

Benton Harbor Drinking Water Study



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by

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Cover Photo: EPA personnel installing a faucet-mounted water filter on a kitchen faucet in Benton Harbor, MI. Taken November 17, 2021.

Foreword

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Abbreviations

AL	Action Level
BCHD	Berrien County Health Department
BRL	Below Reporting Limit
BSD	Back Scatter Detection
CCT	Corrosion Control Treatment
CESER	Center for Environmental Solutions and Emergency Response
CRL	Chicago Regional Laboratory
EDS	Energy Dispersive Spectroscopy
EGLE	Department of Environment, Great Lakes and Energy
FDA	Food and Drug Administration
HDPE	High-Density Polyethylene
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
kDa	Kilodalton
kV	Kilovolt
kW	Kilowatt
L	Liter
LCR	Lead and Copper Rule
LSL	Lead Service Line
mA	Milliamp
MCL	Maximum Contaminant Level
MDHHS	Michigan Department of Health and Human Services
mL	Milliliter
MOR	Monthly Operating Report
nm	Nanometer
OCCT	Optimal Corrosion Control Treatment
ORD	Office of Research and Development
OW	Office of Water
POU	Point of Use
ppb	Parts per billion
RDT	Random Daytime Sampling
SDD	Silicon Drift Detector
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
TEM	Transmission Electron Microscopy
TOC	Total Organic Carbon
XRD	X-Ray Diffraction
-5FF##	Faucet Filtered Sample, initial 5 second flush (## indicates sequential number)
-FF##	Faucet Filtered Sample, next 1 L
-PF##	Pitcher Filtered Sample of the first 1 L from tap (no 5 second flush)
-UF##	Unfiltered Sample, 2 nd L
-FFL##	Faucet Filtered Sample collected at ~7 th L
-PFL##	Pitcher Filtered Sample collected at ~7 th L
-UFL##	Unfiltered Sample collected at ~8 th L
-SS##	Sequential Samples
-DS##	Fully Flushed Water Quality Samples

-PC##-TM	Unfiltered Targeted Sample for Particle Analysis
-PC##-20	0.2 μm Syringe Filtration
-PC##-45	0.45 μm Syringe Filtration
-PC##-UL	Ultrafiltration

Acknowledgments

The authors wish to acknowledge:

- The residents of Benton Harbor that participated in these studies, for allowing access to their homes and for their cooperation with our sampling teams.
- The Michigan Department of Health and Human Services (MDHHS) and the Michigan Department of Environment, Great Lakes and Energy (EGLE) for providing personnel for sampling and for meaningful discussions about the water system and the sampling protocol.
- The Region 5 Superfund and Emergency Management Division and Community Involvement Coordinators for their involvement in organizing, coordinating, and deploying personnel to ensure this study's success.
- Neptune and Company, Inc. (Contract # EP-C-18-007) for statistical sampling design considerations and evaluation of the design achieved.
- National Student Services Contract (Contract # 68HERH20D0003) for data management and visualization.
- Abonmarche for service line inventory data.
- The 100+ individuals (federal, state, local, contractors) who had a hand in making sure this project was completed.

Executive Summary

The EPA Office of Water (OW) requested the EPA Office of Research and Development (ORD) conduct a water filter effectiveness study in Benton Harbor, Michigan, to address concerns raised by residents of Benton Harbor. ORD designed a study to evaluate water filter effectiveness, identify lead sources, and characterize particles within the plumbing materials of residences in Benton Harbor. This study was carried out in collaboration between EPA Region 5, the State of Michigan and ORD from November 9 – December 17, 2021. Just under 2,000 field samples were collected and analyzed, sampling 215 locations for the water filter effectiveness study (resulting in 199 properly installed and operated water filter study locations) and 26 locations for the sequential sampling study to evaluate premise plumbing and service line lead release. The highlights of each of the three studies are below:

- The water filter effectiveness study results show that all (100%) properly operating water filter samples were below the NSF/ANSI 53 (NSF/ANSI, 2021) and Food and Drug Administration (FDA) bottled water certification (21 C.F.R. § 165.110) requirements of 5 ppb lead (FDA).
- Galvanized iron premise plumbing and service line materials were prevalent throughout the community with 66% of all locations sampled having some galvanized premise plumbing. Results from the sequential sampling study show that the galvanized plumbing may be a source of lead to drinking water, as levels of lead (ranging from 1-25 ppb lead and an average around 6 ppb lead) were observed to persist in sections of the plumbing where galvanized pipes were observed or suspected.
- Lead particulate was identified in the community; however, single, discrete lead-containing nanoparticles (<100 nm) were not widely found or common. Combined with the water filter effectiveness results, Benton Harbor was not having the same issue with certified water filter lead breakthrough due to lead nanoparticulate that was observed by ORD in Newark, New Jersey (Lytle et al., 2020).

1.0 Introduction

The City of Benton Harbor, MI, initially exceeded EPA's Lead and Copper Rule (LCR) lead action level (AL) in 2018, after which the State required the City to conduct monitoring every 6 months according to Michigan's new Lead and Copper Provisions of the Michigan Safe Drinking Water Act (State of Michigan, Act 399 of 1976). The system continued to exceed the lead AL during five additional monitoring periods from January 2019 to June 2021; however, for the two monitoring rounds ending in December 2021 and June 2022 (EGLE, 2019, 2021a, 2022), the 90th percentile was at or below the lead AL. In response to the AL exceedances, the Michigan Department of Health and Human Services (MDHHS), through the Berrien County Health Department (BCHD), began providing the community with faucet-mounted water filters and pitcher water filters certified for NSF/ANSI 53 for lead reduction, to reduce the level of lead in tap water (FOX 17 News 2019; NSF/ANSI, 2021). In March 2019, the City began adding an 70% orthophosphate and 30% polyphosphate blended (70/30 blend) corrosion-control inhibitor at a target residual of 1.5 mg PO₄/L (EGLE, 2019, 2020). Based on the State of Michigan Department of Environment, Great Lakes and Energy's (EGLE) evaluation of subsequent monitoring results, in its February 2020 designation of optimal corrosion control treatment (OCCT) (EGLE, 2020), EGLE directed the City to change to a minimum 90% orthophosphate chemical to achieve a 3 mg PO₄/L orthophosphate residual in the distribution system. The system then made the switch to a 90% orthophosphate and 10% polyphosphate (90/10) blend in March 2020 (EGLE, 2021c).

Public concerns were raised over the effectiveness of water filters as well as the need for public education on proper water filter use (e.g., to provide information on how to properly install and maintain the filters). To support the State's response and to address concerns raised in a Safe Drinking Water Act petition filed on behalf of the residents of Benton Harbor, EPA's Office of Water (OW) requested that EPA Office of Research and Development (ORD) conduct a filter effectiveness study (Petitioners, 2021). The study was designed to address concerns that beginning in April 2020 lead was found in some LCR compliance samples above 150 parts per billion (ppb) (the maximum lead concentration in water tested for the NSF/ANSI 53 certification) and questions about whether lead nanoparticles might be forming in the water that were small enough to pass through certified filters. The lead nanoparticulate consideration was raised because of previous research ORD had conducted in Newark, New Jersey (Lytle et al., 2020). In Newark, ORD found low soluble (dissolved) lead concentrations once orthophosphate was added; instead, lead was present as mobile lead orthophosphate nanoparticles. In several Newark homes sampled, the presence of lead nanoparticulate resulted in certified filters not meeting the then NSF/ANSI 53 standard for lead (Lytle et al., 2020) of 10 ppb. On September 30, 2021, a joint press release was issued by BCHD, MDHHS, and EGLE stating that bottled water would be made available to the residents of Benton Harbor for the foreseeable future (EGLE, 2021b). Then on October 6, 2021, the state of Michigan issued a recommendation that Benton Harbor residents should use "bottled water for cooking, drinking, and brushing teeth" (MDHHS & EGLE, 2021).

A preliminary ORD literature review (manuscript in preparation) on the performance of NSF/ANSI 53 certified filters indicates that filters tested in the field almost always perform to their certification standard. However, at OW's request, and out of an abundance of caution, ORD designed and, with the assistance of EPA Region 5 and MDHHS, implemented a statistically-sound water filter effectiveness study. Sampling began on

November 9, 2021 and concluded on December 17, 2021. During that period, water from properly installed and operated water filters was collected from 199 Benton Harbor locations. In addition to the water filter effectiveness study, ORD designed two additional concurrent lead assessment studies: the first to assess lead source contributions in premise plumbing, and the second to characterize lead particles. For lead source evaluations, sequential profile sampling was performed in 26 Benton Harbor locations. To characterize lead particles, particle size fractionation and particle composition characterization was conducted at these same 26 homes. These additional studies are important considerations for corrosion control treatment (CCT) effectiveness and for characteristics of lead-containing particles that could jeopardize water filter effectiveness.

The objective of this report is to summarize results from the: (1) water filter effectiveness, (2) sequential profile, and (3) particle size fractionation studies.

2.0 Methods

The protocol and methods used in the Benton Harbor water studies are briefly described in the following pages. For further detail, the sampling protocol for the study conducted in Benton Harbor has been attached to Appendix A. Drinking Water Sampling Protocols for Benton Harbor Water Study, Version 2.5, 12/10/2021, and the associated Quality Assurance Project Plan is in Appendix B. Benton Harbor, MI Filter Performance Screening and Assessment Study, Revision 0, 11/5/2021.

2.1 Water Filter Effectiveness Study Statistical Design and Analysis

Design

The statistical design of the water filter effectiveness study was focused on whether properly operated and certified water filters were performing as they should according to their certification, which says that filtered water sample concentrations should be at or below 5 ppb lead. EPA worked with the contract statistician, Neptune and Company, Inc., to determine an appropriate sample size for evaluating water filter effectiveness in the community. The objective for the sample size calculations was to determine the 95% lower confidence bound of a 95% effective rate (95% of water filters performing as certified). An initial estimate of the percentage of filters performing as certified was needed to calculate sample size. Previously conducted water filter effectiveness field studies from Flint, MI (Bosscher, Lytle, Schock, Porter, & Del Toral, 2019) and Newark, NJ (CDM Smith 2019) were evaluated, and demonstrated that 98-100% of NSF/ANSI 53 certified water filters were effective in producing filtered water at or below 10 ppb lead (certification standard at the time of the studies¹). Using a Clopper-Pearson ‘exact’ binomial equation, confidence intervals were calculated by Neptune and Company, Inc. for various sample sizes using the lowest observed filter effectiveness rate of 98% from the field studies (Clopper & Pearson, 1934). From those assessments it was estimated that at a 98% filter effectiveness rate (98% of filters having an effluent at or below the certification standard for lead), water filter samples from 200 unique locations would be needed to prove that 95% of water filters are effective in the

¹ Prior to December 2019 water filters certified to NSF/ANSI 53 were required to have a filtered effluent of 10 ppb lead or less; but with the 2019 publication update the standard was lowered to 5 ppb lead or less (NSF, 2020).

community with 95% confidence.

An additional consideration of the sampling design was the distribution of samples across the water filters being provided in the community by the BCHD (89% faucet-mounted water filters and 11% pitcher water filters, based on BCHD records provided to EPA on September 27, 2021). Statistical advice received on the study design suggested sampling 178 (out of 200) faucet-mounted water filters and 22 (out of 200) pitcher water filters at a minimum, and to collect additional samples from pitcher water filters if possible.

Analysis

An evaluation of water filter performance in the community and adherence to the sample design was evaluated via the Clopper-Pearson ‘exact’ binomial equation (Clopper & Pearson, 1934). Unfiltered and filtered metal concentrations resulting from the water filter effectiveness study were analyzed via the $1-\alpha$ (probability) confidence interval for μ (mean of the population) based on the Student’s t distribution (Casella & Berger, 2001). Confidence intervals provided the range, in which there is 95% confidence that the true mean of the sample concentration was captured. The effect of stagnation time and service line status on unfiltered lead concentrations was evaluated using a log-transformed two-variable linear regression model.

2.2 Sampling Site Selection

Single-family residences served by the Benton Harbor Water Treatment Plant that were provided by BCHD with PUR® or Brita® faucet-mounted water filters or ZeroWater® pitcher water filters were targeted by EPA for the water filter efficacy sampling effort. The distribution of water filter types sampled from locations during the study reflected the distribution of water filter types provided to residents by the BCHD (Figure 1). Residences sampled for the water filter effectiveness study were confirmed by the sampling team to not have whole-house water filters, water softeners, or reverse osmosis units under the kitchen sink. Furthermore, schedulers targeted single-family residences with known lead service lines (LSLs), or with Benton Harbor documentation of being likely (assumed) to have an LSL. EPA completed best efforts to schedule sampling at the approximately 200 locations identified by Benton Harbor as known LSLs as of early December 2021, including locations on Smith Court where long branched LSLs (>100 ft) had been reported. (USEPA, 2022b). EPA and its partners contacted over 600 residents, distributed over 270 doorhangers, and met with residents in over 238 households regarding the filter efficacy study.

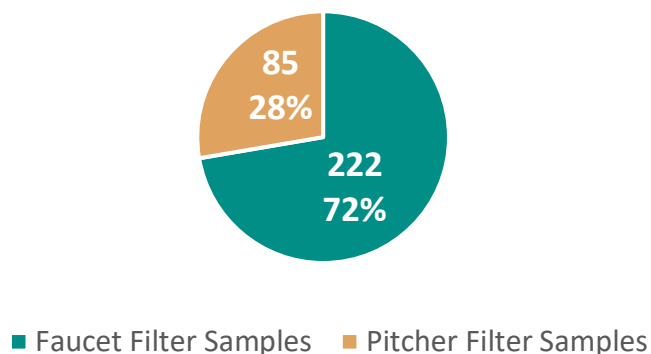


Figure 1. Distribution of faucet-mounted and pitcher water filters sampled in water filter effectiveness study.

For the concurrent lead assessment study, a smaller subset of locations within Benton Harbor were sampled to understand lead sources present, any leaded particulate, and the state of CCT. This study included sequential sampling and targeted particulate sampling with different size filters to assess lead sources and particles present within the drinking water (USEPA, 2022a). The MDHHS had already conducted some sequential profile samples within the City prior to EPA's study. For the concurrent lead assessment study, EPA evaluated MDHHS' sequential data and prioritized locations that had higher and consistent (if data from multiple sampling events were available) sequential profile lead levels and known or assumed LSLs. However, site selection was heavily influenced by resident availability and willingness to participate in the study. The MDHHS data was also used to target the water volume with historically high lead concentrations at each site for the particulate analysis. The peak lead concentration from the previous MDHHS sampling(s) was selected for a one-liter (1-L) particulate characterization analysis.

During the home visits for both the water filter efficacy and concurrent lead assessment studies, the sampling team collected information from the residents and made observations (if allowed by the resident), including but not limited to details about the customer side service line material, interior premise plumbing pipe materials, type of water filter, operating status of the water filter, use of whole house water filters/softeners, and water stagnation time.

2.3 Water Filter Study Sampling Protocol

The water filter effectiveness study was designed to evaluate whether properly certified and operated faucet-mounted and pitcher water filters reduced lead to at or below 5 ppb. For this study, properly operated faucet-mounted water filters included those that had a green or yellow indicator light when the samples were taken, and only had cold water run through them (indicator lights on the faucet-mounted water filters were volume based with 100-gallon capacities). Properly operated pitcher water filters were within the total dissolved solids (TDS) operating bounds for the ZeroWater® filters, and only had cold water run through them.

Initially, no special instructions regarding water stagnation time were provided to residents in advance of water filter effectiveness sampling. Water samples were collected at random stagnation times (random daytime (RDT) samples) as reported by the residents. After reviewing data on samples collected in November, it was noted that most of the reported stagnation times were 1 hour or less. To gather more varied stagnation times and particularly longer stagnation times which can be associated with higher lead levels, a revision was made to the sampling protocol (Appendix A. Drinking Water Sampling Protocols for Benton Harbor Water Study, Version 2.5, 12/10/2021). For residences who had a scheduled appointment for sample collection the week of 11/29/21, during the confirmation call schedulers encouraged those residents to stagnate their water (2-6+ hours) prior to the sampling visit. For all residences that were scheduled (receiving their sample appointment date/time) on or after 11/29/21, those residents were required to stagnate their water for 6+ hours prior to the sampling visit. If a resident was unable to accommodate the request for stagnation the scheduler made a note, did not schedule that location, and moved on to the next priority site.

