosing a sampling location with lead-bearing plumbing materials or using a sampling method that did not capture all lead release locations in a water system, especially since only one house was sampled per system and the volume of water collected was 125 mL.

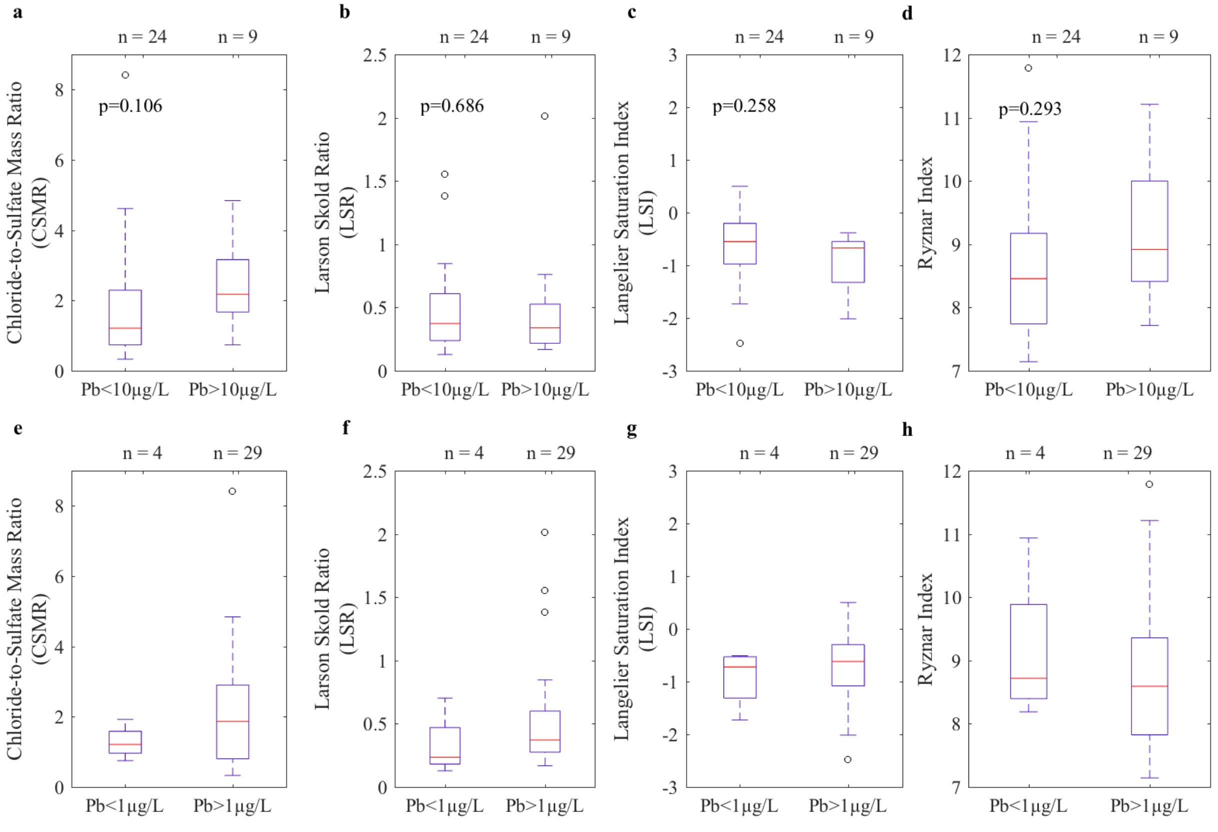


Figure 9. Sampling Campaign 1: The Chloride-to-Sulfate Mass Ratio, Larson-Skold Ratio, Langelier Saturation Index, and Ryznar Index distributions and comparisons for samples from PRASA and non-PRASA systems. (a-d) Binning cutoff concentration of 10 µg/L. The p-value for the Kruskal-Wallis test is reported. (e-h) Binning cutoff concentration of 1 µg/L.

However, while not statistically significant, the median CSMR values are higher in both categorical lead bins. For high WLLs that were greater than 10 μg/L, the median CSMR value is 2.2 in comparison to 1.2 for the low WLLs, and for detectable WLLs greater than 1 μg/L, the median CSMR value was 1.9 μg/L in comparison to 1.2 for non-detect WLL. There is a 1.0-unit difference in median CSMR values for high and low WLLs and a 0.8-unit difference in CSMR values for detect and non-detect WLLs. All of these values are above the critical threshold of 0.77, and the difference between them is the same magnitude that produced the highest observed lead release in some studies [44]. However, it is important to note that in some cases of the same studies, increasing the CSMR above the threshold of 1.0 had little *additional* adverse effects, but severe corrosion problems still generally occurred [44].

Larson-Skold Ratio. The LSR varied across sampling sites for SC 1, ranging from a minimum value of 0.1 to a maximum value of 2.0, with an average value of 0.5 and a median value of 0.4. Waters with a Larson-Skold Ratio (LSR) above 0.2 to 0.3 are said to be corrosive towards cast iron and steel [16], but other research suggests the threshold for corrosivity is higher, around ratios of 0.8 to 1.2 [95]. In SC 1, 85% of sampling sites were above an LSR of 0.2, with 61% above 0.3, and 12% above 0.8. There was no statistically significant difference ($p = 0.686$) in LSR values between samples with high WLLs (>10 μg/L) and samples with low WLLs (<10 μg/L) (Figure 9b). The median LSR for detected lead compared to non-detected lead was greater at 0.4 compared to 0.2. For the sampling sites that had an LSR ratio of above 0.8, there were also detectable levels of iron. However, the iron levels from these sampling sites were not on the high end of the range of observed iron concentrations in this study. The average iron concentration for these samples was 318 μg/L, when across sampling sites for SC 1 the maximum observed iron concentration was 3847 μg/L with an average iron concentration of 940 μg/L. The lack of relationship between the

LSR and lead and iron concentrations does not mean that the parameter is not important as there is a high risk for Type II error.

Langelier Saturation Index and Ryznar Index. The LSI and RI indices were evaluated to determine if the potential exists for calcium carbonate precipitation. LSI ranged from a high positive value of 0.5 to a low negative value of -2.5 with an average of -0.78. Only two sampling sites had a positive LSI value (Sites 26 and Site 27). The RI was also high for many systems, with a range of 7.1 to 11.8 with an average of value of 8.8. There was no statistically significant difference ($p_{LSI} = 0.258$, $p_{RI} = 0.293$) in LSI or RI values between samples with high WLLs (>10 μg/L) and samples with low WLLs (<10 μg/L) (Figure 9c, d). However, the median value of the RI (8.9) for the high WLL bin (> 10 μg/L) was higher than the median value of the RI (8.5) for the low WLL bin (< 10 μg/L).

Historically, it was recommended that LSI value should be positive, indicating that the water is supersaturated with respect to $CaCO_3$ and a scale layer will form. Supersaturation according to the RI, which is closely related to the LSI, occurs at values less than six (6) [99], [100]. It has been demonstrated, however, that $CaCO_3$ scale layers are not protective against lead corrosion [17], [18]. Notwithstanding, only 5% of systems had an LSI > 0 and 100% of systems had an RI > 6, indicating that many Puerto Rican systems were undersaturated with respect to calcium carbonate.

The absence of relationships between corrosion indices and lead demonstrates not only the limitations in the corrosion indices but also limitations in the experimental design. In previous work, these guidelines values have been shown to be inconclusive for predicting lead release. A study by Cantor (2017) showed that across eight (8) different water systems the CSMR, LSR, and the LSI were not found to correlate with observed lead release from a Process Research Solutions

(PSR) distribution system monitoring station. The distribution system monitoring stations have a lead source such that lead can be released if the water has corrosive characteristics against lead. In this study, there was no prior knowledge to guarantee that every sampling site had a lead source.

CSMR specifically applies to scenarios where there is a galvanic connection between lead (e.g., pipe or solder) and copper (e.g., pipe or fixture). LSR was developed to predict corrosion towards cast iron pipes, and while this ratio is not explicit for corrosion of lead plumbing, indirect forms of lead release can occur from iron if lead sorbs onto iron particulates or scales [19], [20]. When the CSMR or LSR suggest corrosive waters but no lead levels greater than 10 μg/L are observed (17 of 24 samples for CSMR threshold of 0.77), it can indicate that either 1) the corrosion mechanism supposedly captured by the index is not relevant or 2) the sampling site did not contain lead plumbing. In contrast, when the CSMR or LSR suggest non-corrosive waters but lead levels greater than 10 μg/L are observed (1 of 9 samples for a CSMR threshold of 0.77), then the corrosion index is not representative of the actual corrosion mechanism. Based on the CSMR and LSR, the results from this study show that many Puerto Rican distribution systems have aggressive water quality conditions. While there are known limitations of using these indices individually and as proxy for predicting lead release, they have greater evaluating power when combined together to provide motivation for future studies.

Turbidity

Only two of the samples that exhibited a turbidity of greater than 1 NTU had corresponding higher WLLs with observances of 5.7 μg/L and 615 μg/L. The site that had a turbidity of 3.1 NTU had a WLL of 5.7 μg/L and the site that had a turbidity of 10.6 NTU had a WLL of 615 μg/L. The higher turbidities observed with a higher WLLs could indicate particulate forms of lead release since turbidity is a proxy for the number of particles in the water, and thus lead-bearing particles could be present if there were mechanisms for particulate lead release. However, there was no statistically significant difference (p = 0.419) when comparing turbidity concentrations between samples with high WLLS (> 10 µg/L) and samples with low WLLs (< 10 µg/L) (Figure 10a).

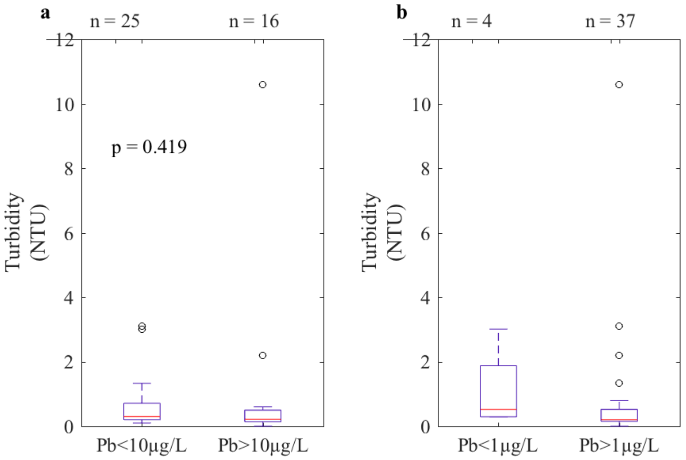


Figure 10. Sampling Campaign 1 & Sampling Campaign 2: Turbidity distributions and comparisons for samples from PRASA and non-PRASA systems. (a) Binning cutoff concentration of 10 µg/L. The p-value for the Kruskal-Wallis test is reported. (b) Binning cutoff concentration of 1 µg/L.

Trace Metal Constituents

Trends between WLLs and other trace elements were evaluated to identify if the presence of lead was also associated with other trace metals found in plumbing materials. Each statistic test investigated whether elevated levels of lead were accompanied by elevated levels of other metals. Relationships between metals other than lead were not explored. Moving forward, aluminum and iron concentrations both exceeded secondary MCLs in many systems at point-of-use locations. Eight (8) samples exceeded 50 µg/L of aluminum and 39 samples exceeded 300 µg/L of iron. One sampling site exceeded the MCL of antimony with a concentration of 36 and 53 µg/L in SC 1 and SC 2, respectively. No other exceedances of primary or secondary maximum contaminant levels were measured.

Table 11. Sampling Campaign 1 & Sampling Campaign 2: Trace metal results for aluminum, cadmium, copper, iron, nickel, antimony, tin, and zinc. The results from Sampling Campaign 2 are indented and shaded in grey.

System Type	***Site #***	***Community***	***Al (μg/L)***	***Cd (μg/L)***	***Cu (μg/L)***	***Fe (μg/L)***	***Ni (μg/L)***	***Sb (μg/L)***	***Sn (μg/L)***	***Zn (μg/L)***
PRASA	1	Sabana Grande	79.2	0.099	401	714	24.6	<MDL	2.97	528
		Sabana Grande 2	67.2	0.034	139	928	13.4	<MDL	<MDL	202
	2	Lajas	6.59	0.436	268	2275	56.3	0.95	<MDL	1642
		Lajas 2	3.87	0.020	202	2690	43.7	<MDL	<MDL	138
	3	Hormigueros	6.02	<MDL	70.2	599	9.71	<MDL	<MDL	3.84
	4	Arecibo	13.6	<MDL	669	1261	27.1	1.94	<MDL	67.1
	5	Utuado	51.9	<MDL	21.2	680	13.4	<MDL	<MDL	11.0
	6	Vega Alta	18.7	<MDL	198	449	8.50	<MDL	<MDL	37.2
	7	Humacao	24.6	<MDL	565	140	3.65	<MDL	0.336	146
	8	Gurabo	31.2	<MDL	89.9	520	9.34	3.05	<MDL	8.08
	9	Trujillo Alto	8.29	<MDL	652	601	11.5	<MDL	<MDL	33.9
	10	San Juan	37.5	0.008	396	705	26.2	<MDL	7.35	163
		San Juan 2	20.0	<MDL	161	764	14.0	<MDL	0.647	106
	11	Adjuntas	81.4	0.038	20.5	450	7.72	<MDL	<MDL	236
	12	Coamo	50.4	<MDL	216	664	12.2	<MDL	1.738	96.6
	13	Santa Isabel	3.10	0.015	100	1718	38.0	<MDL	<MDL	160
	14	Juana Díaz	4.52	0.021	228	1586	34.0	< DL	1.124	111
	15	Yauco	7.96	<MDL	2.77	958	16.7	< DL	<MDL	120
	16	San Germán	26.2	<MDL	772	86.5	7.37	1.41	<MDL	57.8
		San Germán 2	20.9	<MDL	1119	78.6	7.65	1.96	<MDL	78.8
	17	Mayagüez	7.36	<MDL	86.5	673	13.6	<MDL	<MDL	13.9
	18	Aguada	32.5	<MDL	43.4	901	17.3	<MDL	<MDL	6.11
	19	Aguadilla-Pueblo	27.5	<MDL	316	900	19.7	<MDL	<MDL	62.6
	20	Isabela	17.5	<MDL	147	1009	20.8	0.81	<MDL	30.1
	21	Moca	11.0	<MDL	718	985	23.3	1.02	<MDL	328
		Moca 2	2.89	0.514	914	1052	25.3	<MDL	<MDL	462
	22	Aguadilla-Base Ramey	35.6	<MDL	94.7	981	18.8	<MDL	<MDL	21.0
	23	Ponce	2.11	0.088	865	2270	52.6	35.6	<MDL	461
	24	Guayama	16.8	0.507	299	286	11.6	52.9	20.0	1363
		Guayama 2	9.69	0.717	688	260	16.9	<MDL	6.98	2076
NON-PRASA	25	San German	21.7	<MDL	20.3	101	8.23	<MDL	<MDL	20.7
	26	Yabucoa	117	<MDL	46.9	358	3.50	<MDL	<MDL	34.3
	27	Villalba	4.71	0.141	72.0	1293	17.3	<MDL	<MDL	113
	28	Guayama	45.0	<MDL	29.5	951	15.6	<MDL	<MDL	34.0
	29	Patillas-Don Conde	6.27	0.078	100	1176	26.5	<MDL	<MDL	67.4
	30	Patillas-Tanque 2	21.4	<MDL	81.5	395	7.07	<MDL	<MDL	448
	31	Patillas-Tanque 1	20.4	0.049	155	3847	8.77	1.80	<MDL	91.4
		Patillas-Tanque 1 2	8.32	<MDL	63.3	412	7.12	<MDL	<MDL	37.3
	32	Patillas-El Real	4.55	0.030	217	160	4.55	<MDL	<MDL	171
	33	Patillas-Mulas	6.99	<MDL	87.4	195	3.01	<MDL	143	15.3
		Patillas-Mulas 2	5.90	<MDL	164	172	3.67	<MDL	8.28	21.1
	33a	Community Tap	6.83	0.065	84.9	352	10.4	<MDL	<MDL	455
	33b	Raw Water Intake	21.6	<MDL	2.67	208	3.23	<MDL	<MDL	1.70
	33c	River Source Water	13.2	<MDL	1.28	174	3.23	<MDL	<MDL	1.15
SPRING	34	Maricao/Sabana	115	<MDL	0.64	277	9.15	<MDL	<MDL	1.63
	35	Utuado	6.54	<MDL	0.12	1515	26.3	<MDL	<MDL	<MDL
	36	Manati	<MDL	<MDL	0.42	2982	58.8	<MDL	<MDL	<MDL
	37	Caguas	1.89	<MDL	0.57	469	7.78	<MDL	<MDL	<MDL
	38	Adjuntas	38.5	<MDL	0.55	982	16.5	<MDL	<MDL	0.548
	39	Mayagüez-Quemado	<MDL	<MDL	0.24	1032	21.3	<MDL	<MDL	<MDL
	40	Mayagüez-Río Cañas	5.27	<MDL	0.25	542	10.9	<MDL	<MDL	<MDL

Figure 11 shows the distribution and comparisons of different trace metals for SC 1 and SC 2. Antimony, tin, and cadmium were three metals where the Kruskal-Wallis test was not performed because many of the samples had non-detectable levels of the trace element. However, trends can be observed with these metals.