While only properly operated water filters were considered as valid samples, the sampling team observed inadequately maintained water filters (i.e., red or malfunctioning light, hot water was used through the filter, or TDS reading outside of the operating limit), and the water was still sampled through these water filters. When compromised water filters were observed, the EPA sampling team provided water filter education

to the resident and replaced the water filter cartridge (following manufacturer instructions). If the faucet-mounted water filter or pitcher water filter was compromised, the replacement water filter was sampled if the newly installed water filter cartridge did not require a conditioning step. If a conditioning step was necessary, EPA attempted to schedule a follow-up sampling visit for a later date. All samples were collected without altering or removing aerators on the faucet.

2.3.1 Faucet-Mounted Water Filter Sampling Procedure

First, with the water filter in the “on” position, the cold-water tap was turned on and the first 5 seconds of filtered water (-5FF##) was collected in a 500 mL or 250 mL wide-mouth high-density polyethylene (HDPE) bottle. This (-5FF##) sample is not considered proper use since according to the faucet-mounted water filter operation instructions, the first 5 seconds of use is to be wasted rather than consumed; however, this water sample was collected and analyzed for metals. Immediately following the 5 second flush sample, without turning the water off and taking care not to spill, a 1-L sample of filtered water was collected in a wide-mouth HDPE bottle (-FF##, 1st liter). Next, the water filter was switched to bypass mode without turning the water off, and a 1-L sample of unfiltered water was collected (-UF##, 2nd liter).

2.3.2 Pitcher Water Filter Sampling Procedure

Any water that was found to be in the pitcher on sampler arrival was transferred to another container so that the pitcher was completely empty to start. The cold-water tap was turned on, and a first draw unfiltered 1 L sample (-PF##) was collected in a 1-L HDPE bottle. Immediately following without turning off the water, a second unfiltered 1 L sample (-UF##) was collected without allowing any water to spill. The first liter of water that was collected (-PF##) was turned “end over end” five times to mix and then poured into the empty pitcher water filter. Once the sample passed completely through the water filter the filtered water was poured into a new sample bottle for laboratory analysis (-PF##). Some water poured into the pitcher water filter has the potential to be retained within the water filter (when the filter is new), so that the volume of pitcher filtered water was slightly less than the influent volume. If the filtered water sample did not have enough volume to reach the 1 L mark on the sample bottle, an additional sample of water was collected and filtered in the pitcher until there was enough filtered water effluent to fill the bottle.

2.3.3 Service Line Water Filter Study Samples

After a review of preliminary data, beginning with samples collected on and after 12/2/21, an additional pair of samples were collected during water filter sampling visits (Appendix A. Drinking Water Sampling Protocols for Benton Harbor Water Study, Version 2.5, 12/10/2021). These samples targeted water in contact with the service line that was approximated to be at the 7th liter based on review of past MDHHS sequential profile lead data. The intent was to find higher lead concentrations to challenge the water filters by targeting water that had a greater chance to capture the lead contribution directly from known or assumed LSLs (if present). Once the first unfiltered sample (-UF##, 2nd liter) was collected, the cold water was allowed to run (if a faucet-mounted water filter, the filter was in bypass mode) while filling and wasting 1 L sample bottles until 4 L of water had been flushed after the initial two 1 L samples (-FF## or -PF## and then -UF##). Then filtered service line and unfiltered service line samples were collected as described below:

Faucet-Mounted Water Filter Sites: The water filter was switched to the on position and the first 5 seconds of filtered water was wasted, then a 1 L service line sample of filtered water was collected (-FFL##, 7th liter). Immediately following the service line (-FFL##, 7th liter) sample, without turning off the water, the water filter was switched to bypass mode and a 1 L sample of unfiltered water was collected (-UFL##, 8th liter).

Pitcher Water Filter Sites: A 1 L service line sample was collected (-PFL##, 7th liter). Immediately following the service line sample without turning off the water, a second 1 L sample (-UFL##, 8th liter) was collected. The -PFL## sample was then filtered through the pitcher water filter as previously described.

2.3.4 Temperature and Free and Total Chlorine Measurements

Once all water filter study samples had been collected, the cold (unfiltered) water was allowed to run for an additional 5 minutes. After completing the flush, a Hach (Hach Company, Loveland, CO) SL1000 portable parallel analyzer was used according to Hach Method 10260 (EPA approved DPD (N, N-diethyl-p-phenylenediamine) to measure free and total chlorine. Free chlorine levels less than 0.2 mg Cl₂/L (screening level determined by the state of Michigan) were resampled after an additional 5 minutes of flushing. If the sample still contained less than 0.2 mg Cl₂/L free chlorine, the MDHHS member of the sampling team collected a water sample for bacteriological (total coliform) analysis. MDHHS was responsible for microbiological analyses (i.e., total coliform and E. coli) and reporting results back to residents. Additionally, a NIST traceable thermometer was used to measure the flowing water temperature. Field equipment was unavailable for two water filter effectiveness study sites (locations 3351 and 3554), in those cases water samples were taken back to the field office within two hours of sampling and analyzed for free and total chlorine.

2.3.5 Not True Paired Samples

While at least two sequential 1-L samples were taken from each residence (filtered and unfiltered), the samples cannot be misconstrued as actual pairs. Lead in drinking water is a variable contaminant and is closely related to the individual sections of plumbing and lead sources the water sits in contact with (1 L samples representing ~20 ft of ½” copper type M) (Triantafyllidou et al., 2021). Therefore, the actual lead concentrations loaded onto the water filter in this study are unknown, and it cannot be assumed that if the unfiltered sample associated with a location was below the reporting limit (BRL) that the water which was filtered also had an initial lead concentration BRL. The same applies for a lead detect in the unfiltered sample, meaning lead-laden water of the same concentration may or may not have passed through the water filter. Lead concentrations going onto the water filter could be higher or lower than what was observed in the unfiltered sample.

There is no methodology possible to get an actual paired field sample, where the concentration of lead going onto the water filter is known. It is conceivably possible when sampling pitcher water filters as a portion of the water collected to be filtered could be preserved and analyzed. However, there remains uncertainty in distributing any present particulate lead, between the water collected, and the water that goes through the

pitcher filter. This discrepancy highlights the necessity of ensuring a statistically representative number and distribution of water samples are collected (see Section 2.1), so that the sample size is large enough to capture the variability in multiple plumbing configurations, water filter use patterns, and lead concentrations.

2.4 Sequential Sampling Protocol

Residents were instructed by EPA to flush cold water through the faucet in the intended sampling location for 5 minutes at least 6 hours prior to their scheduled sampling. This pre-flush was only conducted at sequential sampling locations and was not part of the water filter effectiveness study protocol. The purpose of the pre-flush was to fill the plumbing with fresh water from the water main, so that after the stagnation time the sequential sampling would provide more representative information on the sources of lead for each specific volume of water sampled. Once the resident completed the 5-minute flush, they then turned off the faucet and did not use any water in the house. Sequential samples were collected by EPA only after the resident verified that water in the entire home had been stagnant for 6+ hours.

The first two sequential samples in the profile were collected in 125 mL HDPE bottles to identify smaller lead containing premise plumbing components near the tap (i.e., faucet and connected plumbing) (-SS01 and -SS02). The rest of the sequential samples were collected in 500 mL HDPE bottles (-SS##), except that a 1 L HDPE bottle was included in each set of sequential samples targeting the anticipated highest lead concentration for particle size fractionations (particulate characterization sample) (-PC##-TM). The location of the 1 L sample bottle within the sequential set was predetermined by identifying the location of the peak lead level observed in sequential samples that were previously collected from the locations by MDHHS. The number of sequential sample bottles equated to approximately 16 L per site, unless previous sequential sample results from the residence suggested that a larger or smaller number of samples were necessary to collect water from the sample tap to the water main.

Bottles were prelabeled and arranged in sequential order on a nearby surface. The cold-water tap was turned on (bypass mode if a faucet-mounted water filter was present) so that the first volume of water out of the tap was carefully collected (lower flow rate) in the first sequential sample bottle (125 mL). Immediately following the first sequential sample, without turning the water off and taking care not to spill, the second sample was collected. After the first two 125 mL bottles the flow rate was increased and sampling continued until all bottles allocated for the sampling site were filled.

Once sequential sampling was complete, the cold water was allowed to continue flushing at the maximum flow rate for an additional 5 minutes. After 5 minutes of flushing, three 500 mL HDPE sample bottles were collected, and temperature was measured. The first flushed sample was analyzed for metals, the second and third samples were analyzed for background water quality including alkalinity and total organic carbon (TOC). Water was also collected and analyzed on-site, if possible, for free chlorine, total chlorine, and total alkalinity. Free and total chlorine were measured using a Hach (Hach Company, Loveland, CO) SL1000 portable parallel analyzer according to Hach Method 10260 (EPA approved DPD (N, N-diethyl-p-phenylenediamine) method) and Hach Method 10280 (also for the SL1000) was used to measure total alkalinity. Total alkalinity Hach Chemkeys® were unavailable for one field visit to location 3446, in that case there are no field measurements for total alkalinity, but that location does have laboratory results. Free chlorine levels less than 0.2 mg Cl₂/L were resampled after an additional 5 minutes of flushing. If the sample still

contained less than 0.2 mg Cl₂/L free chlorine, the MDHHS member of the sampling team collected a water sample for bacteriological (total coliform) analysis. MDHHS was responsible for microbiological analyses (i.e., total coliform and E. coli) and reporting results back to residents. As a last step, flow rate was reduced to the width of a pencil and four Erlenmeyer flasks of water were collected with no headspace; these samples were analyzed for pH in the field laboratory.

2.5 Particulate Sampling Protocol

2.5.1 Water Filtrations- Particulate Fractionation

Sample filtrations and solid sample collection occurred on the 1 L peak-targeted sequential sample, within 2 hours of sample collection to reduce the likelihood that metal particulate could continue to change over time. Once back at the field laboratory, the 1 L bottle was turned “end over end” five times to mix before a portion of water was screened for lead using the Kemio™ heavy metals analyzer (Figure 2). The Kemio™ was used only as a screening technique in the field and Kemio™ results were not used for any subsequent data analysis, all water samples were analyzed via ICP-MS for lead. At the beginning of the study this step was used as a screening mechanism to only complete the filtrations when the lead concentration measured ≥ 9.5 ppb. Beginning on November 23, 2021, all samples were filtered regardless of Kemio™ reading, as it was suspected that the presence of particulate lead in a sample may have caused a false low Kemio™ reading. This change in the sampling protocol is why only 16 samples were filtered for solids analysis, and not all 26 sequential sampling locations.

After Kemio™ analysis, the 1 L bottle was turned “end over end” again, five times to mix before water was used for each of the various filtrations detailed below. For the syringe filtrations, each syringe was rinsed with 5 mL of sample water (rinsed and wasted) before drawing up sample water (Figure 2). Then 50 mL of water from the 1 L sample bottle was filtered through a 0.45 µm syringe filter into a 60 mL sample bottle, to identify the fraction of particulate lead (particle size >0.45 µm). This step was repeated from the 1 L bottle with a 0.2 µm syringe filter into a separate 60 mL sample bottle, to determine the colloidal lead fraction (particle size <0.2 µm). For ultrafiltration the stirred cell has been observed to adsorb some soluble lead. For this reason, a pre-conditioning step was developed for the stirred cell by filling it with 250 mL of sample water for at least 5 minutes to saturate the stirred cell with lead. This conditioning water was then wasted, and the cell was refilled with 250 mL of sample water that underwent filtration. This sample water was filtered through a 30 kDa ultrafilter into a 125 mL bottle for laboratory analysis, to determine the soluble fraction of lead (Figure 2). 30 kDa was determined to correlate with pore sizes smaller than 10 nm. The remaining sample in the 1 L bottle was retained for total metals analysis (Figure 2). All filtrations and the remaining sample were then field preserved according to Section 2.6.

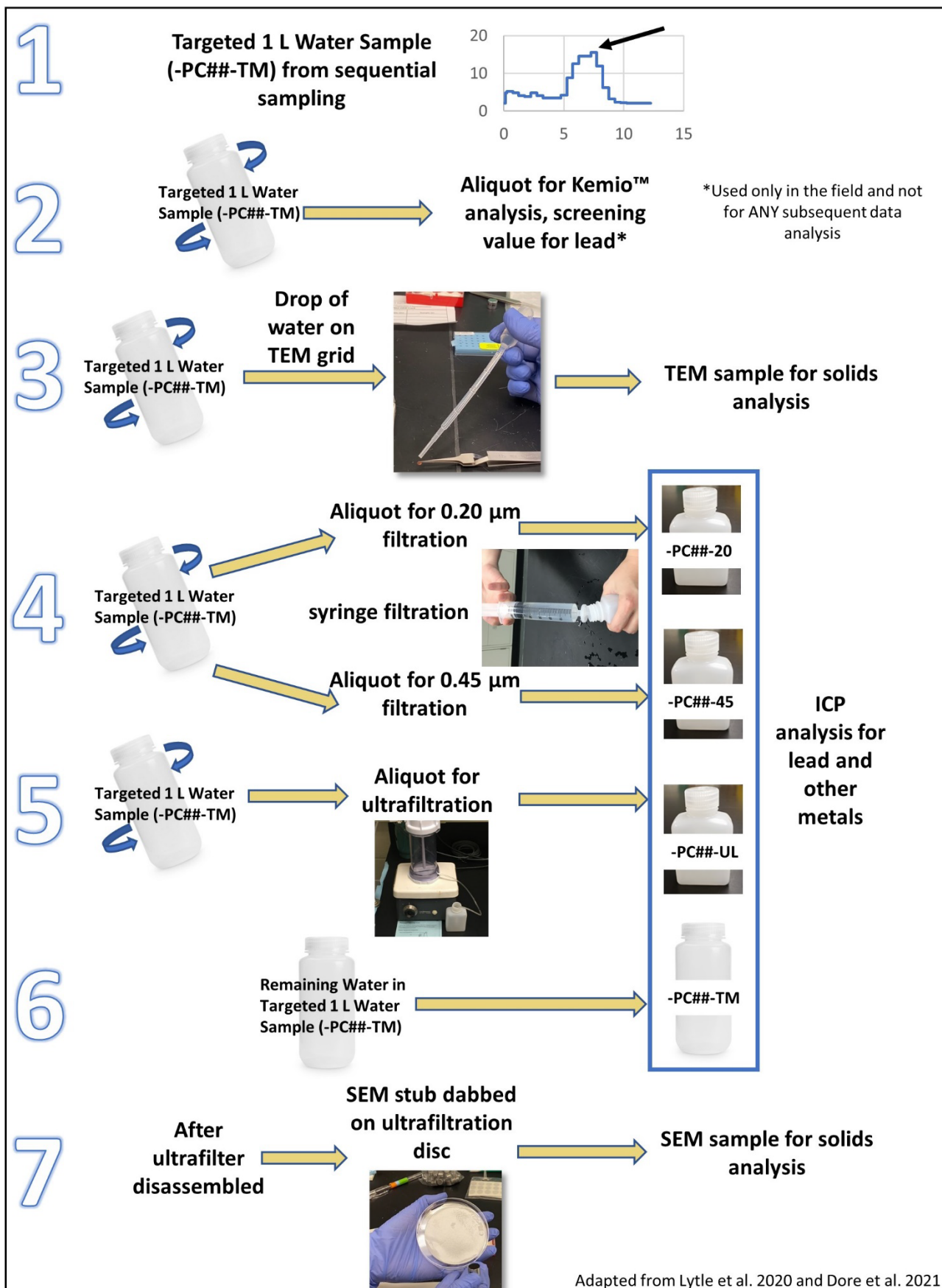


Figure 2. Sample filtrations and solid sample collection from the 1 L peak-targeted sequential sample.

2.5.2 Particulate Sampling and Solids Analysis

Lead particulate analysis for size, morphology, and elemental composition, was conducted in ORD's Advanced Materials and Solids Analysis Research Core (AMSARC) in Cincinnati, OH using transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and powder X-ray diffraction (XRD). TEM samples were prepared by collecting water from the targeted 1 L sample bottle in a disposable pipette and placing a drop of water on a 3-mm formvar/carbon coated copper TEM grid (Figure 2). The water drop was allowed to evaporate under ambient conditions so that any particles in the water were left behind on the copper grid. The samples were then examined using a JEOL JEM 2100 TEM (JEOL USA Inc., Peabody, MA) with accelerating voltage of 200 kV coupled with an Oxford X-max[®] 80 mm² silicon drift detector (SDD) EDS system running AZtec[®] software (Oxford Instruments America Inc., Concord, MA).

For SEM analysis, a SEM stub specimen mount with a carbon adhesive tab was used to collect particles from the ultrafiltration discs by lightly dabbing the adhesive on the surface of the disc (Figure 2). Then the solids were directly analyzed with a JEOL JEM7600FE SEM at a working distance of 8 mm and accelerating voltage of 15 kV (JEOL USA Inc., Peabody MA). The elemental composition of particles were identified using an Oxford X-max[®] 50 mm² SDD EDS system, spectra were analyzed using AZtec[®] software (Oxford Instruments America Inc., Concord, MA).

Powder XRD analyses were performed directly from the ultrafiltration discs, to identify crystalline solids retained by each of the filters. A 32 mm diameter disk was cut from the center of each filter and mounted on a quartz zero-background plate. An unused 'blank' of the ultrafilter was prepared and mounted in the same manner as the samples to evaluate the characteristic diffraction pattern of the filter material. Samples were analyzed using a PANalytical X'Pert Pro[®] theta-/theta powder diffractometer using Cu K α radiation generated at 1.8 kW (45 kV, 40mA) and an X'celerator[®] RTMS detector. Samples were spun at 1 revolution/s to improve particle statistics. Patterns were collected in continuous scan mode, from 5 to 89.994° 2 θ at a scan speed of 0.01181°/s, with data binned into 0.0167113° steps. Diffraction patterns were analyzed using Jade+ version 9.8 software and the 2021 ICDD PDF-4+ database.

2.6 Water Sample Preservation and Analysis

Samples collected for metals analysis were field preserved with nitric acid to pH <2. Samples collected for background water quality parameters and TOC were placed in a cooler with ice and reduced to a temperature of <6° C (See Table 1 for methods and preservation requirements). TOC samples were also field preserved to pH <2 using sulfuric acid. All water samples were taken by courier to EPA Region 5's Chicago Regional Laboratory (CRL) in Chicago, Illinois, generally within 48 hours, for analysis. CRL analyzed metals samples by EPA Methods 200.8 (lead, copper, zinc) and 200.7 (aluminum, calcium, cadmium, chromium, iron, potassium, magnesium, manganese, sodium, nickel, phosphorus, silica, and tin). The reporting limit for lead was 0.5 ppb, other analyte reporting limits are in Table 1. Some samples were analyzed with higher reporting limits due to dilutions; those analytes, their reporting limits, and associated samples are in Table 2. Background water quality samples were not collected at each water filter study site; those analyses were only conducted on fully flushed water during the concurrent sequential sampling study.

In accordance with the target minimum of one per 20 samples, over 100 field blanks were collected,

associated with the approximately 1,800 field samples for metals analysis. Field blanks were filled with Milli-Q® water (lab distilled water that is passed through a mixed bed resin column before use) at the field laboratory, capped and taken out to sampling sites. During the sampling visit, the field blank bottle was uncapped and left open in the sampling location while samples were collected. Once all samples had been collected at the sampling location the bottle was capped and placed in the cooler and subsequently field-preserved with the rest of the samples. No field blanks were found to contain lead above the reporting limit of 0.5 ppb.

The data were validated against the laboratory and field performance requirements before data analysis was performed. A pooled analysis of variance based on replicate analyses of field samples suggests a standard deviation of 0.26 ppb lead for samples that fall above the reporting limit of 0.5 ppb to 30 ppb lead.

Analyte	Instrumentation	Method	Reference	Reporting Limit	Units	Sample Volume/Bottle Type	Preservation	Hold Time
Total Organic Carbon (TOC)	Combustion	CRL SOP	AIG021D ¹	2	mg/L	Single 500 mL/HDPE ² bottle	<6° C; H ₂ SO ₄ to pH<2; No headspace	28 days (48 hour hold time for NO ₂ and NO ₃)
Total Alkalinity	Titrimetric pH 4.5	CRL SOP	AIG005A ³	20	mg CaCO ₃ /L	Single 500 mL/HDPE bottle	<6° C	48 hours for PO ₄ , NO ₂ and NO ₃ ; 14 days for alkalinity; 28 days for the rest
Orthophosphate (PO ₄)	IC ⁴	CRL SOP	AIG045A ⁵	0.25	mg/L			
Fluoride (F ⁻)	IC	CRL SOP	AIG045A	0.02	mg/L			
Chloride (Cl ⁻)	IC	CRL SOP	AIG045A	0.12	mg/L			
Nitrite (NO ₂ – as Nitrogen)	IC	CRL SOP	AIG045A	0.12	mg/L			
Nitrate (NO ₃ – as Nitrogen)	IC	CRL SOP	AIG045A	0.12	mg/L			
Sulfate (SO ₄)	IC	CRL SOP	AIG045A	0.12	mg/L			
Lead (Pb)	ICP-MS ⁶	CRL SOP	SOP ⁷	0.50	ppb	Single HDPE bottle (1L, 500mL, 125mL, or 60mL)	HNO ₃ to pH<2	6 months (if acid-preserved within 14 days)
Copper (Cu)	ICP-MS	CRL SOP	SOP ⁷	2	µg/L			
Zinc (Zn)	ICP-MS	CRL SOP	SOP ⁷	10	µg/L			
Aluminum (Al)	ICP-AES ⁸	CRL SOP	SOP ⁹	0.5	mg/L			
Calcium (Ca)	ICP-AES	CRL SOP	SOP ⁹	0.5	mg/L			
Cadmium (Cd)	ICP-AES	CRL SOP	SOP ⁹	0.002	mg/L			
Chromium (Cr)	ICP-AES	CRL SOP	SOP ⁹	0.005	mg/L			
Iron (Fe)	ICP-AES	CRL SOP	SOP ⁹	0.08	mg/L			
Potassium (K)	ICP-AES	CRL SOP	SOP ⁹	0.8	mg/L			
Magnesium (Mg)	ICP-AES	CRL SOP	SOP ⁹	0.2	mg/L			
Manganese (Mn)	ICP-AES	CRL SOP	SOP ⁹	0.008	mg/L			
Sodium (Na)	ICP-AES	CRL SOP	SOP ⁹	0.4	mg/L			
Nickel (Ni)	ICP-AES	CRL SOP	SOP ⁹	0.012	mg/L			
Phosphorus (P)	ICP-AES	CRL SOP	SOP ⁹	0.2	mg/L			
Silica (Si, as SiO ₂)	ICP-AES	CRL SOP	SOP ⁹	0.2	mg/L			
Tin (Sn)	ICP-AES	CRL SOP	SOP ⁹	0.02	mg/L			

Table 1. Collection and analytical method requirements for general water chemistry and inorganic analyses performed at the Chicago Regional Laboratory (CRL).

¹ Standard operating procedure AIG021D for the analysis of organic carbon, total, in water based on standard method 5310B

² High-Density Polyethylene

³ Standard operating procedure AIG005A for the analysis of alkalinity in water based on standard method 2320B

⁴ Ion Chromatography

⁵ Standard operating procedure AIG045A for the analysis of anions in water by ion chromatography based on EPA method 300.0

⁶ Inductively Coupled Plasma-Mass Spectrometry

⁷ Standard operating procedure for the analysis of metals by ICP-MS, EPA method 200.8/SW-846 6020B Using the Agilent 7700x, Metals 001 version 11

⁸ Inductively Coupled Plasma-Atomic Emission Spectroscopy

⁹ Standard operating procedure for the analysis of metals by ICP, EPA method 200.7/6010D Using the Thermo 6500 Duo, Metals003A version 9

Analyte	Instrumentation	Reporting Limit	Samples Analyzed with Different Reporting Limit
Zinc (Zn)	ICP-MS ¹	50 µg/L	BH4730-PC03-TM ²
Nickel (Ni)	ICP-AES ³	0.06 mg/L	BH4588-5FF01 ⁴
Phosphorus (P)	ICP-AES	1 mg/L	BH4862-5FF01
		2.5 mg/L	BH2937-5FF01
Potassium (K)	ICP-AES	4 mg/L	BH4862-5FF01, BH4394-5FF01, BH3389-5FFh01 ⁵
		10 mg/L	BH2937-5FF01
Silica (Si, as SiO ₂)	ICP-AES	1 mg/L	BH4362-5FF01, BH4522-5FF01, BH2323-5FF01, BH3457-5FF01, BH4723-5FFe01 ⁶ , BH2505-5FFh01, BH2267-5FF01, BH4862-5FF01, BH4703-5FFe01, BH3268-5FF01, BH4315-5FF01, BH2827-5FF01, BH3312-5FF01, BH3368-5FF01, BH4303-5FF01, BH4300-5FF01, BH5449-5FF01, BH3389-5FFh01
Sodium (Na)	ICP-AES	2 mg/L	BH4862-5FF01, BH4394-5FF01, BH3389-5FFh01
		5 mg/L	BH2937-5FF01

Table 2. Alternative Reporting Limits in Data.

¹ Inductively Coupled Plasma-Mass Spectrometry

² PC##-TM- Particle characterization- total metals sample (associated with sequential sampling study)

³ Inductively Coupled Plasma-Atomic Emission Spectroscopy

⁴ 5FF##- Five second flush sample (associated with faucet-mounted water filter study samples)

⁵ 5FFh##- Five second flush sample, hot water use (associated with faucet-mounted water filter study samples)

⁶ 5FFe##- Five second flush sample, improper use (associated with faucet-mounted water filter study samples)

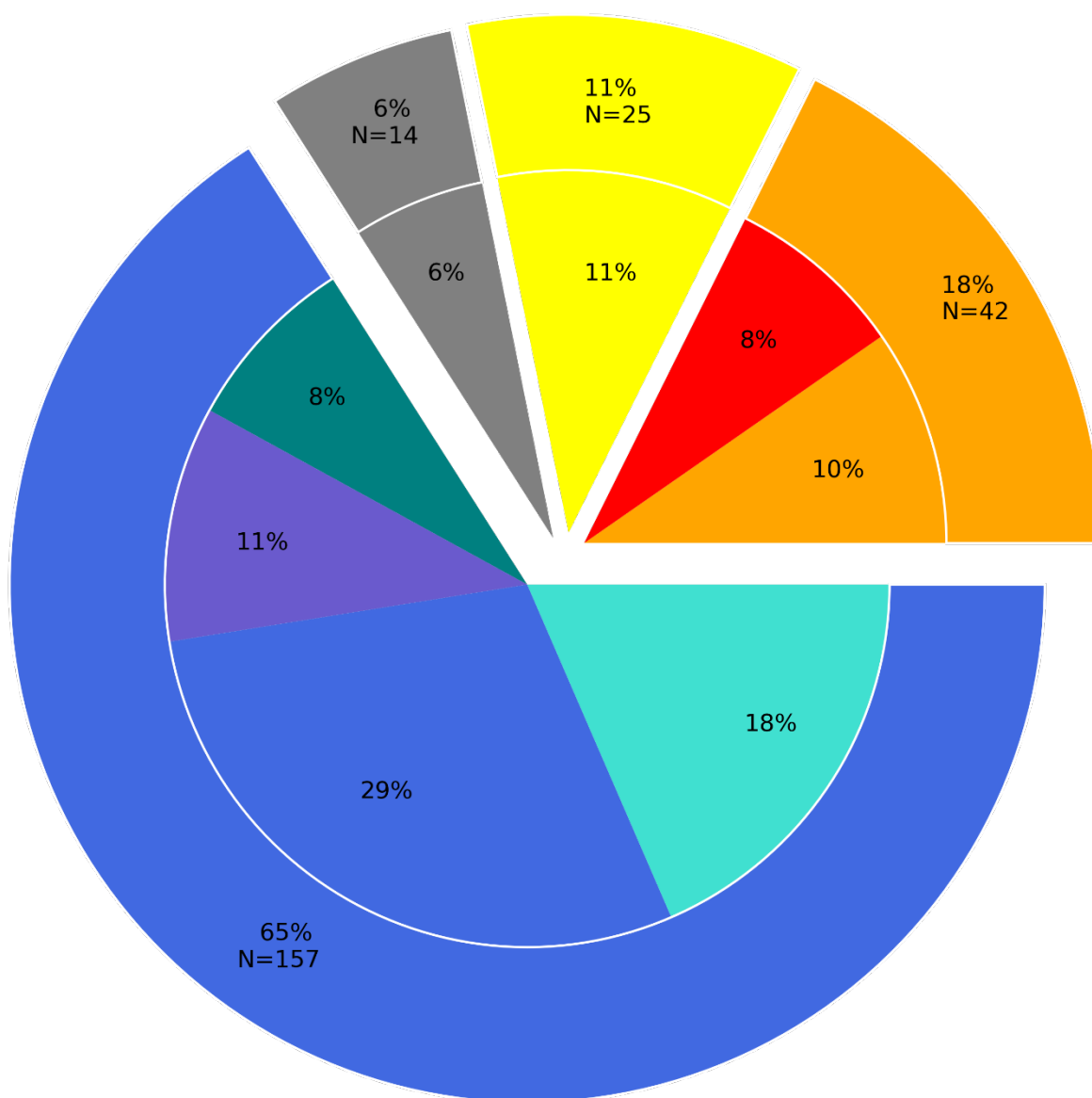
3.0 Results and Discussion

3.1 Premise Plumbing and Service Line Observations

The types of premise plumbing materials observed by the sampling teams are summarized in Figure 3. Premise plumbing is defined in this study as any plumbing materials downstream of the meter (typically located just inside the foundation) and within the residential structure. Galvanized pipe was the most common material observed in sampled homes. Of the 238 study locations visited, 157 (66%) locations were observed to have galvanized iron premise piping alone or in combination with other materials. This is a particularly noteworthy observation as galvanized pipe can contain lead and can accumulate lead over time when downstream of an LSL (AWWARF-TZW, 1996; Clark, Masters, & Edwards, 2015; HDR, 2009; McFadden, Giani, Kwan, & Reiber, 2011; Pieper, Tang, & Edwards, 2017; Sandvig et al., 2008). Eighteen percent (42) of the locations had copper containing plumbing, 11% (25) contained plastic plumbing, and at 14 locations (6%) the premise plumbing was not observed. Forty-six (46) of the study locations have copper containing premise plumbing with the potential for leaded solder as their build years are on or prior to the prohibition of leaded solder (containing more than 0.2% lead) in 1986 (USEPA, 2022d).

The service line type for the 199 valid water filter study locations at time of sampling is shown in Figure 4. The service line data is based on visual observations collected by Abonmarche. At each service connection the service line was visually observed at both the curb stop (excavation and exposure of both sides of the curb stop) and meter (inside the residence). One-hundred and thirty-three (66%) of the 199 valid water filter effectiveness study sample sites had known LSLs, this includes 5 full LSLs, 18 lead to copper service lines, and 110 lead to galvanized iron service lines (Figure 4). Although EPA was not able to gain access for every one of the approximately 200 locations identified by Benton Harbor as known LSLs (as of early December 2021) for sampling, the percentage of confirmed LSL sites in the study (66%) exceeds the percentage of confirmed LSLs in the community at the time (4-6%). Some assumed LSL sites turned out to be non-LSL sites, but these data are still represented in the filter study. There are 30 copper to copper service lines, 34 copper-galvanized iron service lines, 1 full galvanized iron service line, and 1 full PEX service line represented in the filter study data.

Premise Plumbing Percentage N = 238



- Copper N=23
- Copper/Plastic N=19
- Plastic N=25
- Not observed N=14
- Galvanized iron/Copper/Plastic N=19
- Galvanized iron/Copper N=25
- Galvanized iron N=69
- Galvanized iron/Plastic N=44

Figure 3. Premise plumbing materials observed from all study locations.