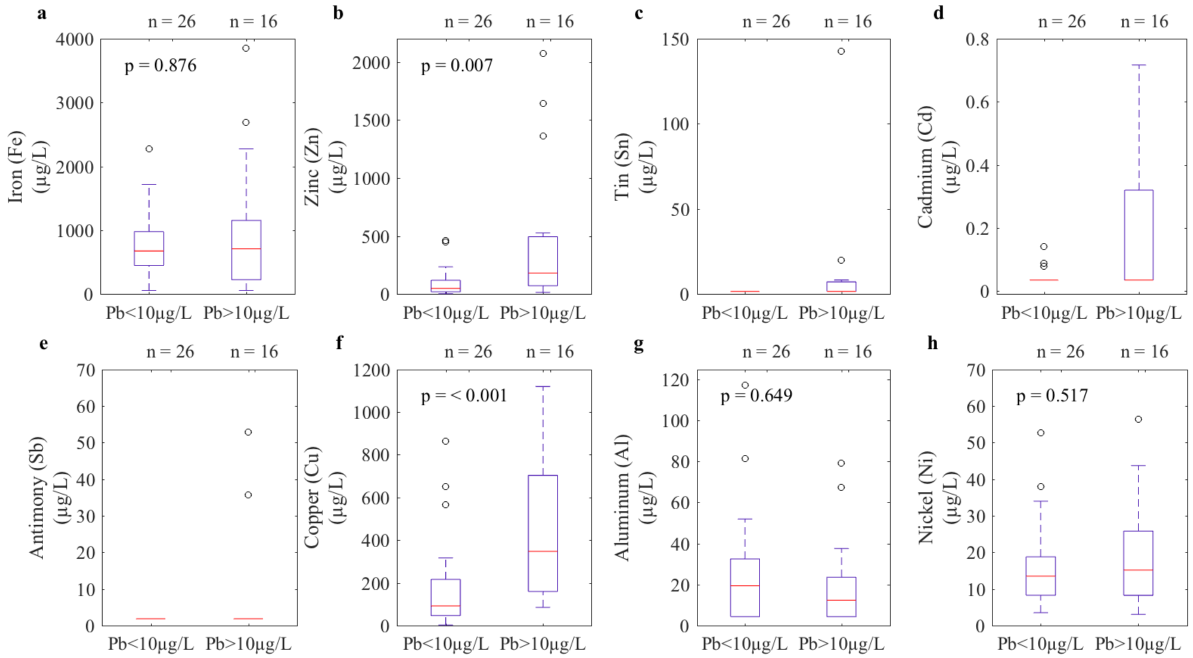


Figure 11. Sampling Campaign 1 & Sampling Campaign 2: Trace metal distributions and comparisons for samples from PRASA and non-PRASA systems. (a-h) Binning cutoff concentration of 10 µg/L. The p-value for the Kruskal-Wallis test is reported.

Antimony, tin, and aluminum had visually indistinguishable median concentrations. Only considering PRASA and non-PRASA systems from SC 1 and SC 2, 76% of systems had non-detectable levels of antimony. However, 24% (10 out of 42 sampling sites) did have detectable levels of antimony. Interestingly, 5 of those 10 samples had high WLLs (>10 µg/L) in SC 1, and 3 of those 10 samples were resampled sites in SC 2, presenting that 80% of samples that had high WLLs also observed detectable and sometimes elevated antimony concentrations (Table 11). For tin, 76% of samples were non-detect, representing that 24% (10 out of 42 sampling sites) had detectable levels of tin. Of those 10 samples, 7 had high WLLs (>10 μg/L) observed in SC 1 or SC 2, representing that in 70% of samples tin was detected with elevated WLLs. Moving forward, 60% of samples were non-detect for cadmium concentrations as well, representing that 40% (17 out of 42 sampling sites) had detectable levels of cadmium. Of those 17 samples, 10 had high WLLs (>10 μg/L) observed in SC 1 or SC 2. The high occurrence of lead and these trace metals presents an opportunity for forensic analysis, even though Kruskal-Wallis statistics tests could not be performed with certainty.

Neither iron (p = 0.876), aluminum (p = 0.649), or nickel (p = 0.517) were found to be statistically significant with high or low WLLs (Figure 11a, g, h). However, zinc and copper were shown to have significant differences (Figure 11b, f), showing that the occurrence of lead at concentrations greater than 10 μg/L was also accompanied by elevated concentrations of these two (2) trace metals. Antimony, tin, and cadmium were also found to have a high occurrence of elevated lead with detectable levels of each.

Zinc (p = 0.002) was found to have a statistically significant difference in concentrations between samples with high WLLs (>10 μg/L) and samples with low WLLs (<10 μg/L) (Figure 11b). Zinc, cadmium, and lead have been observed together in water samples when the lead source was the zinc coating on galvanized steel/iron pipe (GIP) since Prime Western Grade zinc coating was made with up to 0.5% lead by weight with a maximum percentage of 1.4% lead by weight in some material prior to 2014 [18], [111]. This Prime Western Grade zinc used in GIP is also made with to 0.2% cadmium, which helps distinguish a GIP lead source from a brass lead source.

Based on these statistically significant observances, ratios between lead, zinc, and cadmium were evaluated and compared to the literature. A systematic lead corrosion study of the scale layers on field collected GIP samples in Flint, MI found that the ratio of Pb:Cd (μg/L:μg/L) was 7, the ratio of Cd:Zn (µg/L:mg/L) was 2.6, and the ratio of Pb:Zn was 18.2 [112]. In that same study, Pieper et. al. (2017) found that the ratio of Pb:Cd was 744, the ratio of Cd:Zn was 2.6, the ratio of Pb:Zn was 1824 in water samples from a profiling effort of the ground zero home. Since the Pb:Cd ratio was much higher in water samples than the expected ratio from a GIP surface coating, there were other sources of lead present besides a sole source of GIP. The hypothesized reason in this study explaining the cooccurrence of these metals was due to sorbed lead onto iron rust layers and subsequent release when corrosion inhibitors were discontinued, since iron was also found to be statistically significant in that study.

For PRASA and non-PRASA systems from SC 1 and SC 2 that had detectable lead and cadmium, the Pb:Cd ratios were well above 7, with a median ratio of 400 and an average ratio of 6,900. Only one sampling site (Site 27) had a Pb:Cd ratio relatively close to 7, and that ratio was 8. The ratio of Pb:Zn (µg/L:mg/L) was on average 1197. The Cd:Zn ratio in this study was on average 2.2. Thus, the high Pb:Cd ratios indicate that GIP corrosion may be present but there were likely other lead sources present besides GIP [112]. As mentioned, Pieper et. al. (2017) determined that the lead release mechanism was attributed to sorption onto iron rust scale layers and subsequent release of those layers. However, for this study, iron was not found to be statistically significant between high and low WLLs. Thus, a potential reason for explaining the cooccurrence of lead, zinc, and cadmium is the dissolution of either constituent into soluble or insoluble forms, instead of sorption onto iron rust layers [111].

Copper also had a statistically significant difference (*p* = <0.001) in concentrations between samples with high WLLs (>10 µg/L) and samples with low WLLs (<10 µg/L*)* (Figure 11f). Brasses are copper alloys and contain many different metals, depending on the brand, and range in composition from 60 to 80% copper, 4 to 32% zinc, 1.5 to 7.5% lead, and less than 6%

tin, with trace amounts of iron, aluminum, nickel, and silicon [45]. The most common form of brass corrosion is dezincification. Generally, dezincification of brass occurs in waters with pH greater than 8.3 with a high ratio of chloride-to-carbonate hardness [17], [18]. Other forms of brass corrosion include general dissolution and impingement attack [18]. The statistical observance of zinc and copper could be an indicator of brass fixtures, such as ball valves or faucets [16], [72], [74], [81]. These observances make sense since a majority of the sampling taps from SC 1 and SC 2 were hose bibs, which are commonly made from different brass alloys, but cannot be said with certainty since a plumbing materials evaluation was not performed.

While the Kruskal-Wallis test was not performed with tin, the high occurrence of tin and lead is suggestive of the lead-bearing plumbing material lead solder (Figure 11c). Tin is a well-known component of lead solder, a common plumbing material that previously was composed of Sn:Pb ratios of 50:50 or 60:40 material composition. The cooccurrence of tin and lead thus could imply the use of lead solder and subsequent solder corrosion. The most common form of solder corrosion is the slow dissolution of solder components [18] due to galvanic corrosion, but particulate lead release has also been found to be a major contributor [20], [57], [58], [113]–[115]. Free chlorine exacerbates the corrosion of copper-lead solder joints more than combined chlorine at varying pH levels, however, in the presence of corrosion inhibitors, combined chlorine exacerbated corrosion more than free chlorine [113]. Other metals such as Cd, Cu, and Zn could also leach from copper pipes and tin-lead solder joints, but the trace amounts of these metals used in the solder makes them poor indicators of lead solder sources [115].

The common form of lead observed as a result of solder corrosion is particulate lead. This lead can be trapped in particulate form in aerator screens, providing a long-term source of dissolved lead, or be mobilized in particulate form [58]. Particulate lead was not measured in this study and examination of aerator screens was not performed. However, based on the high occurrence of detectable tin with high WLLs (70% occurrence) and the significant variation between median tin concentrations between high and low WLLs, it can be speculated that the corrosion of lead solder of an unknown composition is a potential lead source.

Lastly, the overall distribution of lead levels was evaluated based on whether lead levels were detectable or non-detectable for PRASA and non-PRASA systems from SC 1 and SC 2. For copper, most samples that had detectable lead also had detectable or elevated copper concentrations, with the median concentration (181 µg/L) higher in the detectable lead bin category than in the non-detectable lead bin category (32 µg/L) (Figure 12f). The samples that had non-detect lead also exhibited close to non-detect or non-detectable zinc, cadmium, tin, and antimony concentrations. Lastly, samples in the detectable lead category had a wider range of nickel concentrations (3.0 to 56 µg/L) in comparison to samples in the non-detectable lead category (8.2 to 17 µg/L). The occurrence of lead with other trace metals is indicative of corrosion of water distribution plumbing materials.

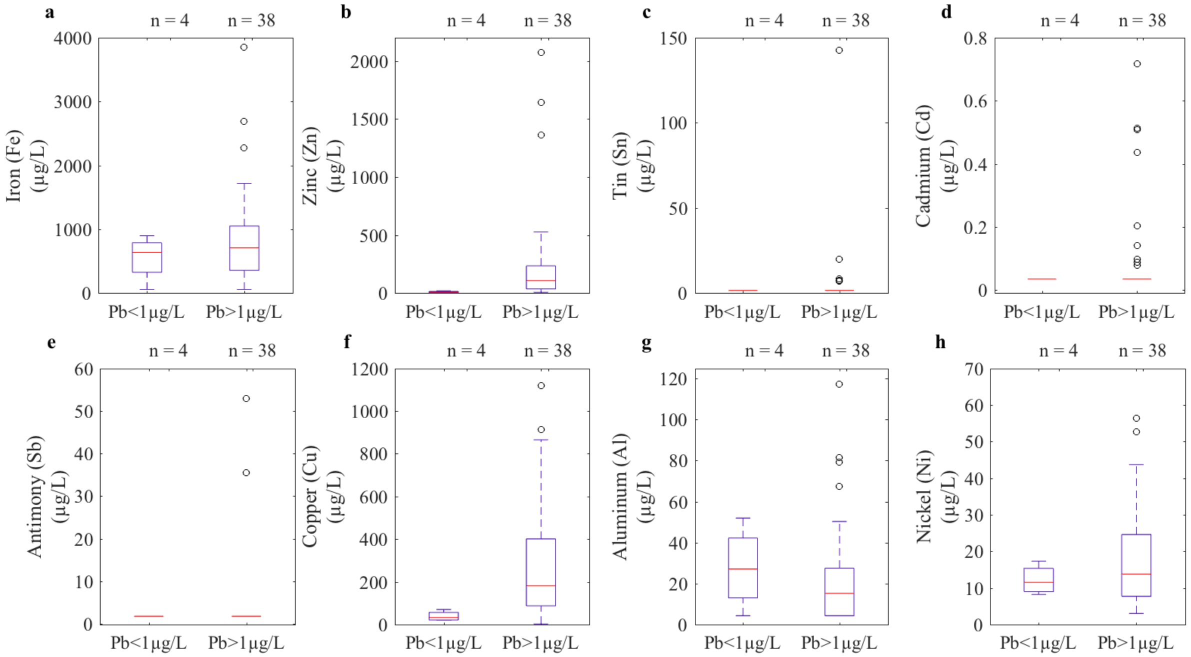


Figure 12. Sampling Campaign 1 & Sampling Campaign 2: Trace metal distributions and comparisons for samples from PRASA and non-PRASA systems. (a-h) Binning cutoff concentration of 1 µg/L.

4.1.4 Analysis of Specific Point-of-Use Taps

Since significant differences were observed between lead and other trace metals, specific taps were analyzed in order to gain a deeper understanding of specific lead sources at each sampling site. Lead and other trace metals were analyzed for relative change (Factor Δ) in concentrations between SC 1 and SC 2 by taking the higher observed concentration and dividing it by the lower observed concentration. If a concentration increased, a positive sign (+) was placed in front of the value and if a concentration decreased, a negative sign (-) was used instead. The full table with specific magnitude changes is provided in Table 12. For simplification, a modified matrix using positive and negative signs to denote the type of co-occurrence of two metals together with the indication of which sampling site corresponded to that occurrence is provided (Table 13). It is important to note that while this process was used to identify potential lead sources, it cannot be used to make definitive conclusions.

Table 12. Sampling Campaign 1 & Sampling Campaign 2: Trace metal concentration differences in samples collected from different communities. A negative factor ∆ indicates a decrease and a positive factor ∆ indicates an increase.

Site #	***System***	***Sampling Campaign***	***Pb*** ***(µg/L)***	***Cu*** ***(µg/L)***	***Al*** ***(µg/L)***	***Cd*** ***(µg/L)***	***Fe*** ***(µg/L)***	***Ni*** ***(µg/L)***	***Sn*** ***(µg/L)***	***Zn*** ***(µg/L)***
1	Sabana Grande	SC 1	35.6	401	79.2	0.099	714	24.6	2.97	528
		SC 2	13.3	139	67.2	0.034	928	13.4	<0.628	202
		Factor ∆	-2.7	-2.9	-1.2	-2.9	+1.3	-1.8	>-4.7[1]	-2.6
2	Lajas	SC 1	33.0	268	6.59	0.436	2275	56.3	<0.301	1642
		SC 2	13.5	202	3.87	0.020	2690	43.7	<0.628	138
		Factor ∆	-2.4	-1.3	-1.7	-21.8	+1.2	-1.3	NA[2]	-11.9
10	San Juan	SC 1	24.0	396	37.5	0.008	705	26.2	7.35	163
		SC 2	8.64	161	20.0	<0.014	764	14.0	0.647	106
		Factor ∆	-2.8	-2.5	-1.9	NA	+1.1	-1.9	-11.3	-1.52
16	San Germán	SC 1	14.2	772	26.2	<0.006	86.5	7.37	<0.301	57.8
		SC 2	18.7	1120	20.9	<0.014	78.6	7.65	<0.628	78.8
		Factor ∆	+1.3	+1.4	-1.25	NA	-1.1	+1.0	NA	+1.4
21	Moca	SC 1	62.0	718	11.0	0.204	985	23.3	<0.301	328
		SC 2	19.8	914	2.89	0.514	1052	25.3	<0.628	462
		Factor ∆	-3.13	+1.3	-3.8	+2.5	+1.1	+1.1	NA	+1.4
24	Guayama	SC 1	37.4	299	16.8	0.507	286	11.6	20.0	1363
		SC 2	23.4	688	9.69	0.717	260	16.9	6.98	2076
		Factor ∆	-1.6	+2.3	-1.7	+1.4	-1.1	+1.5	-2.9	+1.5
31	Patillas-Tanque 1	SC 1	12.2	155	20.4	0.049	3847	8.77	<0.301	91.4
		SC 2	3.2	63.3	8.32	<0.014	411	7.12	<0.628	37.3
		Factor ∆	-3.8	-2.5	-2.5	<-3.5[1]	-9.4	-1.2	NA	-2.5
33	Patillas-Mulas	SC 1	615	87.4	7.0	<0.006	195	3.0	143	15.3
		SC 2	169	164	5.9	<0.014	172	3.7	8.3	21.1
		Factor ∆	-3.6	+1.9	-1.2	NA	-1.1	+1.2	-17.2	+1.4

[1] Calculate by taking the reported concentration from SC 1 and dividing by the detection limit for SC 2, [2] NA – Not applicable since both samples were below the MDL or the higher sample was below the MDL

Table 13. Sampling Campaign 1 & Sampling Campaign 2: Matrix comparison of changes in trace metal concentrations for several systems that exhibited high water lead levels. Each metal is compared against all of relevant measured trace metals for signs of positive or negative "correlation". Numbers correspond to site numbers of each CWS.