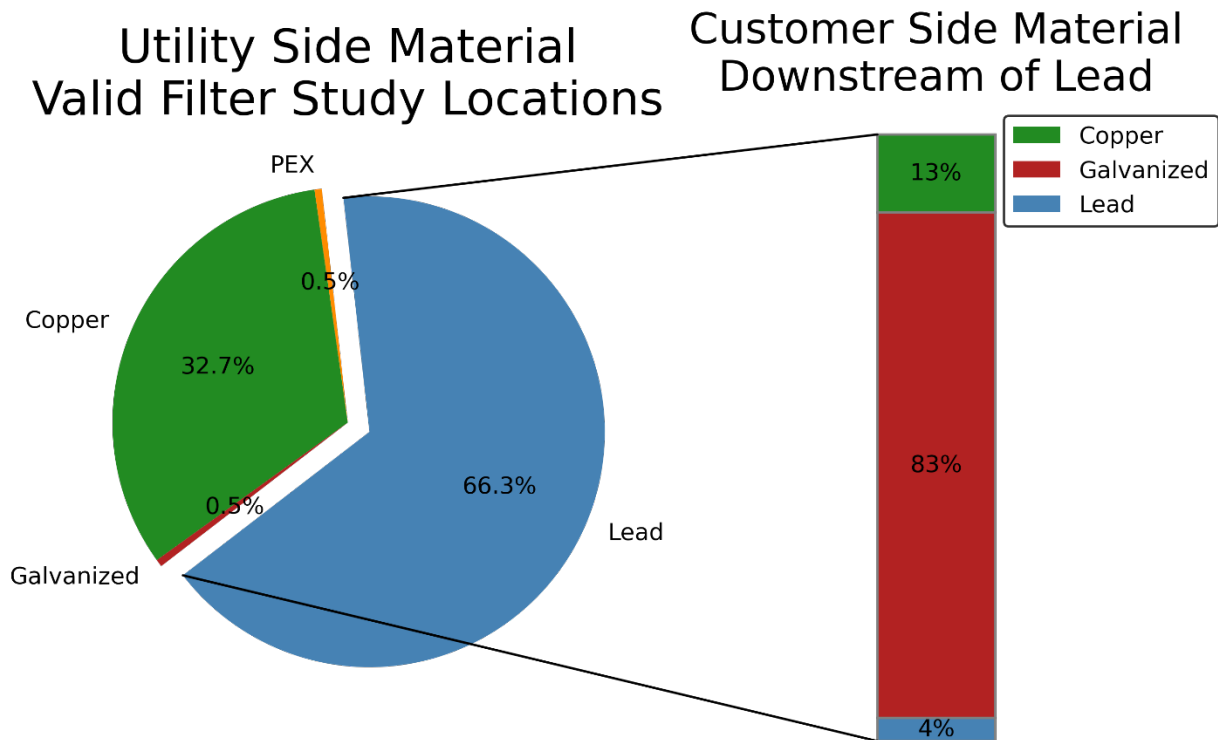


Figure 4. Valid water filter study location utility side service line types at the time of sampling (N=199). Customer side detail included for the utility side lead sites.

Utility side service line designations for residences participating in the sequential sampling study were based on Abonmarche's records (Figure 6). Twenty-four of the twenty-six locations in the sequential sampling study had a lead containing service line, and 83% of those locations also had a customer side galvanized service line (20).

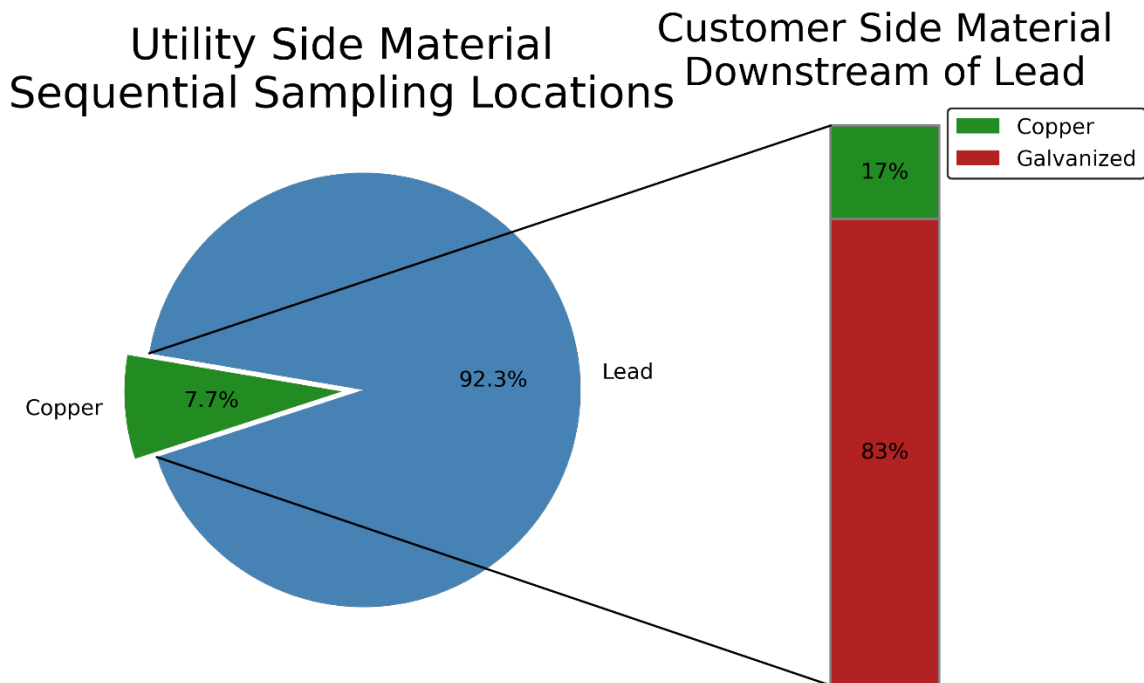


Figure 6. Sequential sampling study location utility side service line types at the time of sampling (N=26). Customer side detail included for the utility side lead sites.

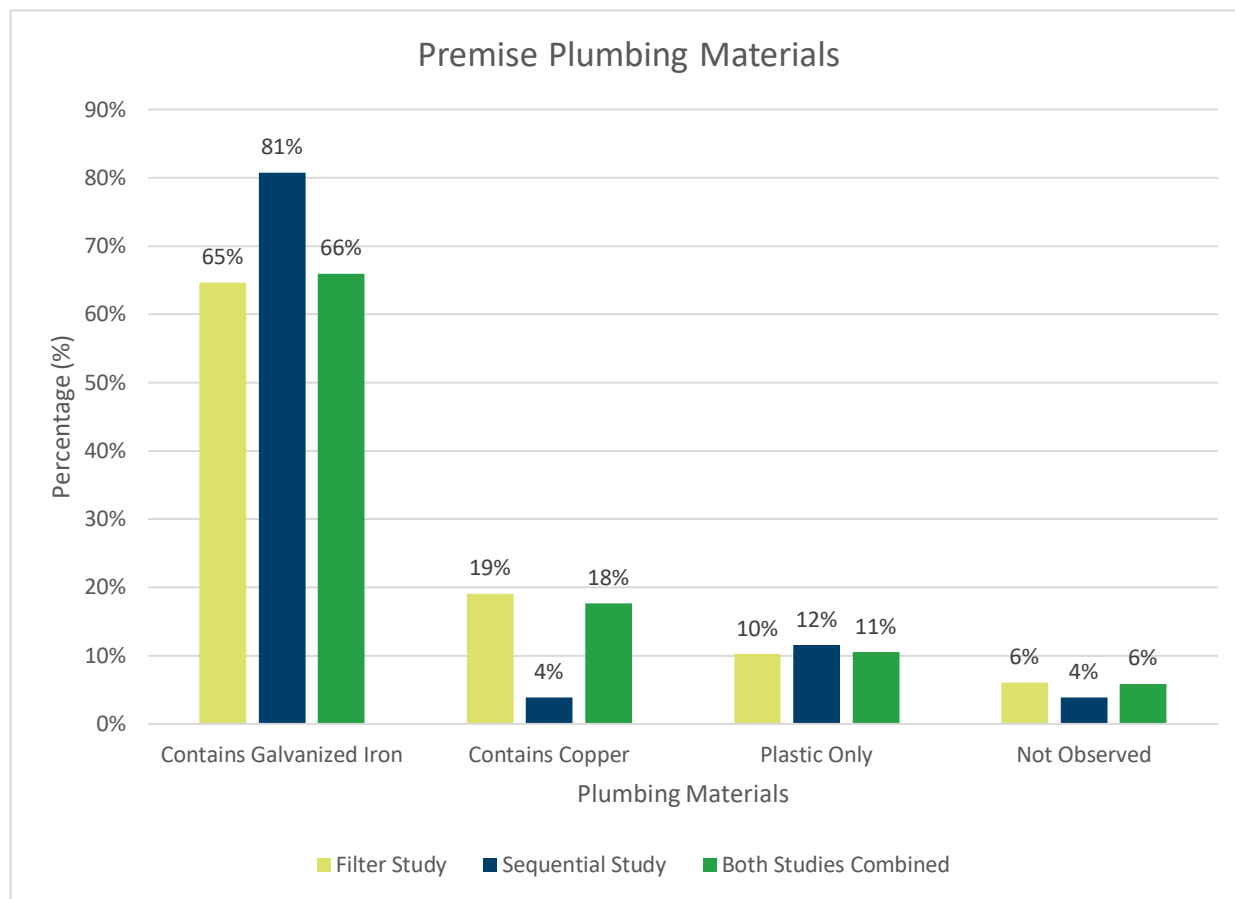


Figure 5. Premise plumbing materials represented in sampling efforts.

The occurrence of galvanized iron piping in this community is noteworthy. 66% of the locations included in this sampling study (water filter effectiveness and sequential) had some galvanized iron piping within their premise plumbing (Figure 5), whether it was galvanized iron only or galvanized iron plus a combination of copper and plastic piping. Additionally, the sequentially sampled homes represented the premise plumbing observed in the filter effectiveness study, while oversampling locations with some galvanized premise plumbing and under sampling copper premise plumbing locations (including copper or copper/plastic plumbing designations) (Figure 5).

3.2 Background Water Quality and Corrosion Control Treatment at Time of Sampling

Benton Harbor is a free chlorine system that treats surface water from Lake Michigan. The system's monthly operating reports (MORs) from 2018 to 2021 were reviewed for insight into the system's recent water quality. Water quality in the distribution system was then evaluated by EPA as part of the sequential sampling study (as described in the methods section). The fully flushed samples associated with the sequential sampling study provide context on background water quality within the residences sampled. These samples also have the potential to pick up metals (such as lead and copper) as the water travels through the premise plumbing to the sampling faucet, which is dependent on many site-specific factors but can provide insight into corrosion control and the presence of lead sources (M. R. Schock, D. A. Lytle, R. R. James, V. Lal, & M. Tang, 2021). At the time of EPA's study, the system had been adding a blended phosphate as CCT for 32 months. For the first 12 months the system used a 70% orthophosphate/30% polyphosphate blend, switching to a 90% orthophosphate/10% polyphosphate blend in March 2020 and continuing that treatment through the course of EPA sampling. Lead concentrations in the fully flushed samples (associated with premise plumbing sampling sites) ranged from BRL <0.5 ppb to 8.7 ppb (Figure 7) and are discussed more in Sequential Profiles for Lead (section 3.6.1).

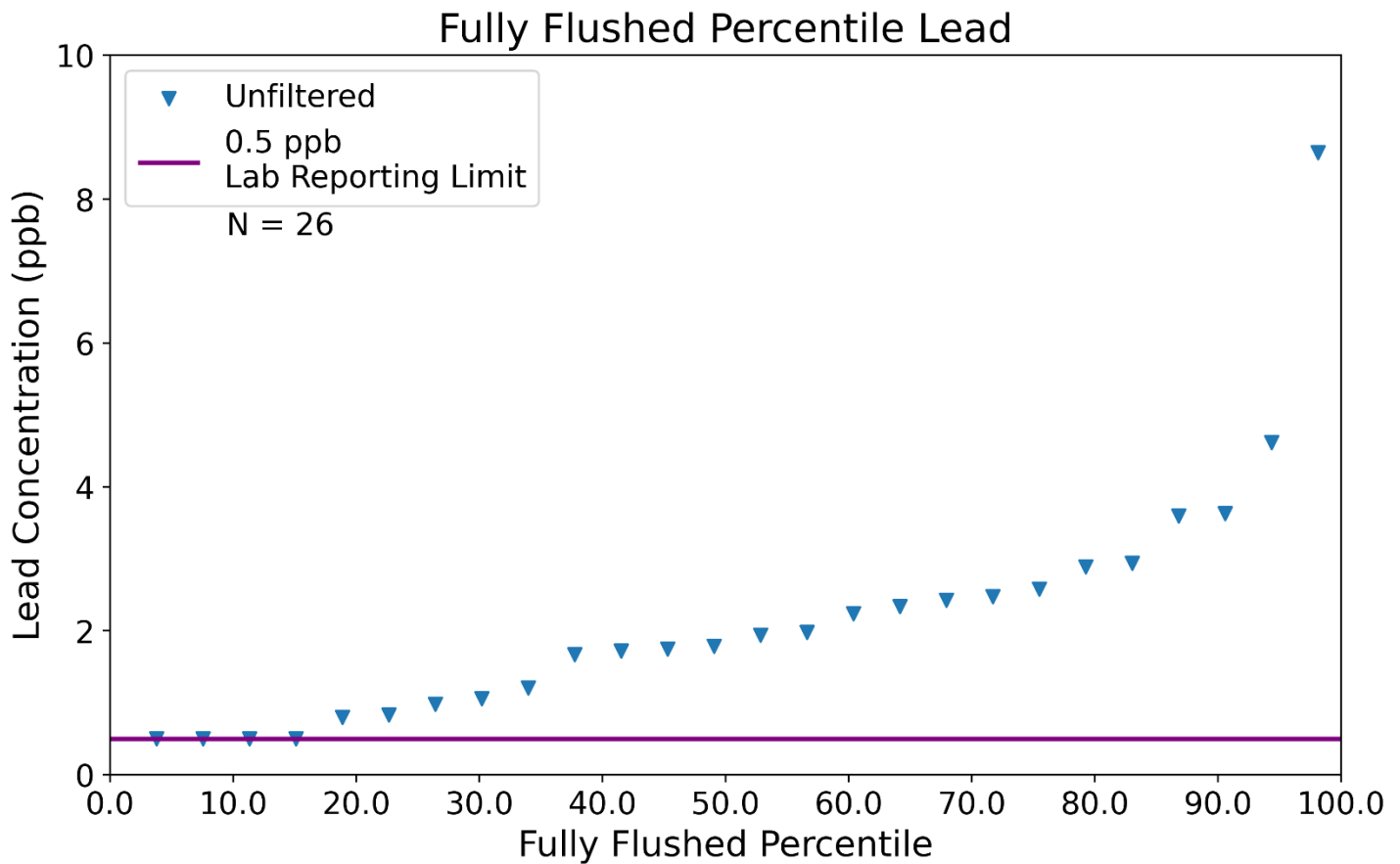


Figure 7. Fully flushed lead concentrations in samples collected during the sequential sampling study.

Comparisons between EPA’s sequential study background water quality samples, and the MOR data recorded during the same time period show relative agreement between measurements. pH measurements at the entry point to the distribution system (“plant tap”) ranged from 7.4-8.2 according to the MOR during the study period with an average of 7.9. From residential tap samples, EPA’s measurements of pH were observed to be a bit lower with an average of 7.69 (Table 3 and Figure 8). Total alkalinity measurements by CRL in the sequential study did not exhibit any variation (all were 120 mg CaCO₃/L), this is because in the laboratory standard operating procedure, data is reported with a maximum of two significant figures and no decimals (ex. ## or ##0) (USEPA, 2021). A Hach Chemkey® method (Hach Method 10280) was also used at 24 of the 26 sequential sampling locations with a range of measurements from 101-117 mg CaCO₃/L (average 106 mg CaCO₃/L). Plant tap total alkalinity as reported on the MORs from the time of the study was an average of 127 mg CaCO₃/L with a range of 110-137 mg CaCO₃/L. Chloride measurements at the plant tap averaged 25 mg/L during the course of the sequential study, while EPA collected chloride measurements from the distribution system were a bit lower between 19-22 mg/L (Table 3). Sulfate also measured lower (32-35 mg/L) in the distribution system than at the plant tap (averaged 39 mg/L) during the same timeframe (Table 3). A few historical measurements indicate the chloride to sulfate mass ratio in the system ranged between 0.6 and 0.7 2021-2022. EPA collected measurements had an average chloride to sulfate mass ratio of 0.6 over the course of the study, indicating a potential for increased galvanic corrosion (Edwards & Triantafyllidou, 2007). The sequential study collected data on orthophosphate residuals measured out in the distribution system, however on receipt of the data many samples had laboratory qualifiers (preservation issues and estimated values). After

also reviewing the total phosphorus (by ICP-AES) measurements, those measurements were converted (Equation 1) from total phosphorus to orthophosphate. The total phosphorus conversions to orthophosphate averaged 4.5 mg PO₄/L which were in line with Benton Harbor’s distribution system monitoring points (average 3.8 mg PO₄/L) and the plant tap (4.1 mg PO₄/L) and higher than the orthophosphate laboratory data with qualifiers (Table 3 and Figure 9).

Equation 1. Conversion of total phosphorus to total orthophosphate.

$$\text{Total Phosphorus} \left(\frac{\text{mg}}{\text{L}} \right) \times 3.066 = \text{Total Orthophosphate} \left(\text{mg} \frac{\text{PO}_4}{\text{L}} \right)$$

Table 3. Benton Harbor background water quality in fully flushed samples, collected from 26 sequential sampling locations.

Parameters	11/9/2021-12/16/2021 N=26
Aluminum (mg/L)	<0.5
Cadmium (mg/L)	<0.002
Calcium (mg/L)	37-43
Chloride (mg/L)	19-22
Chromium (mg/L)	<0.005
Copper (µg/L)	One detect at 2, all others <2
Fluoride (mg/L)	0.15-0.35
Free Chlorine (mg/L)	0.4-2
Iron (mg/L)	<0.08
Lead (ppb)	<0.5-8.7
Magnesium (mg/L)	12-14
Manganese (mg/L)	<0.008
Nickel (mg/L)	<0.012
Nitrate (mg/L as NO ₃)	1.5-2.3
Nitrite (mg/L as NO ₂)	<0.12
pH	7.69 (range 7.62 - 7.80)
Total Phosphorus (mg/L)	1-2
Potassium (mg/L)	1.6-1.9
Silica (Si, as mg/L SiO ₂)	2.4-3.6
Sodium (mg/L)	13-16
Sulfate (mg SO ₄ /L)	32-35
Temperature (°C)	9-18
Tin (mg/L)	<0.02
Total alkalinity (mg CaCO ₃ /L)	120
Total Chlorine (mg/L)	0.7-2.1
Total organic carbon (mg/L)	<2-3
Zinc (µg/L)	<10-86

“<” indicates values BRL for an analyte.

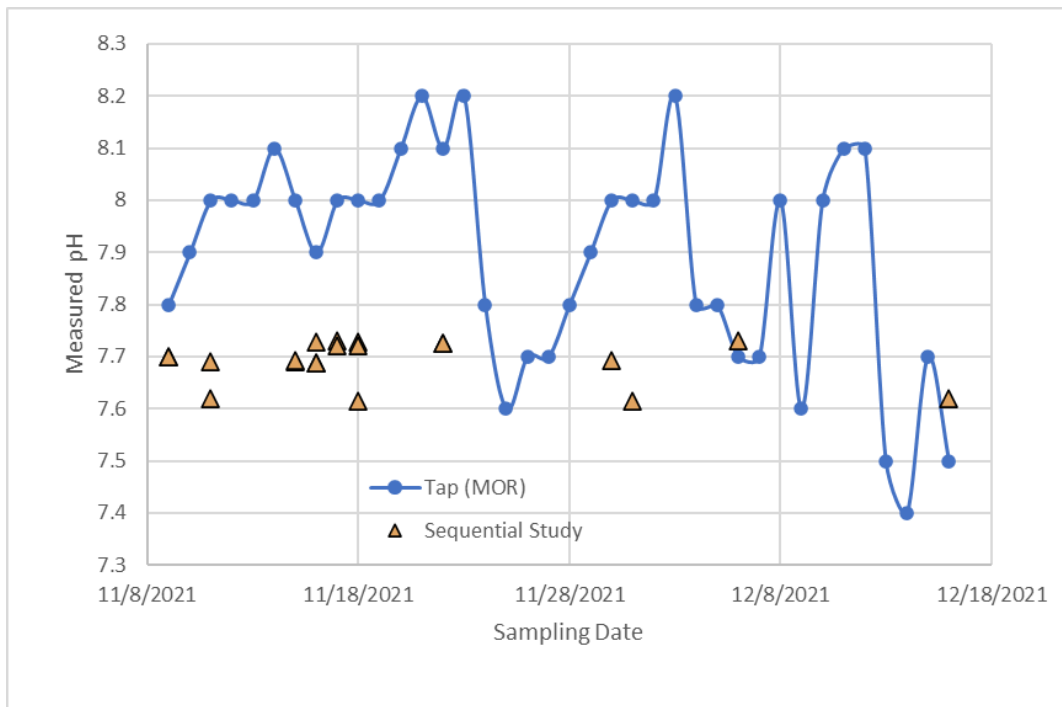


Figure 8. pH Measurements from Plant Tap (MORs) and premise plumbing (Sequential Study, 11/9 - 12/16).

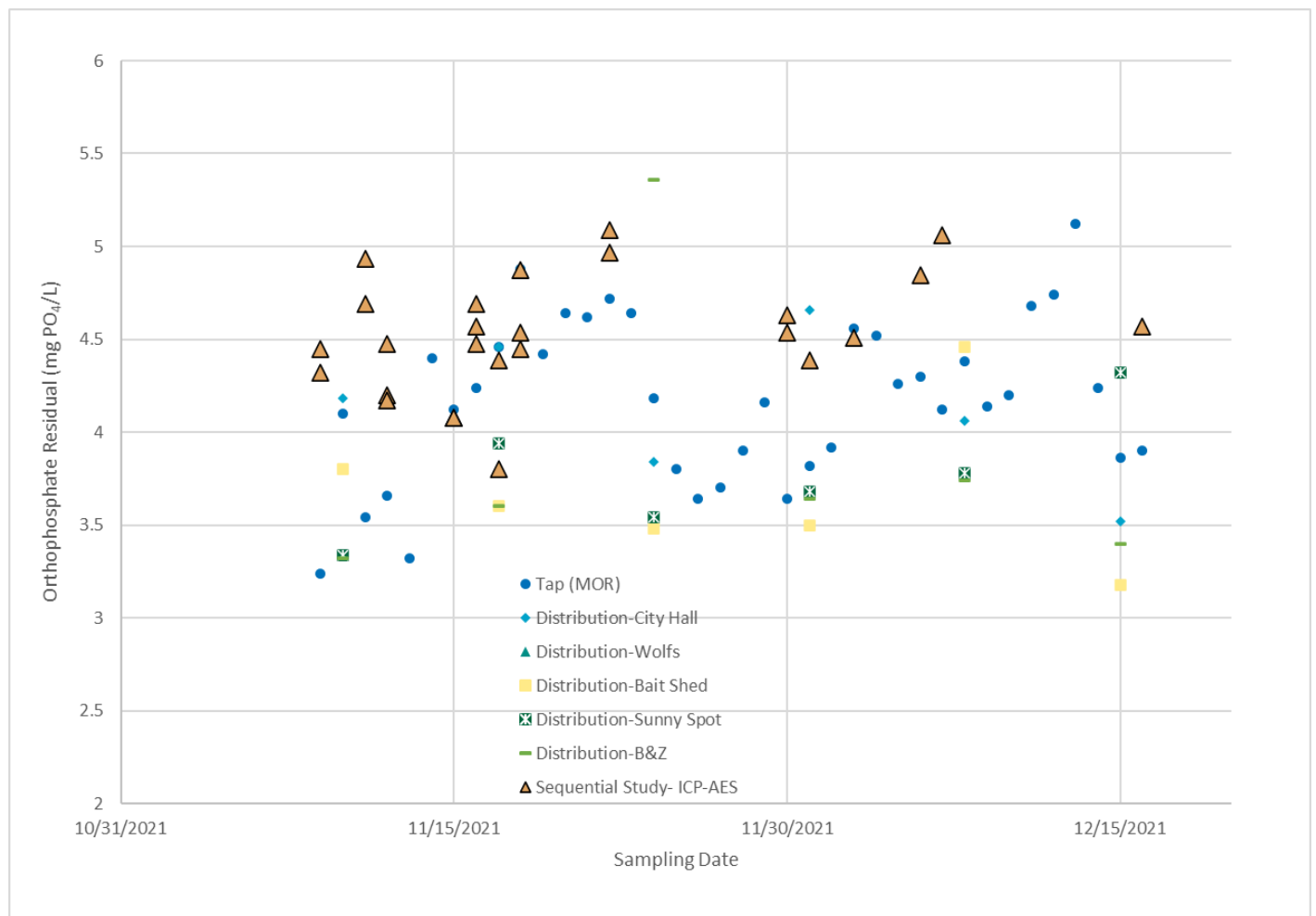


Figure 9. Orthophosphate measurements from plant tap and distribution system monitoring locations (MORs) and EPA's fully flushed sequential sampling study total phosphorus (ICP-AES) results converted to mg PO₄/L (premise plumbing) (11/9 - 12/16).

3.3 Free and Total Chlorine Results

Free and total chlorine water analyses were performed at 236 Benton Harbor locations (two locations had no recorded measurements). Free and total chlorine results ranged between 0.03 and 3.3 mg Cl₂/L and 0.07 and 3.6 mg Cl₂/L, respectively (see Appendix C. Total and Free Chlorine Results by Location). An average of 1.8 mg Cl₂/L free chlorine and an average of 2.2 mg Cl₂/L total chlorine were recorded by the utility in 2021 from the plant tap (MOR). Eleven locations had free chlorine levels <0.2 mg Cl₂/L in the first 5-minute flushed sample, and 8 of those locations still contained <0.2 mg Cl₂/L after an additional 5-minute flush. MDHHS collected samples for microbiological analyses at each location where the free chlorine residual was <0.2 mg Cl₂/L after the two 5-minute flushes, all microbiological analyses at those locations were reported by MDHHS to be non-detect.

3.4 Temperature and Seasonality

The water filter effectiveness study sampling in Benton Harbor began on November 9, 2021 and concluded on December 17, 2021. Seasonal changes to water chemistry can impact metal levels observed in water provided to customers. For example, colder temperatures can reduce the amount and rate of lead released from service line and premise plumbing materials (Deshommes, Prévost, Levallois, Lemieux, & Nour, 2013; Jarvis, Quy, Macadam, Edwards, & Smith, 2018; Masters, Welter, & Edwards, 2016; Ngueta et al., 2014; Schock & Lemieux, 2010). Therefore, this study was designed, organized, and started as rapidly as was logistically possible to minimize the possible effects of the increasingly cold source water. Historically from 2018-2021, minimum water temperatures of 2-2.5 °C in the system occur in January/February, whereas maximum water temperatures of 23-25 °C occur in August.

Temperature of fully flushed samples collected from filter study homes decreased in a linear manner over the study period from ~15 to ~9 °C (Figure 10). During the same time, no apparent decrease in unfiltered lead levels was observed, despite adding a sample that targeted the service line and requesting that residents stagnate their water. However, there are no equivalent water lead data from warmer summer temperatures to compare to the EPA collected fully flushed samples.

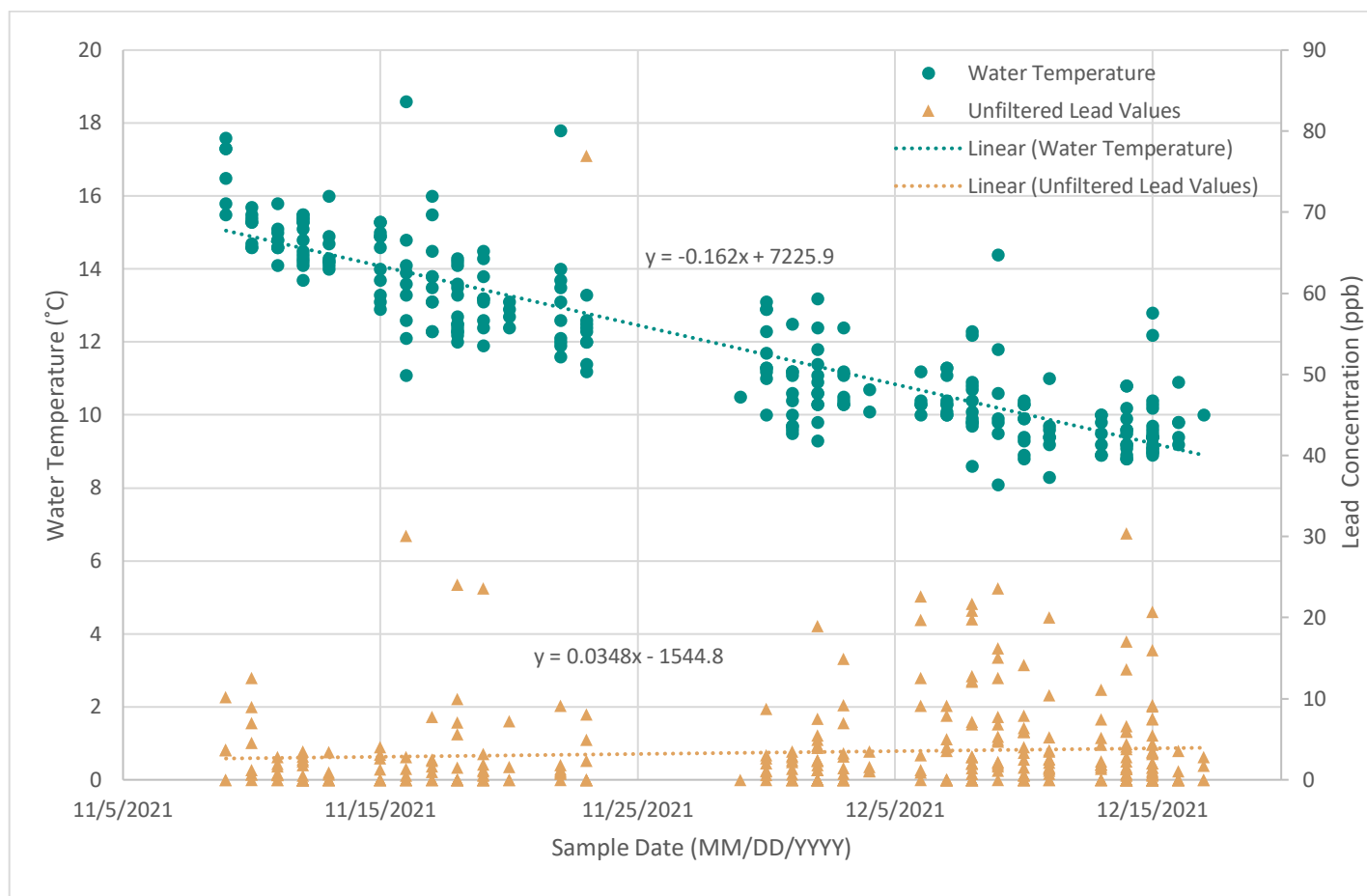


Figure 10. Unfiltered lead concentrations (N=351) and fully flushed water temperatures measured at water filter study locations. Below reporting limit (BRL) samples reported as "0" on this figure.

3.5 Water Filter Study Results

The water filter effectiveness study consisted of water samples collected from 199 locations with properly operated water filters in Benton Harbor (Table 4). In total, 306 pairs of filtered and unfiltered water samples and 1 unpaired filtered water sample (corresponding unfiltered sample was accidentally discarded) were collected. A total of 215 sites were sampled as part of the water filter effectiveness study; however, at some sites samplers encountered compromised filters (red light, hot water use, etc.) (Table 5). In many cases a repeat visit to collect a properly operating filter sample was able to be completed; however, at some locations a second visit was not possible. There were 201 first draw filtered water samples and 106 7th liter filtered water samples (see Table 4). Lead data associated with properly operating water filters has been previously released in a March 2022 data report and is included here for completeness (USEPA, 2022c).

Table 4. A total of 307 properly operated water filters were included in the study. Metadata associated with those samples is included in the table below.

Unique Locations	# Samples/Filter Status		# Samples/Type of Sample		# Samples/Type of Filter	
	Green	Yellow	First Liter	Service Line	Faucet Mount	Pitcher
199	297	10	201	106	222	85

Table 5. Exclusion reasons for the water filter study. The sampling protocol included the sampling of 5 second flush water, but that water was to be wasted per manufacturer instructions and therefore is excluded from the final analysis of properly operated water filters.