		Cu		***Al***		***Cd***		***Fe***		***Ni***		***Sn***		***Zn***	
		+	-	+	-	+	-	+	-	+	-	+	-	+	-
Pb	+	16			16				16	16				16	
	-	21 24 33	1 2 10 31		1 2 10 21 24 31 33	21 24	1 2 31	1 2 10 21	24 31 33	21 24 33	1 2 10 31		1 10 24 33	21 24 33	1 2 10 31

When looking at this matrix it is important to understand that the magnitude of the increase or decrease is not captured. Therefore, even small changes in a concentration could indicate a false trend. The site that stands out the most is San Germán (Site 16), which is always observed by itself with no other systems. As lead concentrations increase, copper, zinc, and nickel concentrations also increase while iron and aluminum concentrations decrease (Table 13).

Many samples saw lead and other trace metal concentrations co-vary negatively together. Sabana Grande (Site 1), Lajas (Site 2), San Jan (Site 10), and Patillas-Tanque 1 (Site 31 are solely observed together three times. In these observances, as lead concentrations decrease, copper, nickel, and zinc concentrations also decrease (Table 13).

In addition, many samples saw lead and other trace metals co-vary in the opposite direction. Moca (Site 21), Guayama (Site 24), and Patillas-Mulas (Site 33) are solely observed together three times. When there is a decrease in lead concentrations there is an increase in copper, nickel, and zinc concentrations. Specifically, for Moca (Site 21) and Guayama (Site 24) there is also an increase in cadmium concentrations (Table 13).

Guayama (Site 24), Patillas-Tanque 1 (Site 31), and Patillas-Mulas (Site 33) were observed together with a decrease in lead concentrations and a subsequent decrease in iron concentrations. However, Sabana Grande (Site 1), Lajas (Site 2), San Juan (Site 10), and Moca (Site 21) saw with a decrease in lead concentrations a subsequent an increase in iron concentrations. Out of these seven (7) communities, Sabana Grande (Site 1), San Juan (Site 10), Guayama (Site 24), and Patillas-Mulas (Site 33) all saw a decrease in lead concentrations with a subsequent decrease in tin concentrations (Table 13).

The clustering of different sites, and furthermore the consistency observed with some of the clustering, could be indicative of different uses of plumbing materials or similar corrosion mechanisms in those systems. At Site 33 in Patillas-Mulas, it was anecdotally reported that the material used to install the tap was lead solder. Based on this information, a specific in-depth analysis of the variations in metals concentrations at that tap was performed.

Patillas-Mulas

As aforementioned, the observance of lead and tin in water samples is an indicator of possible corrosion from lead solder [20], [57], [58], [113]–[115]. During this corrosion process, lead solder has most tendency to be the anodic corrosion site when connected to copper pipe. This tendency decrease slightly when connected to brasses or bronzes [18]. On the other hand, lead solder is cathodic when connected to steel, zinc, or cadmium [18]. During galvanic corrosion of lead solder connected to copper pipe, three galvanic couples exist: Cu-Pb, Cu-Sn, and Sn-Pb. In a study by Subramanian et. al. (1995), lead and tin were released at about a 1:1 ratio until about three (3) to six (6) hours of contact time, where at that point lead release continued to increase while tin release stayed stagnant. Increased lead leaching occurred in waters that had high chloride and sulfate concentrations, despite having higher pH and alkalinity values.

When examining the tin concentrations from SC 1 to SC 2 for Patillas-Mulas (Table 12) there is a 17.2 factor decrease in tin concentration with a corresponding 3.6 factor decrease in lead concentration. While aluminum and iron concentrations consecutively decrease by similar factors (on average -1.2), copper, nickel, and zinc concentrations increase by about similar factors (on average +1.5). The observed high decrease in tin concentrations and smaller decrease in lead concentrations between the two sampling campaigns could be exemplary of the tapered tin release and increased lead release phenomenon if the tap was not used between sampling campaigns. The increases in copper, zinc, and nickel could also indicate an additional lead source, specifically a brass component. This theory is probable because the hose bib connected to the lead solder appeared to be brass, although the exact brand, manufacture, and composition information is unknown.

4.2 Sampling Campaign 3

SC 1 and SC 2 were conducted with a universal sampling approach which had limitations with respect to data interpretation, specifically because the sampling approach did not adhere to U.S. EPA LCR sampling requirements. Making comparisons to historical lead levels and determining the extent of human lead exposure was difficult during the initial phase of the project. The goal of SC 3 was to better assess if the elevated WLLs observed in SC 1 and SC 2 were representative of systemic issues throughout the CWS. SC 3 was conducted using a protocol that better aligned with the U.S. EPA LCR sampling requirements comprising a one-liter 6+ hour stagnation first-draw sample from an indoor kitchen or bathroom tap. Since the two communities that were selected for this in-depth study exhibited elevated WLLs in the first two sampling campaigns (Patillas-Mulas and Lajas), the sampling approach also implemented a sequential volume profiling protocol in order to try and identify if other lead sources within the distribution system. Six (6) houses from each community were sampled and one of those six (6) homes was the same house sampled in SC 1 and SC 2. However, only five (5) houses from the Lajas community were used for statistical analysis since it was discovered that the plumbing system in one of the homes was not used for an extended and unspecified amount of time.

4.2.1 General Water Quality

Table 14 summarizes the general water quality characteristics for Lajas and Patillas-Mulas during SC 3. Average DOC concentrations were similar between the two communities, falling below 1.0 mg_C/L. However, other water quality characteristics were substantially different. The pH of the Lajas community (6.8) was on average 0.5 units lower than the pH of the Patillas-Mulas community (7.3). Conductivity for Lajas was on average 961 μS/cm and for Patillas-Mulas it was 125 μS/cm, almost one order of magnitude difference. Conductivity concentrations for SC 3 were converted to TDS concentrations using Equation 3.3 and compared to calculated theoretical TDS values for spring sources sampled in SC 1. The average TDS value for all spring sources from SC 1 was 223 mg/L with a median value of 203 mg/L. The Patillas-Mulas average TDS value was 68 mg/L and the Lajas average TDS value was 581 mg/L, falling substantially below and above, respectively, the value for natural source waters measured in this study overall.

Table 14. Sampling Campaign 3: Bulk water quality results for Lajas and Patillas-Mulas.

Parameters		***Lajas (n=5)***			***Patillas-Mulas (n=6)***		
		Average	Max	Min	Average	Max	Min
pH		6.8	6.9	6.8	7.3	8.0	7.1
Conductivity	*(μS/cm)*	962	967	956	125	126	124
Alkalinity	*(mg/L as $CaCO_3$)*	334	342	328	33	33	31
Hardness	*(mg/L as $CaCO_3$)*	371	380	344	36	36	36
Free Chlorine	*(mg/L as Cl_2)*	2.1	2.5	1.6	0.0	0.0	0.0
Total Chlorine	*(mg/L as Cl_2)*	2.3	2.7	2.0	0.0	0.0	0.0
DOC	*(mg_C/L)*	0.41	0.48	0.35	0.69	0.72	0.68
Turbidity	*(NTU)*	0.12	0.19	0.04	1.36	3.83	0.72

The average field measured alkalinity (Patillas-Mulas = 33 mg/L as $CaCO_3$, Lajas = 334 mg/L as $CaCO_3$) was similar to the average calculated geochemical alkalinity (Patillas-Mulas = 35 mg/L as $CaCO_3$, Lajas = 382 mg/L as $CaCO_3$), confirming the use of geochemical alkalinity as good indicator of titratable alkalinity and useful for interpreting data from SC 1 and SC 2. The Patillas-Mulas alkalinity was much lower at 33 mg/L as $CaCO_3$, compared to Lajas alkalinity at 333 mg/L as $CaCO_3$. Spring sources across the island from SC 1 and SC 2 had an average alkalinity of 164 mg/L as $CaCO_3$.

Analyzing the water quality of each system comparatively, a lower pH combined with a higher conductivity in Lajas would indicate more corrosive water, but the higher alkalinity could in theory provide corrosion resistance [17], [18]. While Patillas-Mulas had a higher pH and lower conductivity, which could provide capacity to resist corrosion, it had a substantially low alkalinity (<50 mg/L as $CaCO_3$), which shows that the water does not have a large capacity to resists changes in pH, which has been shown to ultimately induce corrosion [17], [18]. The average free chlorine residual for Lajas was 2.1 mg/L as Cl_2, which is right above the Center for Disease Control (CDC) recommended chlorine residual concentration of no more than 2.0 mg/L after 30 minutes of contact time after the initial dose at the treatment plant. Generally, utilities strive for a Cl_2 residual concentration of 0.2 mg/L as Cl_2. However, maintaining high chlorine residuals has shown to increase development of PbO_2 passivation layers, which are rather insoluble, if the ORP of the water is maintained [28], [38]. It is possible that if lead-bearing plumbing materials were present in the Lajas system that these PbO_2 scales would be present.

4.2.2 Observed Water Lead Levels

Three samples per community household were collected and analyzed for lead, copper, and other trace metals: one 6+HS FD sample from an interior fixture, one 6+HS FD from the exterior hose bib, and the third liter from the sequential volume profile of the interior fixture.

Table 15 summarizes collected lead data for SC 3 for each community. Out of the 18 samples collected for Patillas-Mulas 11 were non-detect and out of the 15 samples collected for Lajas eight (8) were non-detect. The maximum interior WLLs and average interior WLLs were similar between the two communities, with concentrations below the U.S. EPA AL in all samples (Interior FD Max_{Lajas} = 4.0 µg/L, Interior FD $Max_{Patillas\text{-}Mulas}$ = 5.0 µg/L, Interior FD Avg_{Lajas} = 1.3 µg/L, Interior FD $Avg_{Patillas\text{-}Mulas}$ = 1.6 µg/L). In addition, no interior 3rd-liter SVP samples observed higher WLLs than the interior FD 6+HS samples with average concentrations less than the project PQL for both systems.

The implications of this suggest that other lead-bearing plumbing materials are not present upstream in the premise plumbing system, however a detailed examination of the plumbing system would need to be performed in order to confirm this speculation. Overall, Patillas-Mulas observed the highest individual WLL at 82 µg/L from the same exterior hose bib tap that exhibited a WLL of 615 µg/L in SC 1 and 169 µg/L in SC 2. While Patillas-Mulas had the highest individual WLL on exterior taps, overall Lajas exhibited higher median concentrations on exterior taps (Exterior FD $\text{Median}_{\text{Lajas}}$ = 4.0 µg/L, Exterior FD $\text{Median}_{\text{Patillas-Mulas}}$ = 2.9 µg/L).

Table 15. Sampling Campaign 3: Descriptive statistics of lead concentrations in µg/L organized by system. One house sampled from Lajas was excluded due to the extended and unspecified amount of stagnation time.

Sampling Campaign 3 July 2018						
Community	Lajas			Patillas-Mulas		
# of Samples	n = 5	n = 5	n = 5	n = 6	n = 6	n = 6
Sampling Location	Interior Fixture	Interior Fixture	Hose Bib	Interior Fixture	Interior Fixture	Hose Bib
Sample Type	FD 6+HS	3rd SVP	FD 6+HS	FD 6+HS	3rd SVP	FD 6+HS
Volume	1L	1L	1L	1L	1L	1L
Above PQL	40%	40%	60%	50%	17%	50%
Pb (µg/L)						
Average	1.3	0.8	2.9	1.6	< 1.0	15.4
Median	< 1.0	< 1.0	4.0	< 1.0	< 1.0	2.3
Maximum	4.0	2.0	4.0	5.0	1.0	82.0
Minimum	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
90th Percentile	2.8	1.4	4.0	3.5	< 1.0	43.5

While overall observed WLLs from this sampling campaign were substantially lower than previous sampling campaigns, there was still detectable WLLs in about half of the samples collected. While these data show that exterior WLLs from SC 1 and SC 2 were not representative of interior WLLs during SC 3, the possibility of human lead exposure cannot be disregarded, as many interior samples still had detectable WLLs. In addition, the exact usage and purposes of water from hose bibs is unknown, and during times of water stress or intermittent water supply, any water that is available is fit for use.

4.2.3 System Corrosion Tendency

Corrosion indices for Lajas and Patillas-Mulas from SC 3 are summarized in Table 16. Patillas-Mulas exhibited a higher average CSMR ratio of 1.56, above the critical threshold value of 0.77. The high CSMR combined with a low alkalinity (33 mg/L as $CaCO_3$) implicate that the water has a higher tendency to be corrosive towards dissimilar metal connections [44]. The averages of other indices were also not within the recommended threshold values with an LSR of 0.8, LSI of -1.5, RI of 10.3, and buffer intensity of 0.2 mol/L per pH unit. The substantial negative value of the LSI and high RI suggest that calcium carbonate precipitation potential is low. The high LSR also suggests that the system has corrosion tendency towards iron plumbing materials, especially since the alkalinity is very low and the hardness was also low (33 mg/L as $CaCO_3$). Patillas-Mulas also did not exhibit a detectable free chlorine concentration in SC 3 (0.0 mg/L as Cl_2) and both initial campaigns SC 1 and SC 2 (Table 14). A higher free chlorine concentration has been shown to increase the ORP of the water and produce insoluble PbO_2 scales. The absence of chlorine residual in the Patillas-Mulas system suggests that these scales are not likely, however the potential for other scale formation is still viable.

Table 16. Sampling Campaign 3: Corrosion index values for Lajas and Patillas-Mulas. One house sampled from Lajas was excluded due to the unknown extensive stagnation time.

Parameters	***Lajas (n=5)***			***Patillas-Mulas (n=6)***		
	Average	Max	Min	Average	Max	Min
CSMR[1]	1.06	1.16	1.01	1.56	1.64	1.43
LSR[2]	0.32	0.33	0.30	0.75	0.76	0.71
LSI[3]	-0.03	0.17	-0.16	-1.52	-0.81	-1.67
RI[4]	6.9	7.1	6.7	10.3	10.5	9.6
Buffer Intensity *(mol/L per pH unit)*	3.97	4.64	2.77	0.19	0.23	0.04

[1] CSMR – Chloride-to-Sulfate Mass Ratio, [2] LSR – Larson-Skold Ratio, [3] LSI – Langelier Saturation Index, [4] RI – Ryznar Index

The corrosion indices for Lajas exhibited a different behavior. Based on the recommended threshold values, the CSMR was the only index in a range that has been associated with increased corrosion potential. The LSR (0.32) was at the threshold 0.3, and well below other recommended thresholds such as 0.8. The Ryznar Index (6.9) was at a level considered to be slightly aggressive and almost neutral. Buffer Intensity (3.97) was substantially above the recommended threshold of 0.1 and the LSI (-0.03) was just slightly negative, indicating that calcium carbonate precipitation was possible and that the water had increased capacity to resist changes in pH. In comparison, the corrosion indices for Site 2 in Lajas from SC 1 (Table 10) were slightly more corrosive, which could be a factor in the higher observed WLLs from that sampling campaign.

4.2.4 Upper Limit of Stagnation Time

During the sampling event, it was determined that one of the houses from the Lajas community was uninhabited and thus excluded from statistical analysis in order to evaluate only homes that were representative of typical water usage patterns. However, this house provides a good analysis of the effects of stagnation time on observed WLLs.

Stagnation time, or the amount of time water sits stagnate in pipes, is the overarching basis around which lead control regulation in the United States was developed. Dissolved lead release is governed by the solubility limits and conditions of lead sources, specifically the pure metal material or the passivation layers on the surface of that metal material. Observations of stagnation curves of lead pipe showed that lead concentration levels approached an equilibrium concentration in about an "overnight" period of time [18], [30], [37], [39]. Thus, worst-case lead exposure could be assumed from long periods of stagnation of normal household water use.

Table 17 displays the lead, copper, bulk water quality, and corrosion index data from this sampling site. The interior stagnation first draw sample, which was collected from a kitchen tap, had a WLL of 137 μg/L. The exterior stagnation first draw sample had a WLL of 7.0 μg/L. The alkalinity was high (334 mg/L as $CaCO_3$), and the conductivity was high (951 μS/cm), on the same magnitude and level as other homes from the same system. The free chlorine concentration of this 2nd liter in the SVP was 1.4 mg/L as Cl_2, which is lower than the main water line free chlorine concentration of 2.0 mg/L as Cl_2. The turbidity of the interior FD 6+HS sample was 0.5 units higher than the turbidity of the exterior FD sample, the 3rd-liter of the interior SVP, and the main distribution line. The higher turbidity indicates more particulate matter in the sample, which could indicate more potential for higher percentages of particulate lead.

Table 17. Sampling Campaign 3 Upper Limit of Stagnation Time House: Water quality data for the sampling site in the Lajas community that was determined to have an unknown upper stagnation time exceeding typical household water usage patterns.

Parameter		***FD Interior Fixture***	***3rd L Interior Fixture***	***FD Exterior Fixture***	***Lajas Community***[1]
Pb	*(µg/L)*	137	4.0	7.0	-
Cu	*(µg/L)*	240	127	104	-
Turbidity	*(NTU)*	0.6	0.13	0.11	-
			Bulk Water Quality		
pH	-		7.1		6.8
Temperature	*(℃)*		32		32
Conductivity	*(µS/cm)*		951		962
Main H_2O Line Turbidity	*(NTU)*		0.15		0.12
Alkalinity	*(mg/L as $CaCO_3$)*		334		334
Hardness	*(mg/L as $CaCO_3$)*		375		371
Free Chlorine	*(mg/L as Cl_2)*		2.0		2.1
Total Chlorine	*(mg/L as Cl_2)*		2.1		2.3
DOC	*(mg_C/L)*		0.4		0.4
PO_4^{2-}	*(mg/L)*		<PQL		<PQL
Cl^-	*(mg/L)*		50.2		50.1
SO_4^{2-}	*(mg/L)*		49.6		47.2
CSMR	-		1.01		1.07
LSR	-		0.33		0.32
LSI	-		0.17		-0.06
RI	-		6.7		7.0
Buffer Intensity	*(mol/L per pH unit)*		2.77		4.21

[1] Results taken as averages between each bulk water quality sample from each sampling site.

The water at this sampling site could be considered corrosive based on the high CSMR (1.01 > 0.77). The positive value of the LSI suggests that the water is supersaturated with respect to $CaCO_3$ and the complex will precipitate as well as a RI near or between recommended threshold values. A high buffer intensity also implies the water has a large capacity to resist changes in pH and the low LSR shows that the water is not aggressive towards cast iron pipe.

Triantafyllidou et. al. (2015) studied the impact of longer stagnation times on elevated WLLs and found varying results depending on the sampling location [116]. In one location, longer stagnation times, specifically 91 to 101 hours, did not significantly increase observed WLLs at the point-of-use location from a lead service line source. In another site, longer stagnation times of greater than 74 hours significantly impacted observed WLLs at the tap. Other studies have found varying results with other metals such as copper and zinc, which were found to reach a maximum concentration in 48 hours in winter months and 24 hours in summer months [117].

The significant level of lead at this tap could be attributed to multiple factors. Since lead dissolution is theorized to reach a maximum concentration many hours before this house was sampled, it should be assumed that this concentration was at maximum solubility and that the months of stagnation had no effect of the observed concentration at the tap. However, studies have shown that extended periods of stagnation can increase lead levels, with a 35% increase in the time period between six (6) to 16 hours [39], with lead levels increasing the most in a time period of 10 hours. As much as 100 μg/L was shown to leach from brass coupons at a pH of 7.0 in a time period of 72 hours [45].

The high concentration of lead observed in the first flush of the uninhabited house is indicative of fixture or fitting corrosion, rather than a lead service line. Lytle and Schock (1996) suggests that the longer stagnation times observed in their studies did have an impact on the observed WLLs. The higher turbidity could also contribute to this observation, as particulate lead is not directly related to solubility limits and stagnation characteristics of lead dissolution. While the turbidity was not over 1 NTU (the recommended threshold for determining acid digestion requirement) the difference in observed values is significant. Based on the possible interaction effects of water quality conditions and the unknown specific stagnation time or plumbing material, it is difficult to say for certain whether the 137 μg/L was a WLL observed at maximum solubility or an artifact of particulate lead release.

CHAPTER 5

CONCLUSIONS

5.1 Prevalence of Elevated Water Lead Levels

This study surveyed water quality from 40 logistically planned but randomly selected sites throughout Puerto Rico that had water available for potable uses. It incorporated a distributed sample set across the island of the three existing types of potable water systems and sources. The initial results of the study found elevated WLLs at hose bib taps from both government-owned and privately-owned systems that were scattered throughout Puerto Rico with no evident pattern or clustering. If differences in sample volume and tap location are neglected, the observed WLLs were on the same order of magnitude of other well-known events such as Washington D.C. from 2001 to 2004 and Flint, MI from 2014 to 2016. The 90th percentile WLL in Washington D.C. was 56 μg/L with some homes exceeding 300 μg/L [38]. In Flint MI, the 90th percentile WLL was 25 μg/L, and in some samples the concentration exceeded 1000 μg/L [118].

This observation of the initial data from SC 1 and SC 2 raised concerns about the extent and severity of lead release in Puerto Rican water distribution systems. However, the initial study design that incorporated a universal sampling approach made it difficult to draw conclusions and direct comparisons to the other well-known events (i.e., Flint, MI and Washington, D.C.). The third sampling campaign, which was designed to help alleviate this issue, also had inherent limitations and, while the results provide useful information regarding the corrosion chemistry and specific system corrosion potential, it could not conclude if lead presence in these systems was representative of the other systems in SC 1 and SC 2 or Puerto Rico as a whole.

5.2 Challenges with Data Set

In order to better understand the lead prevalence in these systems, it is essential to recognize the factors that attribute to the variability of observed WLLs and the unique dynamic between them specific to this study. The sampling approach used to determine lead presence is important when making accurate conclusions on the extent and severity of human lead exposure. In order to have observed WLLs at a tap, there needs to be the intersection of three elements: lead-bearing plumbing materials, a mechanism for lead release, and a sampling approach that captures lead concentrations. If one of these aspects is missing then the result is prone to error, as discussed in Chapter 4. To add to this complexity is the further spatial and temporal variability of each factor and the interrelationship between those factors. There are multiple challenges with this data set that make interpreting and determining the extent of lead release difficult.

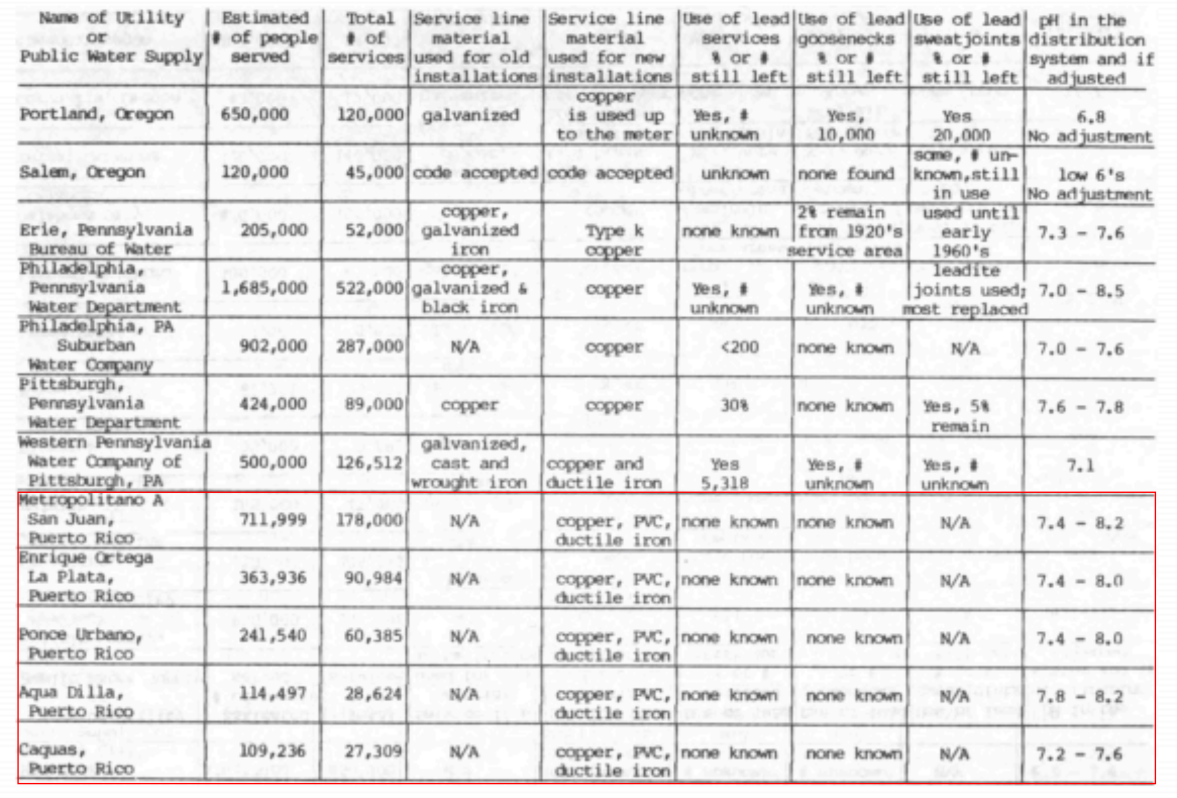
5.2.1 No Baseline Lead Data

When attempting to determine the extent of lead corrosion in these systems, it was important to establish if lead corrosion issues were historically present. In many, and almost all of these systems, there is an absence of publicly available baseline lead data. The 2017 NRDC report stated all but one of the 2015 U.S. EPA LCR violations were attributed to failing to test or monitor for lead in water. This lack of data makes it difficult to place the comparatively small dataset from this study into the context of a large compliance monitoring dataset. Without data available to the public, it is impossible to determine if the results in this study are a glimpse into a larger problem or outliers due to sampling limitations.

5.2.2 Unknown Plumbing Materials in Puerto Rico

When planning a lead corrosion monitoring or sampling event, one of the most important parameters of the study design is the determination of sampling locations that contain lead-bearing plumbing materials. This prioritization of sites is needed to effectively evaluate the extent and severity of corrosion potential for a system. A sampling site could be chosen with corrosive water quality conditions and a mechanism for lead release (e.g., unstable equilibrium conditions, high flow rate, etc.), but if there are not lead-bearing plumbing materials, the constituent concentration result will be prone to Type II error.

Lead pipe was standard practice in many U.S. cities through the 1950's, but the extent and use of the product in off-land states and territories, such as Puerto Rico, is uncertain and not confirmed. A U.S. EPA report from 1984 took an inventory of lead service lines across the country [119]. The excerpt from surveyed utilities from Puerto Rico is shown in Figure 13.



Name of Utility or Public Water Supply	Estimated # of people served	Total # of services	Service line material used for old installations	Service line material used for new installations	Use of lead services % or # still left	Use of lead goosenecks % or # still left	Use of lead sweatjoints % or # still left	pH in the distribution system and if adjusted
Portland, Oregon	650,000	120,000	galvanized	copper is used up to the meter	Yes, # unknown	Yes, 10,000	Yes 20,000	6.8 No adjustment
Salem, Oregon	120,000	45,000	code accepted	code accepted	unknown	none found	some, # unknown, still in use	low 6's No adjustment
Erie, Pennsylvania Bureau of Water	205,000	52,000	copper, galvanized iron	Type k copper	none known	2% remain from 1920's service area	used until early 1960's	7.3 - 7.6
Philadelphia, Pennsylvania Water Department	1,685,000	522,000	copper, galvanized & black iron	copper	Yes, # unknown	Yes, # unknown	leadite joints used; most replaced	7.0 - 8.5
Philadelphia, PA Suburban Water Company	902,000	287,000	N/A	copper	<200	none known	N/A	7.0 - 7.6
Pittsburgh, Pennsylvania Water Department	424,000	89,000	copper	copper	30%	none known	Yes, 5% remain	7.6 - 7.8
Western Pennsylvania Water Company of Pittsburgh, PA	500,000	126,512	galvanized, cast and wrought iron	copper and ductile iron	Yes 5,318	Yes, # unknown	Yes, # unknown	7.1
Metropolitano A San Juan, Puerto Rico	711,999	178,000	N/A	copper, PVC, ductile iron	none known	none known	N/A	7.4 - 8.2
Enrique Ortega La Plata, Puerto Rico	363,936	90,984	N/A	copper, PVC, ductile iron	none known	none known	N/A	7.4 - 8.0
Ponce Urbano, Puerto Rico	241,540	60,385	N/A	copper, PVC, ductile iron	none known	none known	N/A	7.4 - 8.0
Aqua Dilla, Puerto Rico	114,497	28,624	N/A	copper, PVC, ductile iron	none known	none known	N/A	7.8 - 8.2
Caquas, Puerto Rico	109,236	27,309	N/A	copper, PVC, ductile iron	none known	none known	N/A	7.2 - 7.6

Figure 13. Utility response results from a U.S. EPA 1983 inventory of lead-bearing plumbing materials panel discussion. Utilities from Puerto Rico are boxed in red.

The data collected for each system was obtained from phone interviews or mailed questionnaires, however it is important to note that this report did not adhere to the agencies peer and administrative review policies. The main issue for some of the systems included in this report is that accurate record keeping did not exist, and therefore rough estimates of inquired information had to be made by senior staff and operators. For the five utilities from Puerto Rico that participated in the survey, each one claimed “N/A” under the category of “Service Line Material used for Old Installations” which means the question was not asked or there was no response. Overall, the response was “none known” for use of lead service lines or lead goosenecks. The interpretation of this response means to best of their knowledge, at that moment, there was none known, but this does not mean that any survey or confirmation study was conducted to be certain. The result of this seminar for Puerto Rico was that no information was collected about the plumbing materials of any system on the island.

On the other hand, in an NPR new story Rebecca Hersher reported that personal communications with the executive president of PRASA, Eli Díaz-Atienza, stated that Puerto Rico did not use many types of lead-bearing plumbing that were popular during the turn of the century [120]. Physical support or evidence for this statement is unavailable, and therefore concluding that lead pipe was not used in Puerto Rican drinking water distribution systems cannot be said with confidence. In addition, lead pipe is not the only source of lead-bearing plumbing that contributes to elevated WLLs, as discussed in Chapter 2. Overall, the regulation of lead-bearing plumbing materials in Puerto Rico is under the same expectations and laws as all states, and the disconnect between understanding the regulation and composition in a plumbing material that occurs on the mainland occurs in Puerto Rico as well.

To add to the complexity of limited information on lead-bearing plumbing materials, during the urban development of Puerto Rico many construction practices were not always held to code. Homes were built in an ad-hoc fashion with no blueprints, inspections, insurance, or titles to the land underneath it [121]. These construction practices were the overarching reason as to why Hurricane Maria caused so much infrastructure damage and also have long-term effects when trying to understand corrosion issues in Puerto Rican water distribution systems [121].

5.2.3 Variability with Sampling Approaches

By using a universal sampling approach during SC 1 and SC 2 to achieve the original goal of this rapid reconnaissance research project, it became difficult to interpret the collected data with regards to lead, a parameter that was not an initial concern. At the time of sampling plan design, sampling sites were chosen based on the assumed knowledge that every site was served by a different CWS to gain a holistic understanding of water quality issues on the island as a whole after the hurricane. Each CWS had different water quality and water sources (i.e., river, reservoir or lake, groundwater) which contribute to the challenge of making conclusions about the extent of lead corrosion for each system. While certain data have found trends between water quality parameters even when using data from different systems [18], the possibility of selecting a sampling site that did not contain lead-bearing plumbing was still a viable consequence.