Exclusion Reason	Filter Status				Total number of filter samples collected
	Green	Yellow	Red	Malfunction	
5 second flush	151		29		-180
Hot water	18	1	7	3	-29
Red light	-	-	11	-	-11
Malfunction	-	-	-	5	-5
Total properly operating filter samples in study					307

3.5.1 All Unfiltered Water Samples

A total of 351 unfiltered samples were collected as part of the water filter effectiveness study, associated with properly and improperly operating water filters. These include 2nd liter unfiltered samples and targeted 8th liter unfiltered service line samples. Table 6 contains a summary of all the metals analyzed in the unfiltered samples and calculated 95% confidence intervals (range where with 95% confidence the true mean of the samples is expected). All 351 samples were BRL for aluminum and nickel, 350 samples were BRL for chromium and tin, and 347 and 339 samples were BRL for manganese and cadmium respectively (Table 6).

For many of the unfiltered water quality parameter results, such as calcium, magnesium, potassium, sodium, silica, zinc, and phosphorus, the 95% confidence interval captured the range observed in the fully flushed samples collected in the sequential sampling study (Table 3 and Table 6). Additionally, many of the elements in the unfiltered samples that were mainly BRL (aluminum, cadmium, chromium, iron, manganese, nickel, and tin) were also BRL in the fully flushed samples collected in the sequential sampling study. Some variation was seen with copper concentrations, where the unfiltered samples had higher copper concentrations than what was observed in the fully flushed samples. This observation was expected as the unfiltered samples targeted premise plumbing water that had the possibility of being stagnated within copper pipes whereas the fully flushed samples collected in the sequential sampling study were targeting water from the distribution system with no stagnation. The range of lead concentrations in the fully flushed samples exceeded the confidence interval calculated on the unfiltered samples, with a maximum of 8.7 ppb observed in the fully flushed samples. It should be noted that the fully flushed samples were collected from known LSL or high lead

sites selected for the sequential sampling study, whereas the unfiltered samples (as part of the water filter effectiveness study) were collected from a variety of service line material sites (Figure 4).

Table 6. Summary of water filter effectiveness study unfiltered metals results.

Unfiltered samples (N=351)						95% Confidence Interval	
Element	Instrumentation, Units	Percentage of Samples BRL¹	Maximum Concentration	Average*	Standard Deviation*	Low*	High*
Lead (Pb)	ICP-MS ² , ppb	35%	77	3.59	6.39	2.92	4.26
Copper (Cu)	ICP-MS, µg/L	55%	138	5.1	12.0	3.87	6.39
Zinc (Zn)	ICP-MS, µg/L	26%	604	62.8	84.6	54.0	71.7
Aluminum (Al)	ICP-AES ³ , mg/L	100%	BRL	351 samples BRL			
Cadmium (Cd)	ICP-AES, mg/L	97%	0.003	339 samples BRL			
Calcium (Ca)	ICP-AES, mg/L	0%	45	39.3	2.1	39.1	39.5
Chromium (Cr)	ICP-AES, mg/L	99%	0.011	350 samples BRL			
Iron (Fe)	ICP-AES, mg/L	91%	1.73	0.09	0.09	0.08	0.10
Magnesium (Mg)	ICP-AES, mg/L	0%	16	13.0	0.7	12.9	13.1
Manganese (Mn)	ICP-AES, mg/L	99%	0.049	347 samples BRL			
Nickel (Ni)	ICP-AES, mg/L	100%	BRL	351 samples BRL			
Phosphorus (P)	ICP-AES, mg/L	0%	2.6	1.5	0.2	1.4	1.5
Potassium (K)	ICP-AES, mg/L	0%	20	1.7	1.0	1.6	1.8
Silica (Si, as SiO ₂)	ICP-AES, mg/L	0%	5.3	2.92	0.25	2.90	2.95
Sodium (Na)	ICP-AES, mg/L	0%	17	13.8	0.5	13.7	13.9
Tin (Sn)	ICP-AES, mg/L	99%	0.05	350 samples BRL			

*Samples BRL are represented with the analyte reporting limit in these calculations.

¹ Below Reporting Limit

²Inductively coupled plasma-mass spectrometry

³Inductively coupled plasma-atomic emission spectroscopy

Lead concentrations in the unfiltered water samples (which were not passed through a water filter) ranged from BRL (< 0.5 ppb) to a maximum level of 77 ppb lead. Five percent (18 samples) of the unfiltered water samples were >15 ppb, 15% (51) were between 5 and 14.99 ppb and 45% (158) of the unfiltered samples were between 0.5 ppb and 4.99 ppb. Thirty-five percent (124) of the unfiltered samples were BRL for lead (Figure 11).

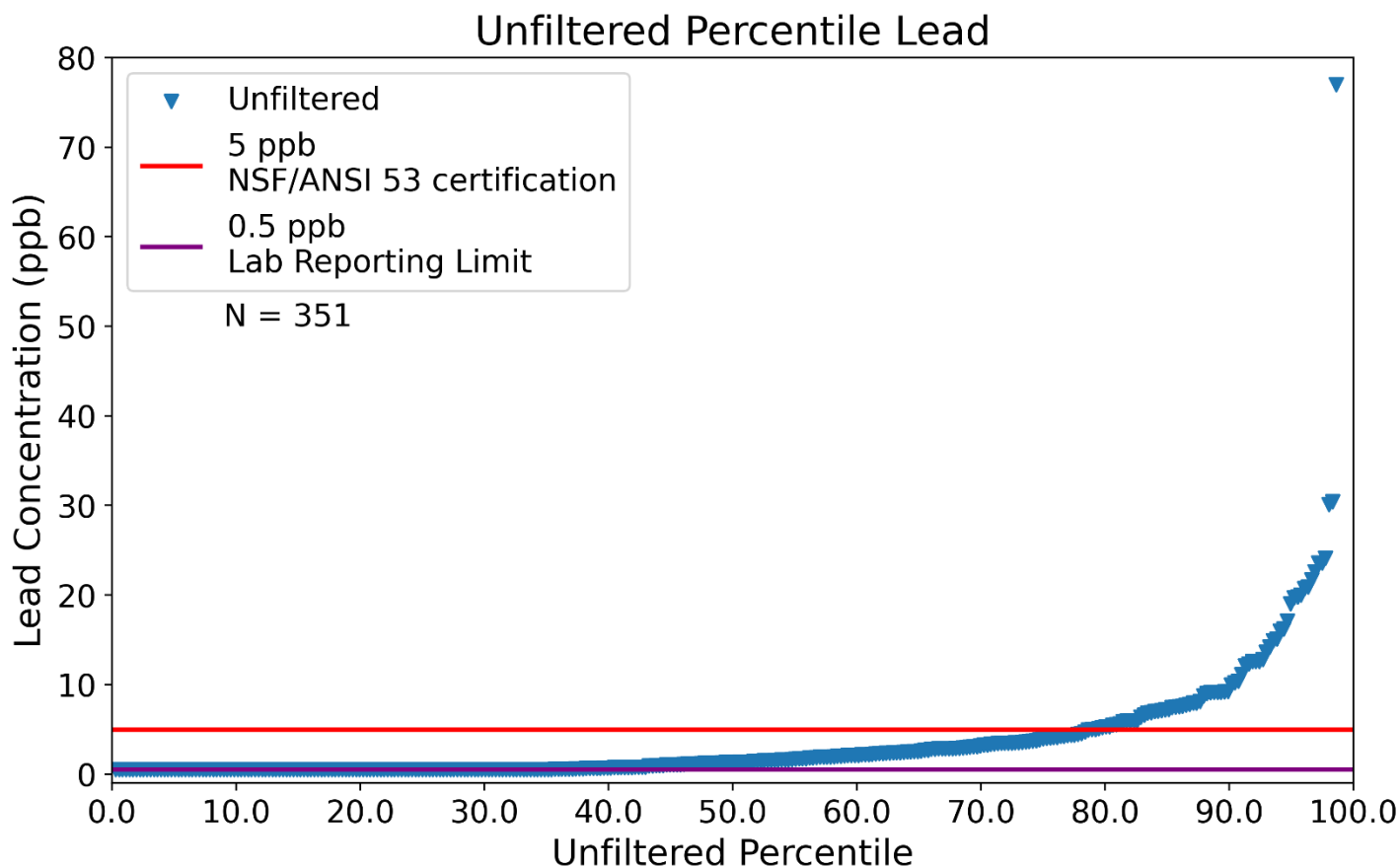


Figure 11. Unfiltered lead concentrations in water from water filter study locations.

The unfiltered lead concentrations associated with the different water filter types, faucet-mounted and pitcher, were evaluated to see if the two water filter types were associated with statistically different lead concentrations. Unfiltered samples at pitcher water filter sites were found to have an average of 3.8 ppb lead, with a 95% confidence interval lower bound of 2.7 ppb and an upper bound of 5.0 ppb (Table 7). Unfiltered samples at faucet-mounted water filter sites were found to have an average of 3.5 ppb lead, with a 95% confidence interval lower bound of 2.7 ppb and an upper bound of 4.3 ppb (Table 7).

Table 7. Unfiltered water lead concentrations by filter type.

Test Sites	Number of Samples	Average lead (ppb)	Lower bound 95%	Upper bound 95%
Pitcher filters	90	3.8	2.7	5.0
Faucet-mounted filters	261	3.5	2.7	4.3

For both confidence intervals, if a sample was BRL, the reporting limit for lead of 0.5 ppb was used in the calculation. Although these averages differ slightly with unfiltered water at pitcher water filter sites having a higher average lead concentration, the difference in the averages is not statistically significant. The error on the laboratory measurement was determined to be 0.26 ppb lead, and a new distribution built on the difference between the two averages (unfiltered water associated with faucet-mounted water filters and pitcher water filters) had a 95% confidence interval that contained “0”; therefore, with 95% confidence there is no statistical

difference between the unfiltered lead concentrations measured from each water filter type site. Additionally, the sampling protocol was altered to attempt to capture higher lead concentrations, by adding in a filtered 7th L and unfiltered 8th L (targeted service line sampling) and by encouraging residents to stagnate their water for at least 6 hours prior to sampling (Figure 12). Neither of these efforts intended to capture higher lead concentrations in the unfiltered water had a significant impact on the lead levels observed, however, the same residences were not sampled under the original protocol and then updated protocol. Although a trend was observed that the 8th liter targeted service line samples (UFL) did have a higher average than the 2nd liter unfiltered samples (UF), 4.7 ppb and 3.1 ppb respectively (BRLs included in the calculation as 0.5 ppb). Due to the violation of normality assumptions with a high proportion of results BRL, when these variables are assessed in a log-transformed two-variable regression model there is no evidence of an effect on lead levels from stagnation time or from the difference between UF or UFL samples.

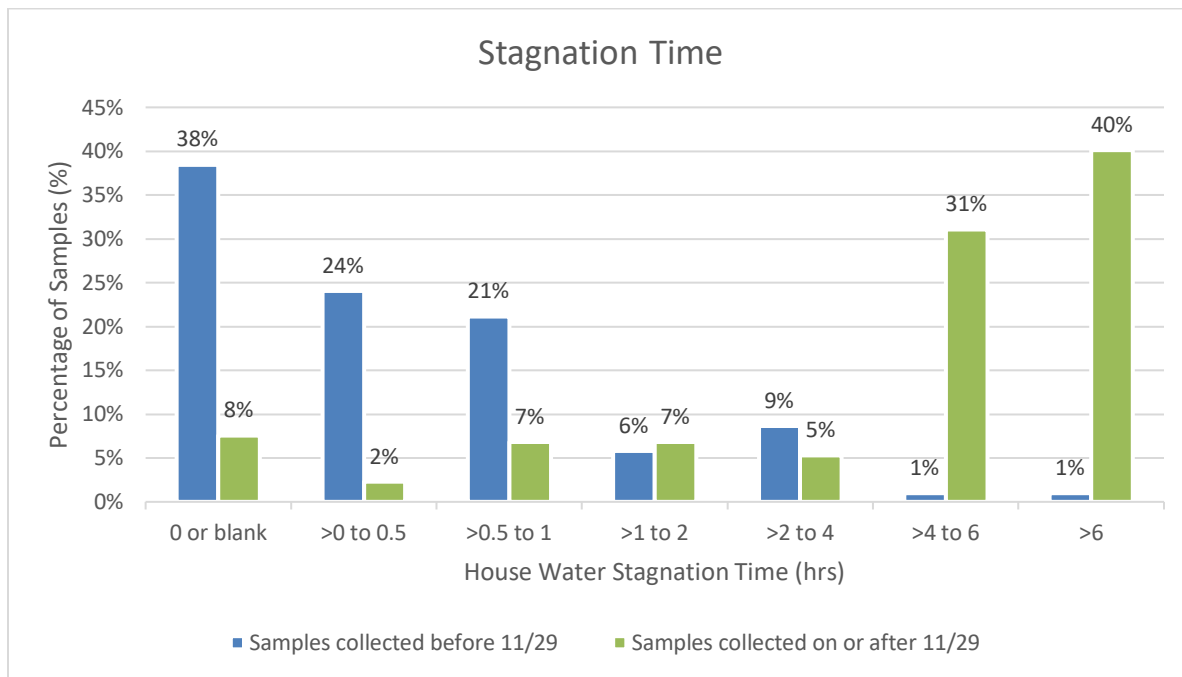


Figure 12. Stagnation times of unfiltered samples collected at different times during the water filter effectiveness study.

3.5.2 Properly Operated Filter Samples

The lead concentrations in water passing through properly operated filters were all below the NSF/ANSI 53 certification standard of 5 ppb and no lead concentrations were greater than 2.5 ppb lead (Figure 13). Most filtered water samples (90%, 277 samples) were BRL for lead (<0.5 ppb). Furthermore, 95% of the samples (291) were below 1 ppb, and 5% of the samples (16) were between 1 ppb and 2.5 ppb lead. Properly operated filtered water samples were collected from 199 unique locations in accordance with the statistical study design (Section 2.1). As all properly operated filtered water samples (first and 7th liter, n=307) were <5 ppb, at 95% confidence at least 98% of locations with properly operated water filters will have filtered water lead concentrations <5 ppb.

In Figure 13 through Figure 20, violin plots are used to visualize the data. These violin plots provide a visual for the numerical distribution of metal concentrations in the datasets, the vertical spread of data points is

in direct relation to metal concentration of the samples, whereas the horizontal spread represents the number of samples at a given concentration. In some cases, due in part to the vast majority of samples for a given analyte being BRL, there are what appear to be horizontal thin lines on the figures with very little spread of datapoints. Somewhat counterintuitive, although the line is thin, it actually represents a high density of samples with a concentration at that value.

All properly operated filtered water lead concentrations were less than 2.5 ppb lead; however, there was a statistical difference observed between pitcher water filters (ZeroWater®) and faucet-mounted water filters (PUR®) (Figure 14). Ninety-nine and a half percent of faucet-mounted filtered water samples were found to be BRL (represented by the straight line and orange diamond at 0.5 ppb) and only one sample was found to be above the reporting limit at 0.73 ppb lead (represented by the orange diamond) (Figure 14). Meanwhile, 29 pitcher water filter samples (out of 85) had lead concentrations at or above the reporting limit, ranging from 0.5 to 2.5 ppb lead (Figure 14). The average concentration for pitcher filtered water samples above the reporting limit was 1.3 ppb lead, with only 4 samples ≥ 2 ppb lead. However, the majority of pitcher filter water samples were still less than 1 ppb lead, and 100% of pitcher water filters were found to be performing as certified.

The two types of water filters in Benton Harbor do operate via different technologies. PUR® faucet mounted water filters are composed of a tightly bound mixture of ion exchange resins and activated carbon. Whereas the ZeroWater® water filters have a 5-stage filtration process which includes: a coarse filter screen, foam distributor, layer of activated carbon and an oxidation reduction alloy, ion exchange resin, finishing with an ultra-fine screen and a non-woven membrane. In addition to the different technologies another potential reason for a difference in performance between faucet-mounted and pitcher water filters is that the ZeroWater® filters do not have the dual certification that the PUR® filters have. The PUR® faucet-mounted water filters distributed by BCHD (e.g., models FM-2000B/FM-3333B) are certified for lead removal under NSF/ANSI 53 and also for class I particulate ($0.5 < 1 \mu\text{m}$) removal under NSF/ANSI 42. Whereas the ZeroWater® pitcher filter (model ZD-018) distributed by BCHD is certified for lead removal under NSF/ANSI 53 but not NSF/ANSI 42 (USEPA, 2018b). As some faucet fixture configurations are incompatible with faucet-mounted water filters, it is important to note that an NSF/ANSI 53 certified pitcher filter still provides lead removal. Based on the results of this study, ZeroWater® pitcher filters in Benton Harbor produce a filtered water complying with NSF/ANSI 53 (NSF/ANSI, 2021) and the bottled water certification (21 C.F.R. § 165.110) requirements of 5 ppb lead (FDA).