Sample Set Size

Under the U.S. EPA LCR, there is a required minimum number of homes that need to be sampled when performing routine monitoring LCR compliance sampling. The number of homes sampled per community varies based on community size. For example, according to the Safe Drinking Water Information System (SDWIS), Patillas-Mulas serves a population of around 650, which requires the collection of 20 LCR compliance samples from 20 unique homes per monitoring period. Lajas serves a population around 47,000, which requires the collection of 60 LCR compliance samples. Only sampling one home per CWS in SC 1 and SC 2 and the small number of homes sampled for each system in SC 3 ($n_{\text{Lajas}} = 5$, $n_{\text{Patillas-Mulas}} = 6$) is not representative of the community as a whole to draw definitive conclusions about the unique extent of lead release in each system.

Sample Volume

Due to the spatial and temporal variability of lead sources and mobilization mechanisms, one variable that becomes of particular importance is the sample volume. The volume of sample collected is a reflection of a location in the water system from which the sample originates. The smaller the sample volume, the easier it is to isolate a fixture or source. In this study, the 125 mL first draw samples from hose bibs most likely capture water unique to the tap fixture [25]. If other lead-bearing plumbing materials were present in any of these systems upstream, the 125 mL sample volume would not capture that, and thus the comparisons between observed WLLs and other water quality parameters is prone to Type II error. The small sample volume is also not representative of water lead levels under normal use patterns where larger volumes would have decreased concentrations due to dilution.

Sample volumes have also been used to determine lead sources within a water system, as discussed in the comparisons of different sampling approaches in Chapter 2 [25]. A sequential volume profiling sampling approach was implemented in SC 3 when three consecutive liters of water were sampled per tap. To capture lead release from a lead service line, though, it is recommended that higher sample volumes between six (6) and (12) liters is more accurate [50], [76]. However, if premise plumbing system configurations are unknown, as in this study, the decision to only sample three liters was made in order to try to gain a more in-depth understanding of lead release but by compromising with the limitations of the study.

5.3 Relationship Between Hurricane Maria and Elevated Lead Levels

The lack of baseline data makes drawing any specific connection between Hurricane Maria and the elevated WLLs in SC 1 and SC 2 impossible. Personal communications with many residents indicate that after Hurricane Maria water quality deteriorated significantly, with specific observances of high turbidity, milky white and dark coloration, and a large amount of particulate matter [122]. The deteriorated water quality conditions could have severely impacted the stability of the water distribution systems. Changes could include altering the bulk water composition which alters the system equilibrium state, for example by changing the ORP or decreasing alkalinity. The initial motivation for the project was to understand the water quality after Hurricane Maria with no preconceived idea of the relevant water quality conditions before the hurricane impact. If during the initial sampling campaigns (SC 1 and SC 2), a 1-liter sample was collected for trace elements, then it might have been possible to make more definitive conclusions about the state of the water distribution systems with respect to the highlighted issue of concern, lead corrosion.

5.4 Risks Associated with Puerto Rico's Water Quality Conditions

Not sampling a large number of homes from each system in SC 1 and SC 2 and not finding elevated WLLs in the small number of interior samples collected during SC 3 is not substantial evidence to dismiss the possibility of more widespread lead corrosion issues. Despite the challenges associated with this project and further not being able to directly relate the observances in water quality characteristics as a direct result of Hurricane Maria, the outcomes of this study indicate that there are still viable, potential risks to public health.

Even months after Hurricane Maria, many residents remained ill and lacked access to potable water. A testimony by Dr. Wendy Matos, executive director of the University of Puerto Rico's faculty practice plan and supervisor of 470 doctors, revealed that many of her patients still lacked access to potable water and suffered from waterborne illness and disease at higher rates and greater risks such as gastroenteritis, conjunctivitis, and dermatological conditions such as dermatitis, scabies, and pediculosis, with positive test results for shigellosis and leptospirosis [123].

5.4.1 Water Availability

Consistent potable water service is unreliable in Puerto Rico. Before Hurricane Maria, reliable water service was not expected, and in the months after the Hurricane residents continued to state that water was only available for several days at a time before being shut off. Due to these delivery interruptions, residents were asked to boil water for three to five minutes for the first three days after supply was restored [124]. While boiling water protects against pathogenic exposure, it does not reduce metals concentrations. These elevated stagnation times, from days to weeks, of the water could intensify observed WLLs at taps that are unrepresentative of normal water usage conditions. Typically, consumers are asked to flush taps before consumption if water has been stagnant for extended amounts of time in order to reduce lead levels. Whether or not residents' flushed taps after these extended periods of water stagnation is unknown.

This inconsistent water availability after Hurricane Maria further tempted people to consume untreated water and collect water from wells located on hazardous superfund sites [125]. While this water was determined to be safe to drink by external analysis, and later in a news release by the EPA, the sampling methods used to collect the samples were not stated in the report [125]–[127]. More specifically, the stagnation time or type of sample (e.g., first draw, flushed, etc.) is unknown. During the U.S. EPA study, volatile organic compounds (VOCs), pathogens, nitrate, and nitrite were monitored from three different wells, but an indication that lead was a monitored parameter was not evident [127]. For the external tests conducted by CNN, only the sample bottle material information was given, which was said to be clean Perrier bottles [125]. No lead data was available for that external test.

The relevant aspect of this information is that the well-head tap used by many of the residents for one of the sites is a hose bib, similar in appearance to many hose bibs tested in this study, as seen in a screenshot of a CNN TV broadcast [8]. This supports the idea that the exact usage and purposes of water from hose bibs cannot be predicted by standard assumptions that all water used for human consumption originates from a kitchen or bathroom tap. This is especially relevant during disaster recovery response periods or times of intermittent water supply. While hurricanes do not often make landfall in Puerto Rico, the consistent unreliability of water services on the island suggest that any water that is available is fit for use.

Figure 14. The hose bib tap at a well-head used to collect water from during water scarcity after Hurricane Maria located on the Dorado Groundwater Contamination Site (a superfund site) in Puerto Rico west of San Juan.

5.5 Implications and Future Work

While the sampling locations and volumes for the first two sampling campaigns deviated from the U.S. EPA LCR, the results show that many public water systems in Puerto Rico can have aggressive water conditions that can result in lead release given susceptible plumbing materials. While it cannot be said for certain that the water with high lead from the first two sampling campaigns is being used for human consumption, it cannot be ruled out either. With unreliable power and water services during natural disaster recovery, any freshwater water that is available is fit for use.

This research highlights the challenges associated with conducting rapid reconnaissance research. One of these challenges is balancing the objectives of the research and following standard methods for quantifying the parameters of interest. When doing this, information critical to interpreting specific data can be sacrificed due to the logistical and financial limitations of the study. Another challenge is correctly associating the impacts of natural disasters on observed response of the target environment, whether that disaster is natural or anthropogenic. To accurately draw connections requires comprehensive baseline monitoring data. What this research did not highlight or address is the many systemic issues stemming from years of prolonged and overlooked attention to infrastructure upgrades. However, even if implicating the effects of a natural disaster are near impossible, this type of research can shed light on problems that stem from more systemic infrastructure issues. Future work is warranted that fully characterizes distribution system conditions in different Puerto Rican drinking water systems. This study supports that there is a critical need to create a comprehensive characterization and collection of baseline monitoring data related to lead corrosion issues.

REFERENCES

[1] R. J. Pasch, Andrew B. Penny, and Robbie Berg, “National Hurricane Center Tropical Cyclone Report: Hurricane Maria (AL152017) 16-30 September 2017.” National Hurricane Center, 10-Apr-2018.

[2] T. Houser and P. Marsters, “The World’s Second Largest Blackout,” *Rhodium Group*, 12-Apr-2018.

[3] OXFAM, “Far From Recovery Puerto Rico Six Months After Hurricane Maria,” Research, 2018.

[4] R. Rosselló, “Request for Federal Assistance for Disaster Recovery: Build Back Better Puerto Rico,” Governers Office, Puerto Rico, Nov. 2017.

[5] M. Panditharatne, “Small Water Systems in Puerto Rico Badly Affected by Maria | NRDC,” *NRDC Expert Blog: Mekela Panditharatne*, 11-Jul-2018.

[6] A. F. Campbell, “Puerto Rican officials claim the water crisis is under control. Reports on the ground tell a very different story.,” *Vox*, 25-Oct-2017. [Online]. Available: https://www.vox.com/policy-and-politics/2017/10/25/16504870/puerto-rico-running-water. [Accessed: 17-May-2018].

[7] Primeraora.com, “AAA anuncia ajustes operacionales,” *Primera Hora*, 29-Sep-2017. [Online]. Available: http://www.primerahora.com/noticias/puerto-rico/nota/aaaanunciaajustesoperacionales-1248390/. [Accessed: 17-May-2018].

[8] E. Lavandera and J. Sutter, “Flirting with another disaster: Puerto Ricans tap into potentially unsafe water,” CNN, 20-Oct-2017.

[9] M. Panditharatne, “New Data: 2 Million Puerto Ricans Risk Water Contamination,” *NRDC Expert Blog: Mekela Panditharatne*, 11-Dec-2017.

[10] M. Panditharatne, “Bacterial Contamination results in Puerto Rico Post Maria,” *NRDC Expert Blog: Mekela Panditharatne*, 11-Dec-2017.

[11] M. Nedelman, “Suspected leptospirosis cases increasing in Puerto Rico after Hurricane Maria,” *CNN*, 24-Oct-2017. [Online]. Available: https://www.cnn.com/2017/10/24/health/leptospirosis-puerto-rico/index.html.

[12] World Health Organization (WHO), “Leptospirosis,” *WHO*. [Online]. Available: http://www.who.int/zoonoses/diseases/leptospirosis/en/. [Accessed: 07-Apr-2019].

[13] World Health Organization (WHO), “Lead in Drinking Water Background document for development of WHO Guidelines for Drinking-water Quality,” WHO/SDE/WSH/03.04/09/Rev/1, 2011.

[14] U.S. Environmental Protection Agency, “Lead and Copper Rule Revisions White Paper.” Oct-2016.

[15] R. Brown, N. McTigue, and D. Cornwell, “Controlling Lead in Drinking Water,” Water Research Foundation & American Water Works Association (AWWA), Web Report #4409, 2015.

[16] American Water Works Association (AWWA) and J. Edzwald, *Water Quality & Treatment: A Handbook on Drinking Water*. 2010.

[17] American Water Works Association (AWWA), R. E. Giani, and C. P. Hill, *M58 Internal Corrosion Control in Water Distribution Systems*, 2nd ed. Denver, CO: American Water Works Association, 2017.

[18] A. R. F. and D.-T. W. AwwaRF and TZW, *Internal Corrosion of Water Distribution Systems*, 2nd ed. Denver, CO: American Water Works Association, 1996.

[19] S. Triantafyllidou and M. Edwards, “Lead (Pb) in Tap Water and in Blood: Implications for Lead Exposure in the United States,” *Critical Reviews in Environmental Science and Technology*, vol. 42, no. 13, pp. 1297–1352, Jul. 2012.

[20] E. Deshommes, L. Laroche, S. Nour, C. Cartier, and M. Prévost, “Source and occurrence of particulate lead in tap water,” *Water Research*, vol. 44, no. 12, pp. 3734–3744, Jun. 2010.

[21] HDR Engineering, Inc., “An Analysis of the Correlation between Lead Released from Galvanized Iron Piping and the Contents of Lead in Drinking Water,” HDR Engineering, Bellevue, WA, Summary Report, Sep. 2009.

[22] M. R. Schock, R. N. Hyland, and M. M. Welch, “Occurrence of Contaminant Accumulation in Lead Pipe Scales from Domestic Drinking-Water Distribution Systems,” *Environ. Sci. Technol.*, vol. 42, no. 12, pp. 4285–4291, Jun. 2008.

[23] M. R. Schock, “Causes of temporal variability of lead in domestic plumbing systems,” *Environ Monit Assess*, vol. 15, no. 1, pp. 59–82, Jul. 1990.

[24] Y. Xie, “Dissolution, Formation, and transformation of the Lead Corrosion Product PbO2: Rates and Mechanisms of Reactions that Control Lead Release in Drinking Water Distribution Systems,” PhD, Washington University at St. Louis, 2010.

[25] AwwaRF, *Lead Control Strategies*. Denver, CO: The Foundation and American Water Works Association, 1990.

[26] D. Guo, “Corrosion Scale Characteristics and Lead Oxide Dissolution in Chloraminated Water,” Ph.D., University of Western Toronto, 2018.

[27] L. W. Wasserstrom, S. A. Miller, S. Triantafyllidou, M. K. Desantis, and M. R. Schock, “Scale Formation Under Blended Phosphate Treatment for a Utility With Lead Pipes,” *Journal - American Water Works Association*, vol. 109, no. 11, pp. E464–E478, 2017.

[28] D. A. Lytle and M. R. Schock, “Formation of Pb(IV) oxides in chlorinated water,” *American Water Works Association. Journal; Denver*, vol. 97, no. 11, pp. 102-114,20, Nov. 2005.

[29] M. R. Schock, “Understanding Corrosion Control Strategies for Lead,” *Journal - American Water Works Association*, vol. 81, no. 7, pp. 88–100, Jul. 1989.

[30] M. R. Schock and F. G. Lemieux, “Challenges in addressing variability of lead in domestic plumbing,” *Water Science & Technology*, vol. 10, no. 5, pp. 793–799, Dec. 2010.

[31] C. Cartier, R. B. Arnold, S. Triantafyllidou, M. Prévost, and M. Edwards, “Effect of Flow Rate and Lead/Copper Pipe Sequence on Lead Release from Service Lines,” *Water Research*, vol. 46, no. 13, pp. 4142–4152, Sep. 2012.

[32] E. J. Kim and J. E. Herrera, “Characteristics of Lead Corrosion Scales Formed during Drinking Water Distribution and Their Potential Influence on the Release of Lead and Other Contaminants,” *Environ. Sci. Technol.*, vol. 44, no. 16, pp. 6054–6061, Aug. 2010.

[33] L. S. McNeill and M. Edwards, “Importance of Pb and Cu Particulate Species for Corrosion Control,” *Journal of Environmental Engineering*, vol. 130, no. 2, pp. 136–144, Feb. 2004.

[34] K. J. Pieper, L.-A. H. Krometis, D. L. Gallagher, B. L. Benham, and M. Edwards, “Incidence of waterborne lead in private drinking water systems in Virginia,” *Journal of Water and Health; London*, vol. 13, no. 3, pp. 897–908, Sep. 2015.

[35] K. J. Pieper, L.-A. Krometis, D. Gallagher, B. Benham, and M. Edwards, “Profiling Private Water Systems to Identify Patterns of Waterborne Lead Exposure,” *Environ. Sci. Technol.*, vol. 49, no. 21, pp. 12697–12704, Nov. 2015.

[36] A. F. Cantor, “Diagnosing corrosion problems through differentiation of metal fractions,” *Journal - American Water Works Association*, vol. 98, no. 1, pp. 117-126,14, Jan. 2006.

[37] Y. Xie and D. E. Giammar, “Effects of flow and water chemistry on lead release rates from pipe scales,” *Water Research*, vol. 45, no. 19, pp. 6525–6534, Dec. 2011.

[38] T. L. Guidotti *et al.*, “Elevated Lead in Drinking Water in Washington, DC, 2003–2004: The Public Health Response,” *Environ Health Perspect*, vol. 115, no. 5, pp. 695–701, May 2007.

[39] D. A. Lytle and M. R. Schock, “Impact of stagnation time on metal dissolution from plumbing materials in drinking water,” *Journal of Water Supply : Research and Technology - AQUA; Oxford*, vol. 49, no. 5, pp. 243–257, Aug. 2000.

[40] Y. Wang, H. Jing, V. Mehta, G. J. Welter, and D. E. Giammar, “Impact of galvanic corrosion on lead release from aged lead service lines,” *Water Research*, vol. 46, no. 16, pp. 5049–5060, Oct. 2012.

[41] C. K. Nguyen, B. N. Clark, K. R. Stone, and M. A. Edwards, “Role of Chloride, Sulfate, and Alkalinity on Galvanic Lead Corrosion,” *Corrosion*, vol. 67, no. 6, pp. E1–E9, Jun. 2011.

[42] C. K. Nguyen, K. R. Stone, A. Dudi, and M. A. Edwards, “Corrosive Microenvironments at Lead Solder Surfaces Arising from Galvanic Corrosion with Copper Pipe,” *Environ. Sci. Technol.*, vol. 44, no. 18, pp. 7076–7081, Sep. 2010.

[43] C. K. Nguyen *et al.*, “Impact of Chloride:Sulfate Mass Ratio (CSMR) Changes on Lead Leaching in Potable Water,” Water Research Foundation & U.S. Environmental Protection Agency, Denver, CO, #4088, 2010.

[44] C. K. Nguyen, K. R. Stone, and M. A. Edwards, “Chloride-to-sulfate mass ratio: Practical studies in galvanic corrosion of lead solder,” *Journal - American Water Works Association*, vol. 103, no. 1, pp. 81-92,16, Jan. 2011.

[45] M. R. Schock and D. A. Lytle, “Stagnation Time, Composition, pH, and Orthophosphate Effects on Metal Leaching from Brass,” U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-96/103, Sep. 1996.

[46] Y. Zhang and M. Edwards, “Zinc content in brass and its influence on lead leaching,” *Journal - American Water Works Association*, vol. 103, no. 7, pp. 76-83,14, Jul. 2011.

[47] A. A. Abokifa and P. Biswas, “Modeling Soluble and Particulate Lead Release into Drinking Water from Full and Partially Replaced Lead Service Lines,” *Environ. Sci. Technol.*, vol. 51, no. 6, pp. 3318–3326, Mar. 2017.

[48] C. Cartier *et al.*, “Investigating dissolved lead at the tap using various sampling protocols,” *Journal - American Water Works Association*, vol. 103, no. 3, pp. 55-67,10, Mar. 2011.

[49] B. Clark, S. Masters, and M. Edwards, “Profile Sampling To Characterize Particulate Lead Risks in Potable Water,” *Environ. Sci. Technol.*, vol. 48, no. 12, pp. 6836–6843, Jun. 2014.

[50] D. A. Cornwell and R. Brown, “Evaluation of Lead Sampling Strategies,” Water Research Foundation, Project #4569, 2015.

[51] G. Welter, “Typical Kitchen Faucet-Use Flow Rates: Implications for Lead Concentration Sampling,” *Journal - American Water Works Association*, vol. 108, no. 7, pp. E374–E380, 2016.

[52] E. Deshommes, L. Laroche, D. Deveau, S. Nour, and M. Prévost, “Short- and Long-Term Lead Release after Partial Lead Service Line Replacements in a Metropolitan Water Distribution System,” *Environ. Sci. Technol.*, vol. 51, no. 17, pp. 9507–9515, Sep. 2017.

[53] E. Deshommes *et al.*, “Lead Levels at the Tap and Consumer Exposure from Legacy and Recent Lead Service Line Replacements in Six Utilities,” *Environ. Sci. Technol.*, vol. 52, no. 16, pp. 9451–9459, Aug. 2018.

[54] R. A. Brown and D. A. Cornwell, “High-Velocity Household and Service Line Flushing Following LSL Replacement,” *Journal - American Water Works Association*, vol. 107, no. 3, pp. E140–E151, 2015.

[55] J. St. Clair, C. Cartier, S. Triantafyllidou, B. Clark, and M. Edwards, “Long-Term Behavior of Simulated Partial Lead Service Line Replacements,” *Environ Eng Sci*, vol. 33, no. 1, pp. 53–64, Jan. 2016.

[56] E. M. Zhou, “Impact of galvanic corrosion on lead release after partial lead service line replacement,” M.S., University of Toronto (Canada), Canada, 2013.

[57] E. Doré, E. Deshommes, R. C. Andrews, S. Nour, and M. Prévost, “Sampling in schools and large institutional buildings: Implications for regulations, exposure and management of lead and copper,” *Water Research*, vol. 140, pp. 110–122, Sep. 2018.

[58] S. Triantafyllidou, J. Parks, and M. Edwards, “Lead Particles in Potable Water,” *Journal - American Water Works Association*, vol. 99, no. 6, pp. 107–117, Jun. 2007.

[59] A. Sandvig *et al.*, “Contribution of Service Line and Plumbing Fixtures to Lead and Copper Rule Comliance Issues,” AwwaRF & U.S. Environmental Protection Agency (EPA), 91229, 2008.

[60] U.S. Environmental Protection Agency, “Use of Lead Free Pipes, Fittings, Fixtures, Solder and Flux for Drinking Water,” *U.S. EPA*, 03-Aug-2015. [Online]. Available: https://www.epa.gov/dwstandardsregulations/use-lead-free-pipes-fittings-fixtures-solder-and-flux-drinking-water. [Accessed: 08-Apr-2019].

[61] K. J. Pieper, L.-A. Krometis, and M. Edwards, “Quantifying Lead-Leaching Potential From Plumbing Exposed to Aggressive Waters,” *Journal - American Water Works Association*, vol. 108, no. 9, pp. E458–E466, Sep. 2016.

[62] D. A. Cornwell, R. A. Brown, and S. H. Via, “National Survey of Lead Service Line Occurrence,” *Journal - American Water Works Association*, vol. 108, pp. E182–E191, Apr. 2016.

[63] B. Beard and S. Haydt, “Lead Ban Surveillance Project 2015,” Pennsylvania Department of Environmental Protection, Bureau of Safe Drinking Water, Aug. 2015.

[64] P. C. Grevatt (Office of Ground Water & Drinking Water), “U.S. EPA Memo: Clarification of Recommended Tap Sampling Procedures for Purposes of the Lead and Copper Rule,” 29-Feb-2016.

[65] U.S. Environmental Protection Agency, “Quick Guide to Drinking Water Sample Collection Second Edition.” U.S. Environmental Protection Agency, Sep-2016.

[66] U.S. Environmental Protection Agency, “Lead and Copper Rule Monitoring and Reporting Guidance for Public Water Systems,” U.S. Environmental Protection Agency, Washington, D.C., EPA/816/R-10//004, Mar. 2010.

[67] S. Triantafyllidou, C. K. Nguyen, Y. Zhang, and M. A. Edwards, “Lead (Pb) quantification in potable water samples: implications for regulatory compliance and assessment of human exposure,” *Environmental Monitoring and Assessment*, vol. 185, no. 2, pp. 1355–65, Feb. 2013.

[68] M. Bower and C. Hayes, Eds., *Best Practice Guide on the Management of Metals in Small Water Supplies*. London, United Kingdom: IWA Publishing, 2016.

[69] P. Quevauviller and K. C. Thompson, Eds., *Analytical Methods for Drinking Water: Advances in Sampling and Analysis*. John Wiley & Sons, 2006.

[70] M. R. Schock and J. Tully, “Lead Tap Sampling Approaches: What Do They Tell You,” Sep-2016.

[71] E. Deshommes *et al.*, “Evaluation of exposure to lead from drinking water in large buildings,” *Water Research*, vol. 99, pp. 46–55, Aug. 2016.

[72] C. Elfland, P. Scardina, and M. Edwards, “Lead-contaminated water from brass plumbing devices in new buildings,” *Journal - American Water Works Association*, vol. 102, no. 11, pp. 66–76, Nov. 2010.

[73] K. J. Pieper *et al.*, “Evaluating Water Lead Levels During the Flint Water Crisis,” *Environ. Sci. Technol.*, vol. 52, no. 15, pp. 8124–8132, Aug. 2018.

[74] K. J. Pieper *et al.*, “Elevated Lead in Water of Private Wells Poses Health Risks: Case Study in Macon County, North Carolina,” *Environ. Sci. Technol.*, vol. 52, no. 7, pp. 4350–4357, Apr. 2018.

[75] A. F. Cantor, “Summary of the Proposed Lead and Copper Rule From a Perspective Using Process Research Solutions’ Water System Data,” Process Research Solutions, Madison, WI, Dec. 2015.

[76] A. F. Cantor, “Optimization of Phosphorus-Based Corrosion Control Chemicals Using a Comprehensive Perspective of Water Quality,” Water Research Foundation & Water Environment & Reuse Foundation, Project #4586, 2017.

[77] M. A. Del Toral, A. Porter, and M. R. Schock, “Detection and Evaluation of Elevated Lead Release from Service Lines: A Field Study,” *Environ. Sci. Technol.*, vol. 47, no. 16, pp. 9300–9307, Aug. 2013.

[78] M. Edwards, Y. Lambrinidou, R. Scott, and P. Schwartz, “Gaps in the EPA Lead and Copper Rule That Can Allow for Gaming of Compliance,” DC WASA 2003-2009, Oct. 2009.

[79] C. Hass, L. Kock, K. Kelty, D. A. Lytle, and S. Triantafyllidou, “Effectiveness of the Preservation Protocol within the Environmental Protection Agency (EPA) Method 200.8 for Soluble and Particulate Lead Recovery in Drinking Water,” U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-13/222, Dec. 2013.

[80] A. Katner *et al.*, “Weaknesses in Federal Drinking Water Regulations and Public Health Policies that Impede Lead Poisoning Prevention and Environmental Justice,” *Environmental Justice*, vol. 9, no. 4, pp. 109–117, Aug. 2016.

[81] A. Katner *et al.*, “Effectiveness of Prevailing Flush Guidelines to Prevent Exposure to Lead in Tap Water,” *International Journal of Environmental Research and Public Health; Basel*, vol. 15, no. 7, p. 1537, Jul. 2018.

[82] S. Masters, J. Parks, A. Atassi, and M. Edwards, “Inherent variability in lead and copper collected during standardized sampling,” *Environmental Monitoring and Assessment; Dordrecht*, vol. 188, no. 3, pp. 1–15, Mar. 2016.

[83] E. A. Murphy, “Effectiveness of flushing on reducing lead and copper levels in school drinking water.,” *Environ Health Perspect*, vol. 101, no. 3, pp. 240–241, Aug. 1993.

[84] M. Tiemann, “Regulating Lead in Drinking Water: Issues and Developments,” Congressional Research Service, IF10446, Aug. 2016.

[85] “Report of the Lead and Copper Rule Working Group To the National Drinking Water Advisory Council.” Aug-2015.

[86] D. A. Cornwell and D. A. Lytle, “Lead and Copper Research,” *Journal - American Water Works Association*, vol. 110, no. 10, pp. 2–2, Oct. 2018.

[87] D. A. Cornwell, “How Have We Done in Reducing Lead in Water Since the LCR?,” *Journal - American Water Works Association*, vol. 110, no. 10, pp. 30–37, Oct. 2018.

[88] "Regulatory Update At-A-Glance," *Association of Metropolitan Water Agencies*, 06-Nov-2018. [Online]. Available: https://www.amwa.net/update-glance/regulatory-update-glance. [Accessed: 07-Nov-2018].

[89] National Resources Defense Council, "Threats on Tap: Drinking Water Violations in Puerto Rico." May-2017.

[90] American Public Health Association, American Water Works Association, Water Pollution Control Federation, and Water Environment Federation, Eds., *Standard methods for the examination of water and wastewater: including bottom sediments and sludges*. New York: American Public Health Association, 1960.

[91] *Field Measurements: U.S. Geological Survey Techniques of Water-Resources Investigations Chapter A6*, vol. 9. Reston, VA: Geological Survey (U.S.), Various.

[92] P. Brezonik and W. Arnold, *Water Chemistry: An Introduction to the Chemistry of Natural and Engineered Aquatic Systems*, 1st ed. Oxford University Press, 2011.

[93] J. D. Kenny, D. R. Hokanson, and R. R. Trussell, "Technical Note: Calculation of the Langelier Index at High pH," *Journal - American Water Works Association*, vol. 107, no. 3, pp. 82-S3, 2015.

[94] T. E. Larson and R. V. Skold, "Laboratory Studies Relating Mineral Quality of Water To Corrosion of Steel and Cast Iron," *CORROSION*, vol. 14, no. 6, pp. 43–46, Jun. 1958.

[95] P. R. Roberge, *Corrosion Inspection and Monitoring*. 2007.

[96] WatSim, "Water Quality Simulation for Scale and Corrosion Lead & Copper Minimization Quick Reference Guide."

[97] S. J. Masten, S. H. Davies, and S. P. McELMURRY, "Flint Water Crisis: What Happened and Why?," *Journal: American Water Works Association*, vol. 108, no. 12, pp. 22–34, Dec. 2016.

[98] U.S. Environmental Protection Agency, "Optimal Corrosion Control Treatment Evaluation Technical Recommendations for Primacy Agencies and Public Water Systems," United States Environmental Protection Agency, Washington, D.C., EPA/816/B-16/003, Mar. 2016.

[99] T. E. Larson, "Corrosion by Domestic Waters," State of Illinois, Illinois, ISWS-75-BUL59, 1975.

[100] R. R. Cavano, "Saturation, Stability, and Scaling Indices." 2007.

[101] University of New Hampshire, "UNH Researchers Find Unexpected Impact of Hurricanes on Puerto Rico's Watershed," *UNH Today*, 10-Dec-2018. [Online]. Available: https://www.unh.edu/unhtoday/news/release/2018/12/10/unh-researchers-find-unexpected-impact-hurricanes-puerto-ricos-watershed. [Accessed: 26-Mar-2019].

[102] "USGS Water-Quality Information: Frequently Asked Questions." [Online]. Available: https://water.usgs.gov/owq/FAQ.htm#Q19. [Accessed: 08-Apr-2019].

[103] P. Vidon *et al.*, "In the path of the Hurricane: impact of Hurricane Irene and Tropical Storm Lee on watershed hydrology and biogeochemistry from North Carolina to Maine, USA," *Biogeochemistry*, vol. 141, no. 3, pp. 351–364, Dec. 2018.

[104] B. Yoon and P. A. Raymond, “Dissolved organic matter export from a forested watershed during Hurricane Irene,” *Geophysical Research Letters*, vol. 39, no. 18, Sep. 2012.

[105] G. S. Dhillon and S. Inamdar, “Extreme storms and changes in particulate and dissolved organic carbon in runoff: Entering uncharted waters,” *Geophysical Research Letters*, vol. 40, no. 7, pp. 1322–1327, 2013.

[106] J. Manuel, “Nutrient Pollution: A Persistent Threat to Waterways,” *Environ Health Perspect*, vol. 122, no. 11, pp. A304–A309, Nov. 2014.

[107] “Phosphorus: Sources, Forms, Impact on Water Quality - A General Review.” Minnesota Pollution Control, Jul-2007.

[108] U.S. Environmental Protection Agency, “EPA’s 2008 Report on the Environment,” U.S. Environmental Protection Agency, Washington, D.C., EPA/600/R-07/045F, May 2008.

[109] U.S. Environmental Protection Agency, “The Facts About Nutrient Pollution Flyer,” U.S. Environmental Protection Agency, EPA/840/F-12/003, Apr. 2012.

[110] U.S. Environmental Protection Agency, “National Rivers and Streams Assessment 2008-2009: A Collaborative Survey,” U.S. Environmental Protection Agency, Washington, D.C., EPA/84I/R-16/007, Mar. 2016.

[111] B. N. Clark, S. V. Masters, and M. Edwards, “Lead Release to Drinking Water from Galvanized Steel Pipe Coatings,” *Environmental Engineering Science*, vol. 32, no. 8, pp. 713–721, Jun. 2015.

[112] K. J. Pieper, M. Tang, and M. A. Edwards, “Flint Water Crisis Caused By Interrupted Corrosion Control: Investigating ‘Ground Zero’ Home,” *Environ. Sci. Technol.*, vol. 51, no. 4, pp. 2007–2014, Feb. 2017.

[113] N.-H. Lin, A. Torrents, A. P. Davis, M. Zeinali, and F. A. Taylor, “Lead corrosion control from lead, copper-lead solder, and brass coupons in drinking water employing free and combined chlorine,” *Journal of Environmental Science and Health . Part A: Environmental Science and Engineering and Toxicology*, vol. 32, no. 4, pp. 865–884, Apr. 1997.

[114] V. S. Sastri, K. S. Subramanian, M. Elboujdaini, and J. R. Perumareddi, “Inhibition of release of lead into water owing to galvanic corrosion of lead solders,” *Corrosion Engineering, Science and Technology*, vol. 41, no. 3, pp. 249–254, Sep. 2006.

[115] K. S. Subramanian, V. S. Sastri, M. Elboujdaini, J. W. Connor, and A. B. C. Davey, “Water contamination: Impact of tin-lead solder,” *Water Research*, vol. 29, no. 8, pp. 1827–1836, Aug. 1995.

[116] S. Triantafyllidou, M. R. Schock, M. K. DeSantis, and C. White, “Low Contribution of PbO2-Coated Lead Service Lines to Water Lead Contamination at the Tap,” *Environ. Sci. Technol.*, vol. 49, no. 6, pp. 3746–3754, Mar. 2015.