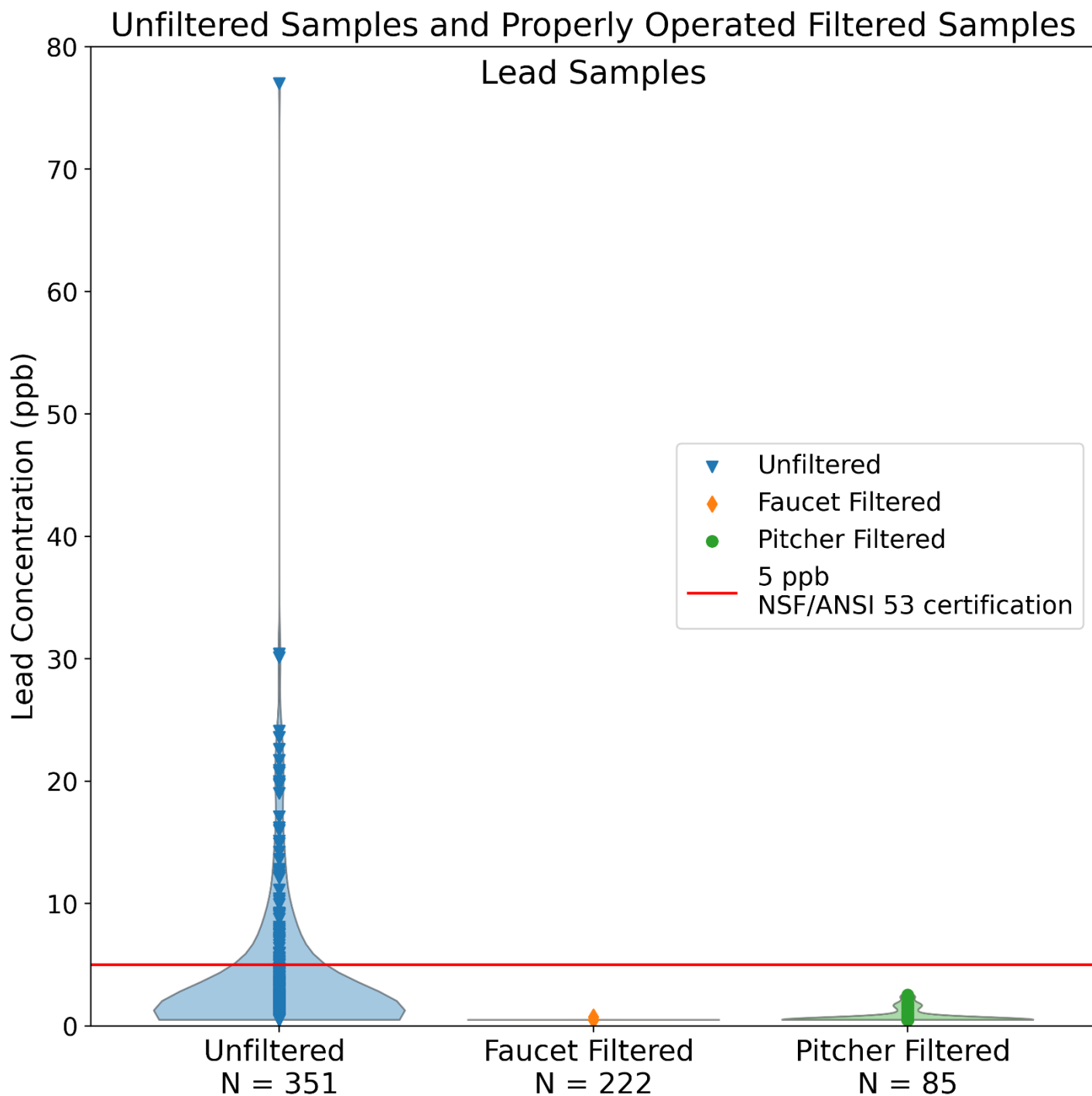


Figure 13. Violin plots of the three types of water filter study samples collected. Samples at or BRL for lead are represented by the widest horizontal line for each of the sample types at 0.5 ppb lead.

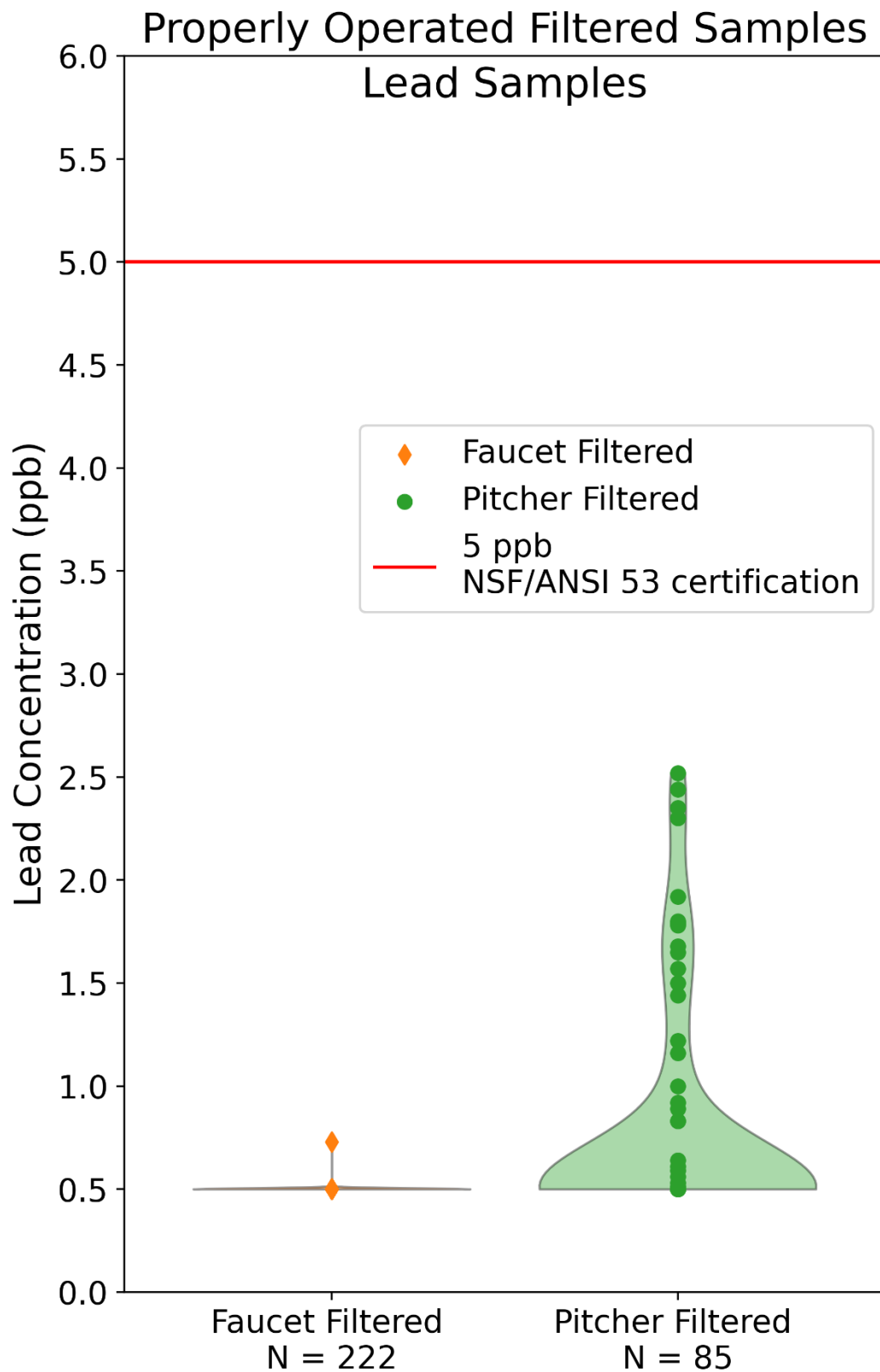


Figure 14. Violin plots of the faucet-mounted water filter and pitcher water filter samples from the previous figure with the y-axis restricted to 6 ppb lead for better resolution of the filtered water data (maximum sample lead concentration in filtered water is 2.5 ppb). Distribution of sample concentrations is shown by spread across the x-axis. Samples BRL are plotted at the reporting limit of 0.5 ppb.

3.5.3 Other Properly Operated Filtered Metals

In addition to lead, another 15 metals were analyzed in the filtered water samples (see Table 8 and Table 9). The water filters have not been certified to remove these additional metals, and they are not included on the water filter model performance data sheets of the most common filters (PUR® FM2000B, 3333B, PFM 100b, PFM 200b, PFM 400h; Brita® FR-200, SAFF-100; and ZeroWater® ZD-018). However, these metals were of interest for overall drinking water quality. Two metals (cadmium and chromium) have an EPA National Primary Drinking Water Regulation and five metals (aluminum, copper, iron, manganese, and zinc) have a Secondary Drinking Water Regulation (USEPA, 40 CFR Part 141, 40 CFR Part 143). Primary Drinking Water Regulations are meant to protect public health by limiting contaminants with a health risk in drinking water, whereas the Secondary Drinking Water Regulations are more for aesthetic concerns. Those chemicals with a Secondary Drinking Water Regulation are not considered to be a risk to human health at the established Secondary Maximum Contaminant Level. None of the properly operated filtered or unfiltered samples in this study had cadmium or chromium concentrations exceeding the maximum contaminant level (MCL). For the Secondary MCLs, the reporting limit for aluminum (0.5 mg/L) was above the secondary MCL, aesthetic standard of 0.05 mg/L. It is unknown how many samples may have exceeded the secondary MCL. However, none of the samples in the water filter study (filtered or unfiltered) had aluminum results above the reporting limit (0.5 mg/L). The only aluminum results above the reporting limit (4 samples) were in the sequential sampling and particulate study (see section 3.8 Other Metals of Concern, for more detail). Just two unfiltered samples exceeded the secondary MCL for iron (0.3 mg/L) at 0.4 and 1.7 mg/L.

Table 8. Summary of properly operated faucet-mounted water filter results.

Properly operated faucet-mounted water filter samples (N=222)						95% Confidence Interval	
Element	Instrumentation, Units	Percentage of Samples BRL ¹	Maximum Concentration	Average*	Standard Deviation*	Low*	High*
Lead (Pb)	ICP-MS ² , ppb	99%	0.73	221 samples BRL			
Copper (Cu)	ICP-MS, µg/L	99%	9	220 samples BRL			
Zinc (Zn)	ICP-MS, µg/L	96%	67	10.4	4.5	9.8	11.0
Aluminum (Al)	ICP-AES ³ , mg/L	100%	BRL	222 samples BRL			
Cadmium (Cd)	ICP-AES, mg/L	100%	BRL	222 samples BRL			
Calcium (Ca)	ICP-AES, mg/L	2%	43	29.1	10.4	27.7	30.5
Chromium (Cr)	ICP-AES, mg/L	99%	0.008	221 samples BRL			
Iron (Fe)	ICP-AES, mg/L	99%	0.09	221 samples BRL			
Magnesium (Mg)	ICP-AES, mg/L	1%	17	12.5	2.8	12.1	12.9
Manganese (Mn)	ICP-AES, mg/L	100%	BRL	222 samples BRL			
Nickel (Ni)	ICP-AES, mg/L	100%	BRL	222 samples BRL			
Phosphorus (P)	ICP-AES, mg/L	0%	4	1.4	0.3	1.3	1.4
Potassium (K)	ICP-AES, mg/L	3%	153	14.1	17.2	11.8	16.3
Silica (Si, as SiO ₂)	ICP-AES, mg/L	0%	11	5.14	1.21	4.99	5.30
Sodium (Na)	ICP-AES, mg/L	0%	224	21.4	17.1	19.2	23.7
Tin (Sn)	ICP-AES, mg/L	100%	BRL	222 samples BRL			

*Samples BRL are represented with the analyte reporting limit in these calculations.

¹ Below Reporting Limit

² Inductively coupled plasma-mass spectrometry

³ Inductively coupled plasma-atomic emission spectroscopy

Table 9. Summary of properly operated pitcher water filter results.

Properly operated pitcher water filter samples (N=85)						95% Confidence Interval	
Element	Instrumentation, Units	Percentage of Samples BRL ¹	Maximum Concentration	Average*	Standard Deviation*	Low*	High*
Lead (Pb)	ICP-MS ² , ppb	66%	2.52	0.76	0.53	0.65	0.87
Copper (Cu)	ICP-MS, µg/L	25%	108	14.0	19.1	9.9	18.1
Zinc (Zn)	ICP-MS, µg/L	82%	69	12.1	7.6	10.5	13.7
Aluminum (Al)	ICP-AES ³ , mg/L	100%	BRL	85 samples BRL			
Cadmium (Cd)	ICP-AES, mg/L	100%	BRL	85 samples BRL			
Calcium (Ca)	ICP-AES, mg/L	92%	2	0.5	0.2	0.5	0.6
Chromium (Cr)	ICP-AES, mg/L	100%	BRL	85 samples BRL			
Iron (Fe)	ICP-AES, mg/L	98%	0.16	83 samples BRL			
Magnesium (Mg)	ICP-AES, mg/L	93%	0.9	0.2	0.0	0.2	0.2
Manganese (Mn)	ICP-AES, mg/L	100%	BRL	85 samples BRL			
Nickel (Ni)	ICP-AES, mg/L	100%	BRL	85 samples BRL			
Phosphorus (P)	ICP-AES, mg/L	100%	BRL	85 samples BRL			
Potassium (K)	ICP-AES, mg/L	100%	BRL	85 samples BRL			
Silica (Si, as SiO ₂)	ICP-AES, mg/L	62%	35	1.17	4.01	0.32	2.02
Sodium (Na)	ICP-AES, mg/L	98%	1	83 samples BRL			
Tin (Sn)	ICP-AES, mg/L	100%	BRL	85 samples BRL			

*Samples BRL are represented with the analyte reporting limit in these calculations.

¹ Below Reporting Limit

²Inductively coupled plasma-mass spectrometry

³Inductively coupled plasma-atomic emission spectroscopy

Water filters also appeared to contribute certain metals to the filtered water; results were greater for potassium, silica, and sodium in filtered samples than in the unfiltered samples (see Figure 15, Figure 16, and Figure 17). The type of water filter (faucet-mounted or pitcher) played a role in what additional metals were contributed. Reasons for the elemental additions by certified filters were not explored in this study, however, one potential cause is due to the differing compositions of the filter media used. Doré et al. (2021) found zeolite resins in faucet-mounted water filter cartridges, which could be a source of silica. Although filtered results were generally greater for potassium, silica, and sodium than in the unfiltered samples, the water filters also removed some of these metals as there were no unfiltered samples BRL, for these elements (Table 6) whereas 17-30% of faucet-mounted and pitcher water filtered samples were BRL for potassium, silica, and sodium (See Figure 15, Figure 16, and Figure 17). For silica and sodium, the samples BRL were all associated with pitcher water filters, potassium BRL samples were also mainly associated with pitcher water filters (85 pitcher filters, out of 91 total water filter samples BRL). Faucet-mounted water filters were found to have higher concentrations of silica and sodium than the unfiltered water (Figure 16 and Figure 17).

Calcium, magnesium, and phosphorus results also experienced a similar pattern with no unfiltered samples BRL (Table 6), but 26-28% of faucet-mounted and pitcher water filtered samples were BRL (see Figure 18, Figure 19, and Figure 20), indicating the water filters also removed some of these metals. For calcium, 83 filtered samples were BRL: 78 pitcher water filters and 5 faucet-mounted water filters (Figure

18). Although calcium was generally able to pass through the faucet-mounted water filter, there is evidence of calcium removal by the faucet-mounted water filters. For magnesium, 81 filtered samples were BRL, of which 79 were pitcher water filters (Figure 19), and for phosphorus all 85 filtered samples BRL were associated with pitcher water filters (Figure 20). Phosphorus was also generally able to pass through the faucet-mounted water filters, and in some filtered samples phosphorus concentrations were higher than what was observed in the unfiltered and background water quality samples (Figure 20). Bearing in mind that all pitcher water filters were from ZeroWater®, the reduction of some metals is expected given the different technology used in the water filter cartridge itself. Also, ZeroWater® filter performance is based on TDS readings as the manufacturer has set a reading of 006 mg/L TDS as the cutoff for water filter replacement; therefore, dissolved constituents in the drinking water are expected to be effectively reduced (below 006 mg/L TDS) by the water filter until the filter has reached capacity (~25 - 40 gallons in an unfiltered water with 051-200 TDS).