[117] Lj. Zlatanović, J. P. van der Hoek, and J. H. G. Vreeburg, “An experimental study on the influence of water stagnation and temperature change on water quality in a full-scale domestic drinking water system,” *Water Research*, vol. 123, pp. 761–772, Oct. 2017.

[118] D. C. Bellinger, “Lead Contamination in Flint — An Abject Failure to Protect Public Health,” *New England Journal of Medicine*, vol. 374, no. 12, pp. 1101–1103, Mar. 2016.

[119] U.S. Environmental Protection Agency, “Plumbing Materials and Drinking Water Quality: Proceedings of a Seminar,” U.S. Environmental Protection Agency, Washington, D.C., EPA/600/9-85/007, May 1984.

[120] R. Hersher, “Puerto Rico’s Tap Water Often Goes Untested, Raising Fears About Lead Contamination,” *All Things Considered*, NPR, 20-Sep-2018.

[121] A. Viglucci and P. A. Raymond, “Half of Puerto Ricos’ housing was built illegally. Then came Hurricane Maria,” *Miami Herald*, 14-Feb-2018. [Online]. Available: https://www.miamiherald.com/news/nation-world/world/americas/article199948699.html.

[122] O. Milman, “Another Flint? Why Puerto Ricans no longer trust water after the hurricane | US news | The Guardian,” *The Guardian*, 08-Aug-2018. [Online]. Available: https://www.theguardian.com/us-news/2018/aug/08/puerto-rico-hurricane-maria-water-quality. [Accessed: 31-Mar-2019].

[123] M. Panditharatne, “Six Months After Maria: Puerto Rico’s Growing Health Crisis,” *NRDC Expert Blog: Mekela Panditharatne*, 21-Mar-2018.

[124] C. Rodriguez, “Water quality in Puerto Rico remains unclear months after Hurricane Maria,” *Kaiser Health News*, PBS, 14-Jun-2018.

[125] J. Sutter and E. Lavandera, “Expert: Water from a polluted Puerto Rico site ‘safe to drink,’” *CNN Investigates*, CNN, 20-Oct-2017.

[126] J. Sutter, “EPA: Puerto Rico Superfund site water is safe,” *CNN*. [Online]. Available: https://www.cnn.com/2017/10/31/health/puerto-rico-water-epa-superfund-test-results/index.html.

[127] U.S. Environmental Protection Agency, “EPA Hurricane Maria Update for Tuesday, October 31,” *United States Environmental Protection Agency*, 31-Oct-2017.

APPENDIX A

Sampling Campaign 1 & Sampling Campaign 2: Detailed Sampling Site Descriptions

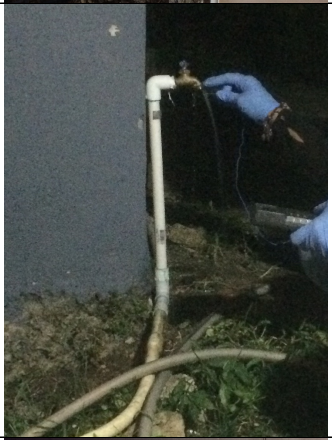
Table A1. Sampling Campaign 1 & Sampling Campaign 2: Detailed sampling site descriptions.

Site Number	***Picture***	***Description***
1		Samples were collected from a house that receives water from PRASA in the municipality of Sabana Grande. The sample port was in an outdoors tub designed to wash clothes (pileta).
		Site was revisited on April 3rd, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
2		Samples were collected from a house that receives water from PRASA in the municipality of Lajas. Samples were collected from a faucet outside towards the back of the house. Owners say that the water they receive comes from Sabana Grande.
		Site was revisited on April 3rd, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
3		The samples were collected from a house that receives water from PRASA in the municipality of Hormigueros. The sample port was in an outdoors tub designed to wash clothes (pileta). Owners of this house alleged that there is a spring that emanates from the inside of the house, they canalized it so that the water comes out of a pipeline. During the hurricane the family and neighbors were getting the water from that spring, but when we went sampling, the spring was dried.

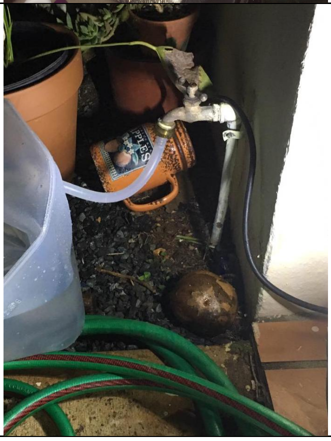
4		Samples were collected from a outdoor tap at Inter American University of Puerto Rico at Arecibo. We got permission to collect water at this site from the Science and Technology Department Head. The faucet had a garden hose connected but was disconnected prior to sample. The faucet was unused that day prior to our arrival. We repeated the sampling at this location on April 19th. Because this second sampling was not done by us but was done by the Department Head after our solicitation, the only sample accompanying our metal sample is pH data.
5		This sample was collected from the female restroom in a high school in the municipality of Utuado. Because of the central location and elevation of this town, it was hit very hard by the hurricane. We had permission from the school's principal to collect this sample and were invited by one of the high school science teachers. However, the faucet that they had dedicated for us to sample was an indoor faucet with the integrated faucet filter. There is no record on how many times was that faucet open prior to us sampling.
6		Samples were collected from a house that receives water from PRASA in the municipality of Vega Alta, in the proximity of the municipality of Dorado. The faucet was located outside the house in front of the main entrance.

7		Samples were collected from a house that receives water from PRASA in the municipality of Humacao. The faucet was located outside the house in front next to the main entrance.
8		Samples were collected from a house that receives water from PRASA in the municipality of Gurabo. The faucet was located outside the house in front next to the main entrance.
9		Samples were collected from a house that receives water from PRASA in the municipality of Trujillo Alto. The faucet was located outside the house in front next to the main entrance.

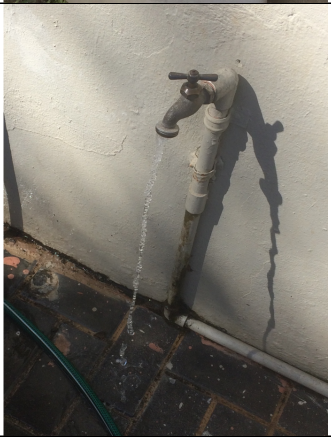
10		Samples were collected from a house that receives water from PRASA in the municipality of San Juan. The faucet was located outside by the back of the house.
		Site was revisited on March 29, 2018, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
11		Samples were collected from a house that receives water from PRASA in the municipality of Adjuntas. The faucet was located outside the house. There are about 5 houses in this location, all of them are family houses. The sample was collected from a faucet that is located in front of a garage where they keep their washing machine. The faucet had a garden hose connected, but the hose was disconnected when we collected the samples.
12		This house receives water from PRASA. Although it is located in the municipality of Coamo, the owners indicate that the water they receive is from the municipality of Barranquitas. The tap was located outside the house and it had a garden hose connected. The hose was disconnected before sampling. At some point, this community was a non-PRASA, that is the second tap that you see in the picture, but no water was flowing out of that tap. We ask around if any of the nearby houses had access to the community water system, but none of them have access.

13		Sample was collected from a house that receives their water from PRASA in the municipality of Santa Isabel. This is a recently constructed house (just before the hurricane). The faucet was located outside, by the back of the house. PVC pipe and brass tap.
14		Samples were collected from a house that receives water from PRASA in the municipality of Juana Díaz. The sampling tap was located outside the house by the front. Water comes through a PVC pipe and a brass tap.
15		Samples were collected from a house that receives water from PRASA in the Municipality of Yauco. The sampling tap was located outside by the front of the house. The tap had a garden hose connected, but the hose was disconnected prior to sampling.

16		Sample was collected from a house that receives water from PRASA in the municipality of San Germán. Sampling port was located outside the house.
		Site was revisited on April 1st, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
17		Samples were collected from a house that receives water from PRASA in the mountainous region of the Municipality of Mayagüez. House is located very close to the spring samples that day (18FEB18MCM01). The sampling tap was located outside the house by the front.
18		Samples were collected from a house that receives water from PRASA in town of Aguada, by the beach in a sector called Espinar. This sector was completely flooded the day of Hurricane María fromf the Culebrina River. The sampling tap was located outside the house by the front.
19		Samples were collected from a house that receives water from PRASA in town of Aguadilla. This area was completely flooded the day of Hurricane María because of the Culebrina River. Site is about 8 min drive from 18FEB18MCM04. The sampling tap was located outside the house by the front.

20		Samples were collected from a house that receives water from PRASA in Municipality of Isabela. Sampling port was outside, by the side of the house.
21		Samples were collected from a house that receives water from PRASA in Municipality of Moca. The tap was located outside, by the back of the house. Sampling port had a garden hose connected but was disconnected prior to sampling.
		Site was revisited on April 1st, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
22		Samples were collected from a house that receives water from PRASA in the Ramey Base area in the Municipality of Aguadilla. The sampling port was located outside, by the front of the house.

23		Water samples were collected from Inter American University of Puerto Rico, Ponce’s Campus. The sampling port was located outside the Student Center.
24		Water samples were collected from Inter American University of Puerto Rico Guayama’s Campus. The sampling port was located outside the building where the administrative offices are located.
		Site was revisited on March 28th, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
25		Sample was collected from a house served by a community potable water system in the municipality of San Germán. Sample was collected from a faucet located outside the house. The faucet had a garden hose connected, but the hose was disconnected it prior to sampling.

26		Samples were collected at the sampling port of a community water system (non-PRASA) in the municipality of Yabucoa, in the south east of the Island. This town is where Hurricane Maria made landfall, with the strongest winds, which were sustained in approximately 155 mph. This site has a surface water and a well to supply the water to the community, but since this is one of the most devastated town, the lack of electricity and the small capacity of their emergency generator resulted in the use almost exclusively of surface water for consumption.
27		Samples were collected from a non-PRASA system at the community sampling port. The “metal” pipe was being directly hit by the sun and those the relatively elevated temperature of the water.
28		Sample was collected from a house served by a community potable water system in the municipality of Guayama. Sample was collected from a faucet located outside by the front of the house. There was no power in the community when this sample was collected.

29		Samples were collected from the sampling port of a community potable water system in the municipality of Patillas. There was no power in the community when this sample was collected.
30		Samples were collected from a house that receives their water from a community water system in the town of Patillas. The samples were collected from outside the house. This is also the sampling port for the community. There was no power in the community when this sample was collected.
31		Samples were collected from a house that receives their water from a community water system in the town of Patillas. The samples were collected from outside the house. This is also the sampling port for the community. There was no power in the community when this sample was collected.
		Site was revisited on March 28th, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.

32		Samples were collected from the sampling port of a community water system in the town of Patillas. The sampling port was located at the base of an electricity pole. The pole was broken due to the hurricane, but the sampling faucet was still intact. There was no power in the community when this sample was collected and the sample was collected late at night.
33		Samples were collected from a house that receives their water from a community water system in the town of Patillas. The samples were collected from outside the house, by the entrance of the house there was a faucet with a garden hose. The garden hose was removed prior to sampling. There was no power in the community when this sample was collected. *First sample was collected at night, the picture is from the second sampling*
		Site was revisited on March 28th, after the initial results indicated high lead levels in the water. Sample for metal analysis was collected from the same faucet that was collected during the first sampling.
33-DIST		As part of the campaign to revisit site 22FEB18TRC08, and in order to try to investigate a high lead measurement, a sample was collected from the community sampling port.

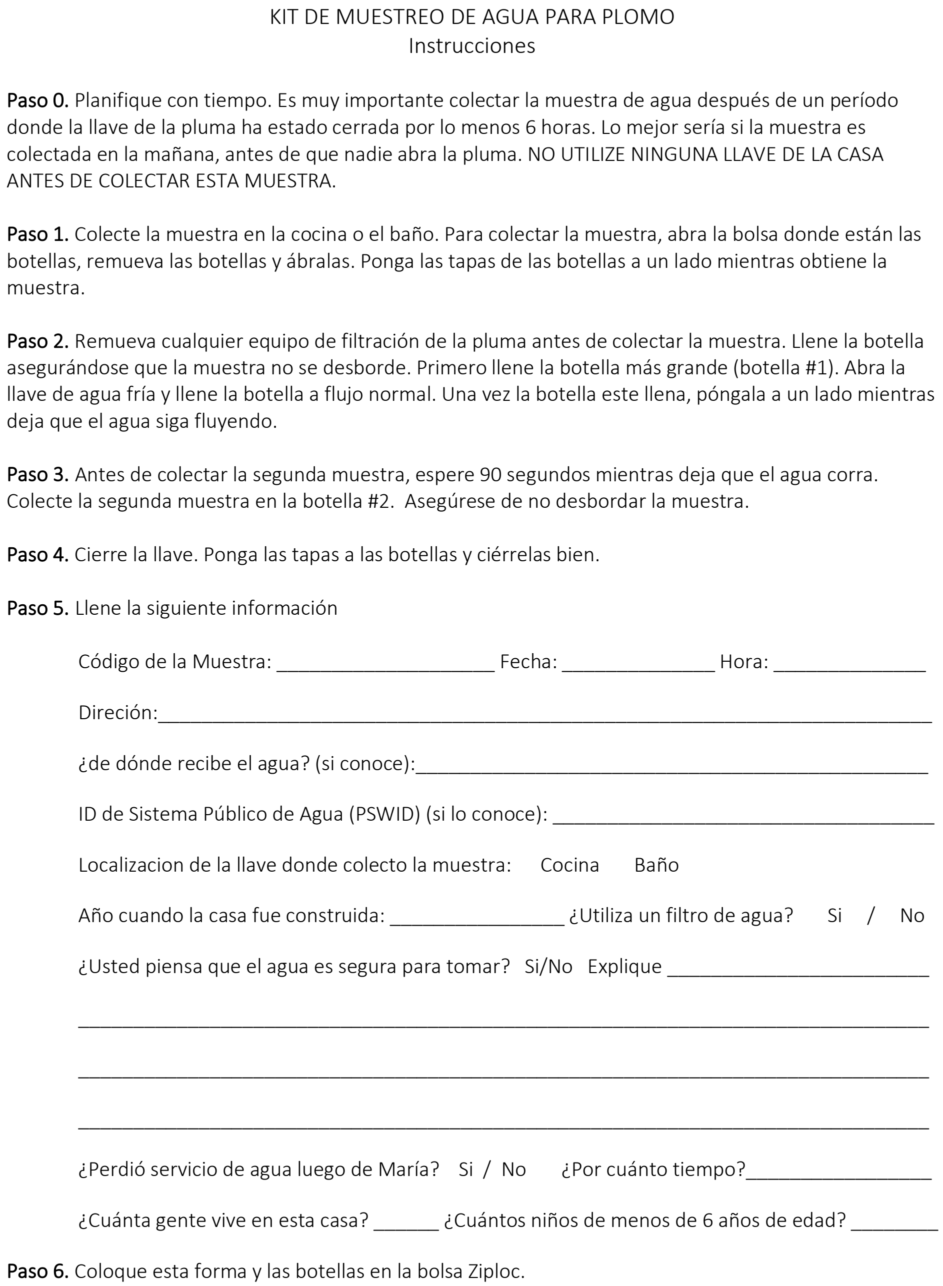
33- RAW		As part of the campaign to revisit site 22FEB18TRC08, and in order to try to investigate a high lead measurement, a raw water sample was collected, water coming directly from the pipe that brings the water to the system
33- RIVER		As part of the campaign to revisit site 22FEB18TRC08, and in order to try to investigate a high lead measurement, raw water sample was collected directly from the river. Because of access issues, the sample was collected downstream of the intake of the system.
34		Samples were collected from a natural spring at the side of road PR-120, at the borderline between the municipalities of Maricao and Sabana Grande. Spring water was flowing through an improvised bamboo pipe. At the same site there was a small water accumulation pond with a metal/aluminum pipe to drain the water. Anecdotal information suggests that hundreds of people collected water at that site during the emergency.
35		Samples were collected from a natural spring at the side of road PR-10 in direction from the Municipality of Arecibo to Utuado. There are several springs along this road. Newspaper articles have featured hundreds of people collecting water from the different springs. The water comes out of a PVC pipe, the source is not observable from the road.

36		Samples were collected from a natural spring at the side of road PR-149, in direction from Manatí to Ciales. Spring water was flowing through an PVC pipe extracting the water from the rocks. At this site there are three springs, all had PVC piping. Anecdotal information suggests that these springs have been available over a long period of time, the authors have indications of people collecting water from these springs even when Hurricane Georges hit the Island in 1998.
37		Samples were collected from a natural spring along highway 52, near the municipality of Caguas. Spring water was flowing through an PVC pipe. There are at least two more springs like this one along this highway, all had PVC piping. Anecdotal information suggests that these springs have been available over a long period of time. Travelers sometimes stop and refill water bottles and even fill up water storage tanks(sisternas) at this site
38		Water samples were collected from a natural spring. Water is coming out of metal pipe from a spring located along road PR-5518 in the Municipality of Adjuntas.

39	 	Water was coming out from a PVC pipe flowing into a bamboo pipe. Water accumulates in a reservoir, if it rains a lot, the water from the reservoir will also run through the bamboo pipe. On the day of collection, there was little flow. Anecdotal information suggests that, when PRASA turns on their well system, near this site, the flow of the spring slows down.
40	 	Samples were collected from a spring in the municipality of Mayagüez, on the border with Las Marias. The water was coming out of a metal pipe. The pipe had a green biofilm growing inside. There were two pipes, one small PVC and one metal, delivering water. Samples were collected from the metal one, because it is the more accessible to the public, it is where most people were collecting water and even taking baths at this place during the emergency. The spring water comes out of the rocks, accumulates in a small artificially made pool and flows through the metal pipe (see pictures below). The accumulation pool is covered by rocks.

APPENDIX B

Sampling Campaign 4: Sampling Kit Materials



KIT DE MUESTREO DE AGUA PARA PLOMO
Instrucciones

Paso 0. Planifique con tiempo. Es muy importante colectar la muestra de agua después de un período donde la llave de la pluma ha estado cerrada por lo menos 6 horas. Lo mejor sería si la muestra es colectada en la mañana, antes de que nadie abra la pluma. NO UTILIZE NINGUNA LLAVE DE LA CASA ANTES DE COLECTAR ESTA MUESTRA.

Paso 1. Colecte la muestra en la cocina o el baño. Para colectar la muestra, abra la bolsa donde están las botellas, remueva las botellas y ábralas. Ponga las tapas de las botellas a un lado mientras obtiene la muestra.

Paso 2. Remueva cualquier equipo de filtración de la pluma antes de colectar la muestra. Llene la botella asegurándose que la muestra no se desborde. Primero llene la botella más grande (botella #1). Abra la llave de agua fría y llene la botella a flujo normal. Una vez la botella este llena, póngala a un lado mientras deja que el agua siga fluyendo.

Paso 3. Antes de colectar la segunda muestra, espere 90 segundos mientras deja que el agua corra. Colecte la segunda muestra en la botella #2. Asegúrese de no desbordar la muestra.

Paso 4. Cierre la llave. Ponga las tapas a las botellas y ciérrelas bien.

Paso 5. Llene la siguiente información

Código de la Muestra: ____________________ Fecha: ______________ Hora: ______________

Direción:____

¿de dónde recibe el agua? (si conoce):____

ID de Sistema Público de Agua (PSWID) (si lo conoce): ______________________________

Localizacion de la llave donde colecto la muestra: Cocina Baño

Año cuando la casa fue construida: ________________ ¿Utiliza un filtro de agua? Si / No

¿Usted piensa que el agua es segura para tomar? Si/No Explique ________________________

____

____

____

¿Perdió servicio de agua luego de María? Si / No ¿Por cuánto tiempo?_________________

¿Cuánta gente vive en esta casa? ______ ¿Cuántos niños de menos de 6 años de edad? ________

Paso 6. Coloque esta forma y las botellas en la bolsa Ziploc.

Figure A1. Sampling Campaign 4: Instruction sheet for residents included in sampling kits.

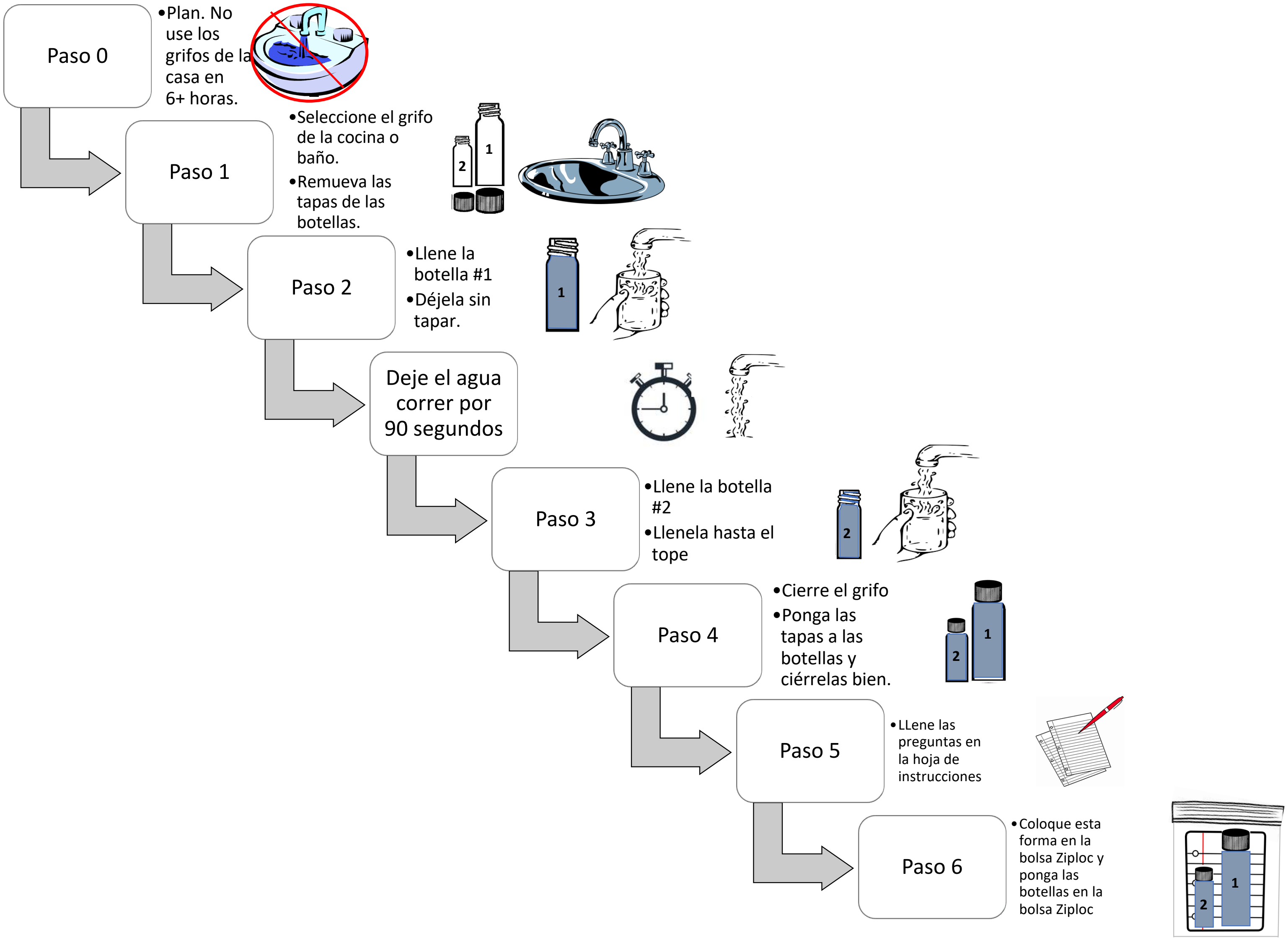


Figure A2. Sampling Campaign 4: Pictogram on the back of the instruction sheet that was included in sampling kits.

APPENDIX C

Detailed Sampling Methods and Analysis Laboratories

Table A2. Sampling Campaign 1, 2, 3, & 4: Parameters measured for all sampling campaigns and the subsequent sampling methods and analysis laboratories.

Parameter		***Sampling Campaign***			
		1	***2***	***3***	***4***
pH	Location	Field			CU Boulder Environmental Engineering Laboratory
	Instrument	Oakton pH 450 or Oakton pH 300 series			OrionStar A211 or Orion VersaStar Pro
	Method	Standard Methods for the Examination of Water and Wastewater 21st Edition. Method 4500 H+ pH Value			
	Description	From free stream flow after water is allowed to equilibrate. Measurements are recorded after stable reading			Probe placed directly in 500 mL sample (SC4-B2)
Temperature	Location	Field			Not measured
	Instrument	Fluke 51 K/J Thermometer			-
	Method	Standard Methods for the Examination of Water and Wastewater 21st Edition. Method 9060 Samples			-
	Description	From free stream flow after water is allowed to equilibrate. Measurements are recorded after stable reading			-

Parameter		***Sampling Campaign***			
		1	***2***	***3***	***4***
Conductivity	Location	Not Measured	Not Measured	CU Boulder Environmental Engineering Laboratory	
	Instrument	-	-	Orion VersaStar Pro	
	Method	-	-	Standard Methods for the Examination of Water and Wastewater 23rd Edition. Method 2510 Conductivity	
	Description	-	-	Place probe directly in 500 mL bulk water quality sample bottle (SC3-B4 or SC4-B2)	
Free Chlorine	Location	Field			Not measured
	Instrument	HACH Free and Total Chlorine Test Kit Model #CN-66			-
	Method	HACH Method Document #2231-88			-
	Description	From free stream flow after water is allowed to equilibrate			-

Parameter		***Sampling Campaign***			
		1	***2***	***3***	***4***
Total Chlorine	Location	Field			Not measured
	Instrument	HACH Free and Total Chlorine Test Kit Model #CN-66			-
	Method	HACH Method Document #2231-88			-
	Description	From free stream flow after water is allowed to equilibrate			-
Turbidity	Location	Field			CU Boulder Environmental Engineering Laboratory
	Instrument	HACH 2100P Turbidimeter			HACH 2100N Turbidimeter
	Method	Standard Methods for the Examination of Water and Wastewater 21st Edition. Method 2130 Turbidity.			HACH Method 8195
	Description	Directly from flow from the tap			Using aliquot from SC4-B1 or SC4-B2

Parameter		***Sampling Campaign*** ***1***	***2***	***3***	***4***
Alkalinity	Location	CU Boulder Environmental Engineering Laboratory	Not Measured	Field	CU Boulder Environmental Engineering Laboratory
	Instrument	HACH Digital Titrator Model #16900	-	HACH Digital Titrator Model #16900	HACH Digital Titrator Model #16900
	Method	HACH Method 8203			
	Description	Post-filtration 2 months after collection 50-100mL aliquot from 500 mL sample	-	Immediately	Pre-filtration Within 2 weeks of collection 50-100mL aliquot from 500 mL sample
DOC	Location	CU Boulder Environmental Engineering Laboratory	Not measured	CU Boulder Environmental Engineering Laboratory	Not measured
	Instrument	Sievers M5310C Laboratory TOC Analyzer	-	Sievers M5310C Laboratory TOC Analyzer	-
	Method	SM Method 5310C and EPA Method 415.3	-	SM Method 5310C and EPA Method 415.3	-
	Description	30 mL aliquot from 500 mL sample 0.7 rinsed GF/F micron filter	-	30 mL aliquot from 500 mL sample 0.45 rinsed GF/F micron filter	-

Parameter		*Sampling Campaign*			
		1	*2*	*3*	*4*
UV_{254}	Location	CU Boulder Environmental Engineering Laboratory	Not measured	CU Boulder Environmental Engineering Laboratory	Not measured
	Instrument	Cary 100-Bio UV/Visible Spectrophotometer	-	Cary 100-Bio UV/Visible Spectrophotometer	-
	Method	-	-	-	-
	Description	Post-filtration 2 mL aliquot from 500 mL sample	-	Post-filtration 2 mL aliquot from 500 mL sample	-
Select Ions	Location	Rocky Mountain Research Station (RMRS) Biogeochemistry Laboratory	Not measured	Rocky Mountain Research Station (RMRS) Biogeochemistry Laboratory	TBD[3]
	Instrument	ThermoFisher Integrion Ion Chromatograph	-	ThermoFisher Integrion Ion Chromatograph	
	Method	Anions: EPA Method 300.0 PO42- SO42- NO42- Br+ Cl- F- Cations: ASTM D6919-03 **Ca+ Mg+ K+ Na+ NH_4^+**	-	Anions: EPA Method 300.0 PO42- SO42- NO42- Br+ Cl- F- Cations: ASTM D6919-03 **Ca+ Mg+ K+ Na+ NH_4^+**	
	Description	Post-filtration 50 mL aliquot from 500 mL sample	-	Post-filtration 50 mL aliquot from 500 mL sample	

Parameter		***Sampling Campaign***			
		1	***2***	***3***	***4***
Trace Elements[1]	Location	Laboratory for Environmental and Geologic Sciences (LEGS) at CU Boulder		Not Measured	TBD
	Instrument	Perkin Elmer SCIEX ICP-MS Model 87Elan DRC-e.		-	
	Method	EPA Method 200.8		-	
	Description	Post-acidification 10 – 20 mL aliquot from 125 mL sample		-	
Pb and Cu[2]	Location	LEGS	LEGS	Denver Water	TBD
	Instrument	Perkin Elmer SCIEX ICP-MS Model 87Elan DRC-e.	Perkin Elmer SCIEX ICP-MS Model 87Elan DRC-e.	Agilent Technologies 7900 series	
	Method	EPA Method 200.8	EPA Method 200.8	EPA Method 200.8	
	Description	Post-acidification 10 to 20 mL aliquot from 125 mL sample	Post-acidification 10 to 20 mL aliquot from 125 mL sample	Post-acidification 250 mL aliquot from 1L sample	

[1] Trace Elements: Ag, Al, As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ge, Hf, H, La, Lu, Mn, Mo, Nb, Nd, Ni, P, Pb, Pd, Pr, Pt, Rb, Rh, Ru, Sc, Sb, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, Y, Yb, Zn, Zr, **Ca+, Mg+, K+, Na+.** The ions in bold were also measured by RMRS.

[2] While lead and copper were measured by LEGS Lab within the "Trace Elements" category, LEGS lab was not used as a resource for the Sampling Campaign 3 and therefore the Denver Water laboratory was used to specifically measure for lead and copper, which is why they are in separate row.

[3] TBD = To be determined

APPENDIX D

Method Reporting Limits and Detection Limits

If an external lab MRL or PQL was given for an analyte of interest, then the highest MRL or PQL was taken as the project PQL. If an analyte did not have a given MRL or PQL by the corresponding lab of analysis, a project PQL was calculated by multiplying by the highest MDL by 5. One-half the project PQL was taken as the value for statistical evaluations across the data sets.

Table A3. Method reporting limits and method detection limits for select trace metals.

Lab		***Limit***	***Pb (µg/L)***	***Al (µg/L)***	***Cd (µg/L)***	***Cu (µg/L)***	***Fe (µg/L)***	***Ni (µg/L)***	***Sb (µg/L)***	***Sn (µg/L)***	***Zn (µg/L)***
Denver Water	SC 3	MRL	1.0	-	-	1.0	-	-	-	-	-
		MDL	1.0	-	-	1.0	-	-	-	-	-
LEGS Lab	SC 1	MDL	0.015	1.707	0.006	0.017	23.029	0.008	0.728	0.301	0.172
LEGS Lab	SC 2	MDL	0.054	1.334	0.014	0.258	17.561	0.064	0.721	0.628	0.595
Project PQL			1.00	8.54	0.07	1.00	115	0.32	3.64	3.14	2.98

Table A4. Method reporting limits and method detection limits for select ions and nutrients.

Lab		***Limit***	Na^+ *(mg/L)*	Ca^{2+} *(mg/L)*	Mg^+ *(mg/L)*	K^+ *(mg/L)*	NO_3^- *(mg/L)*	PO_4^{3-} *(mg/L)*	Br^- *(mg/L)*	Cl^- *(mg/L)*	NH_4^+ *(mg/L)*	F^- *(mg/L)*	SO_4^{2-} *(mg/L)*
RMRS Lab	SC 1 SC 2 SC 3	PQL	0.03	0.1	0.04	0.03	0.02	0.06	0.04[2]	0.05	0.03	0.03	0.01
		MDL	0.01	0.02	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01
LEGS Lab	SC 1	MDL	0.002	0.001	0.0009	0.0055	-	-	-	-	-	-	-
LEGS Lab	SC 2	MDL	0.007	0.013	0.0007	0.0063	-	-	-	-	-	-	-
Project PQL			0.03	0.1	0.04	0.03	0.02	0.06	0.04	0.05	0.03	0.03	0.01

[1] Due to the low concentrations of antimony, a project PQL of 1 [2] The MRL was used instead of the PQL for this constituent