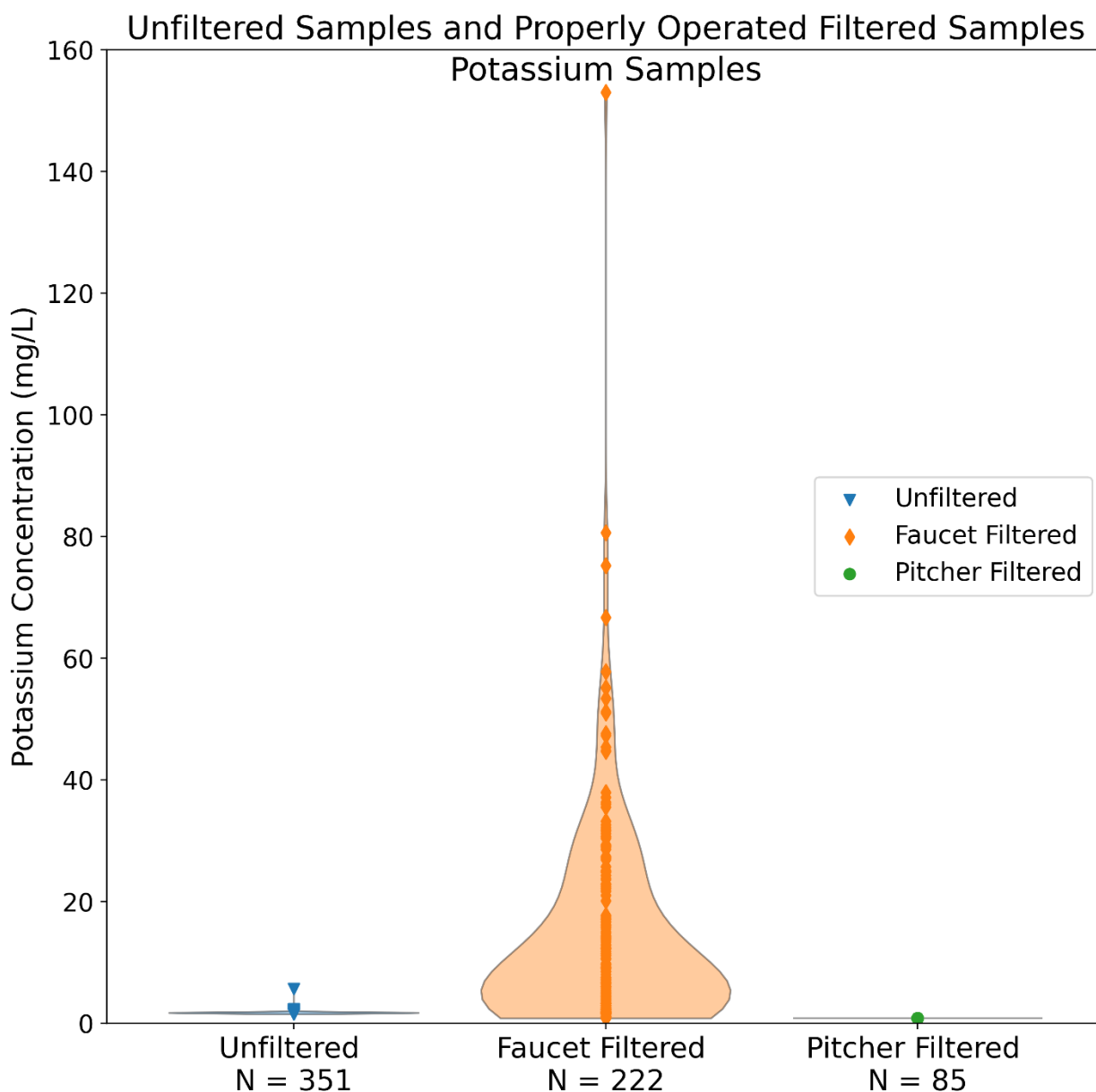


Figure 15. Violin plots of potassium concentrations for: unfiltered, faucet-mounted filtered, and pitcher filtered water. Samples BRL are plotted at the reporting limit of 0.8 mg/L.

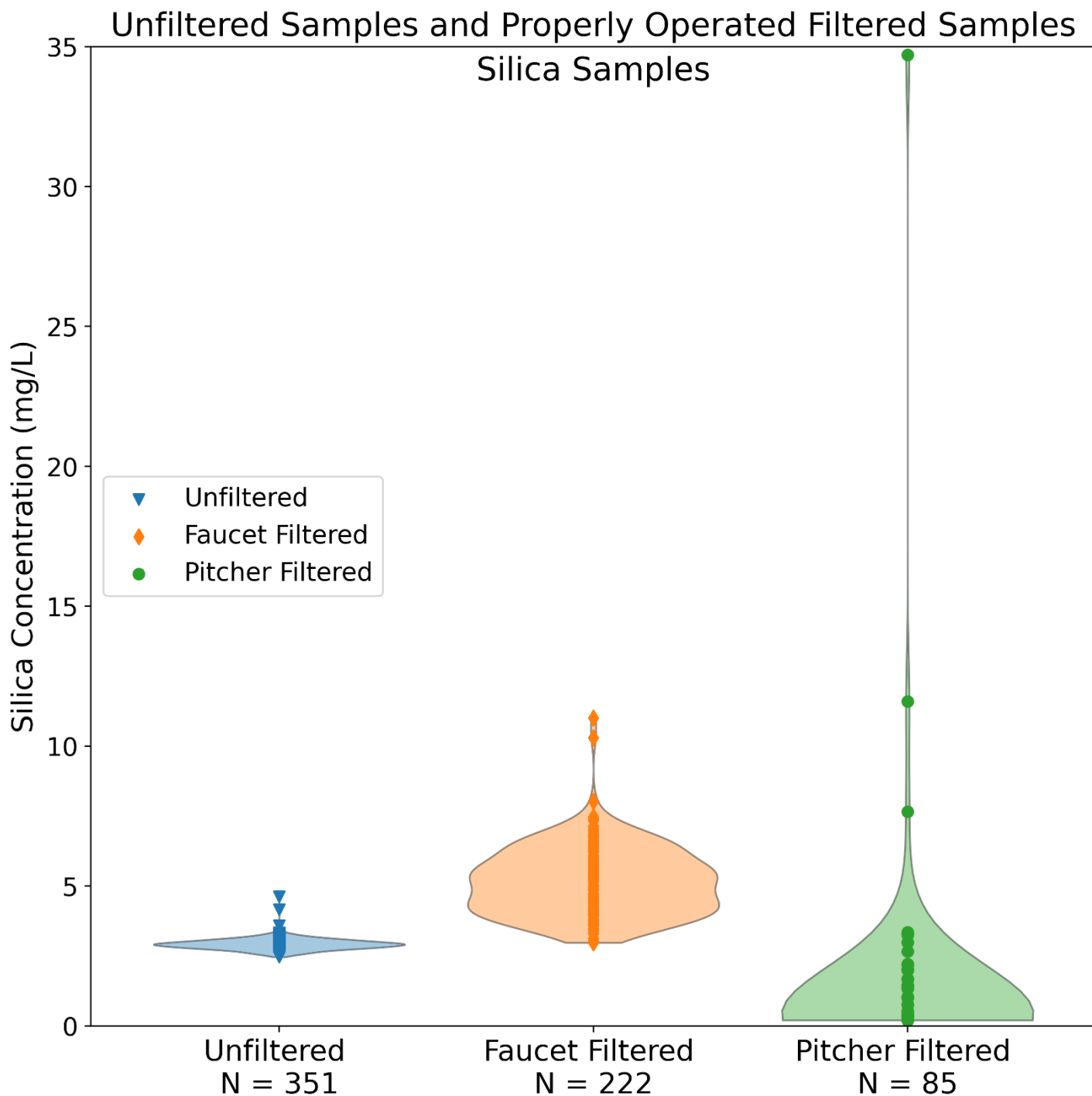


Figure 16. Violin plots for silica concentrations for: unfiltered, faucet-mounted filtered, and pitcher filtered water. Silica was present above the reporting limit in the unfiltered water. Samples BRL are plotted at the reporting limit of 0.2 mg/L.

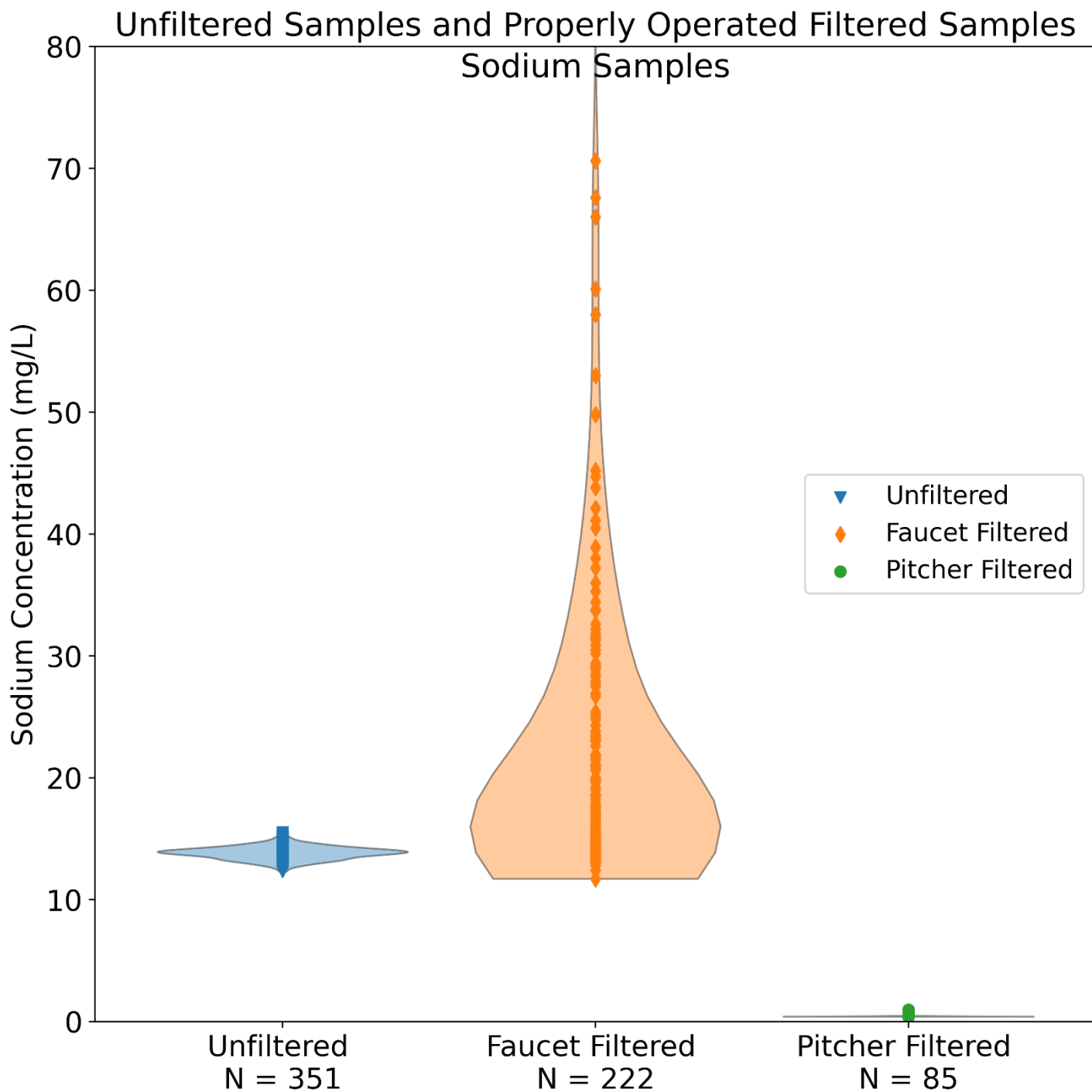


Figure 17. Violin plots for sodium concentrations for: unfiltered, faucet-mounted filtered, and pitcher filtered water. Samples BRL are plotted at the reporting limit of 0.4 mg/L.

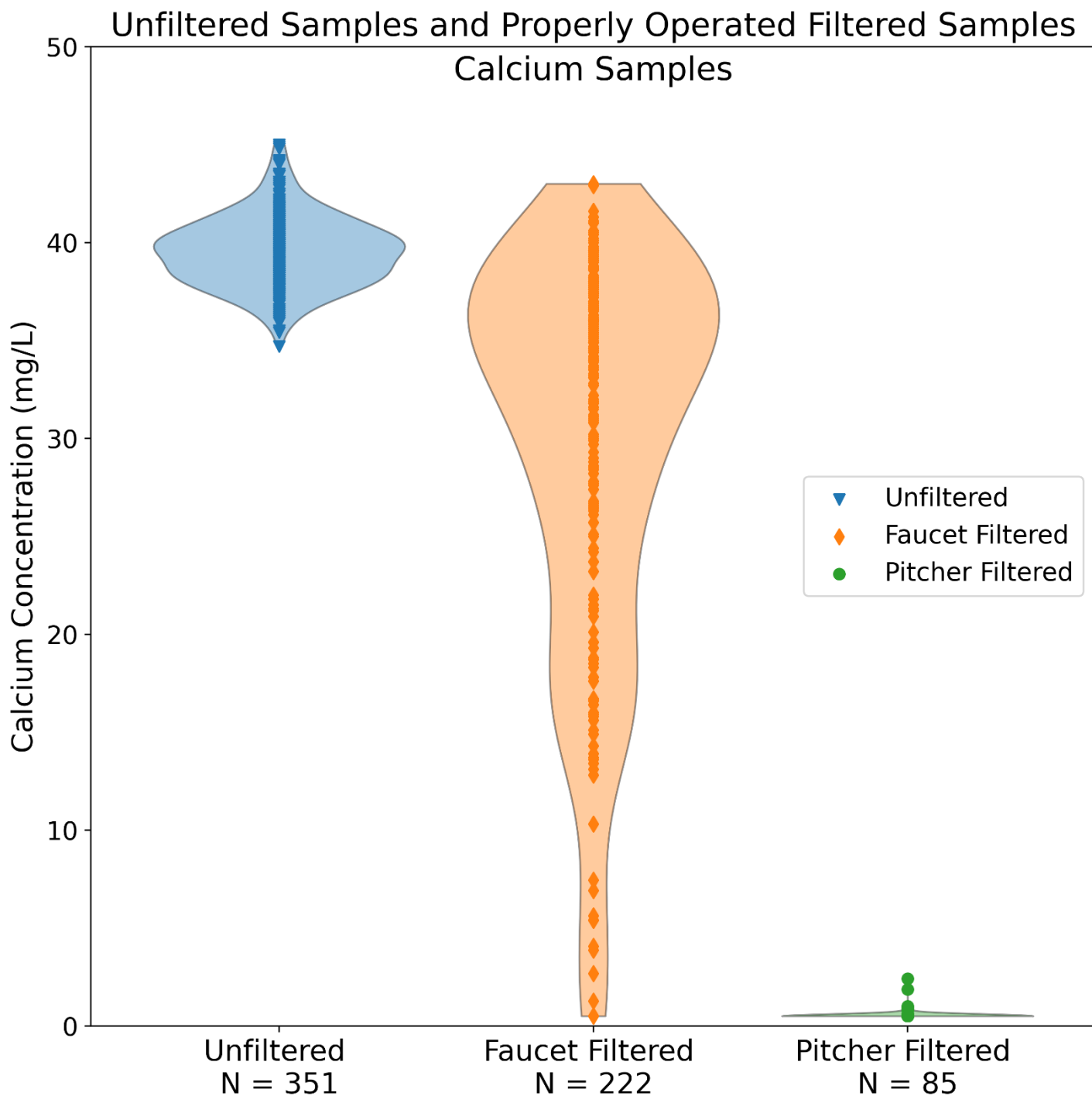


Figure 18. Violin plots for calcium concentrations for: unfiltered, faucet-mounted filtered, and pitcher filtered water. Samples BRL are plotted at the reporting limit of 0.5 mg/L.

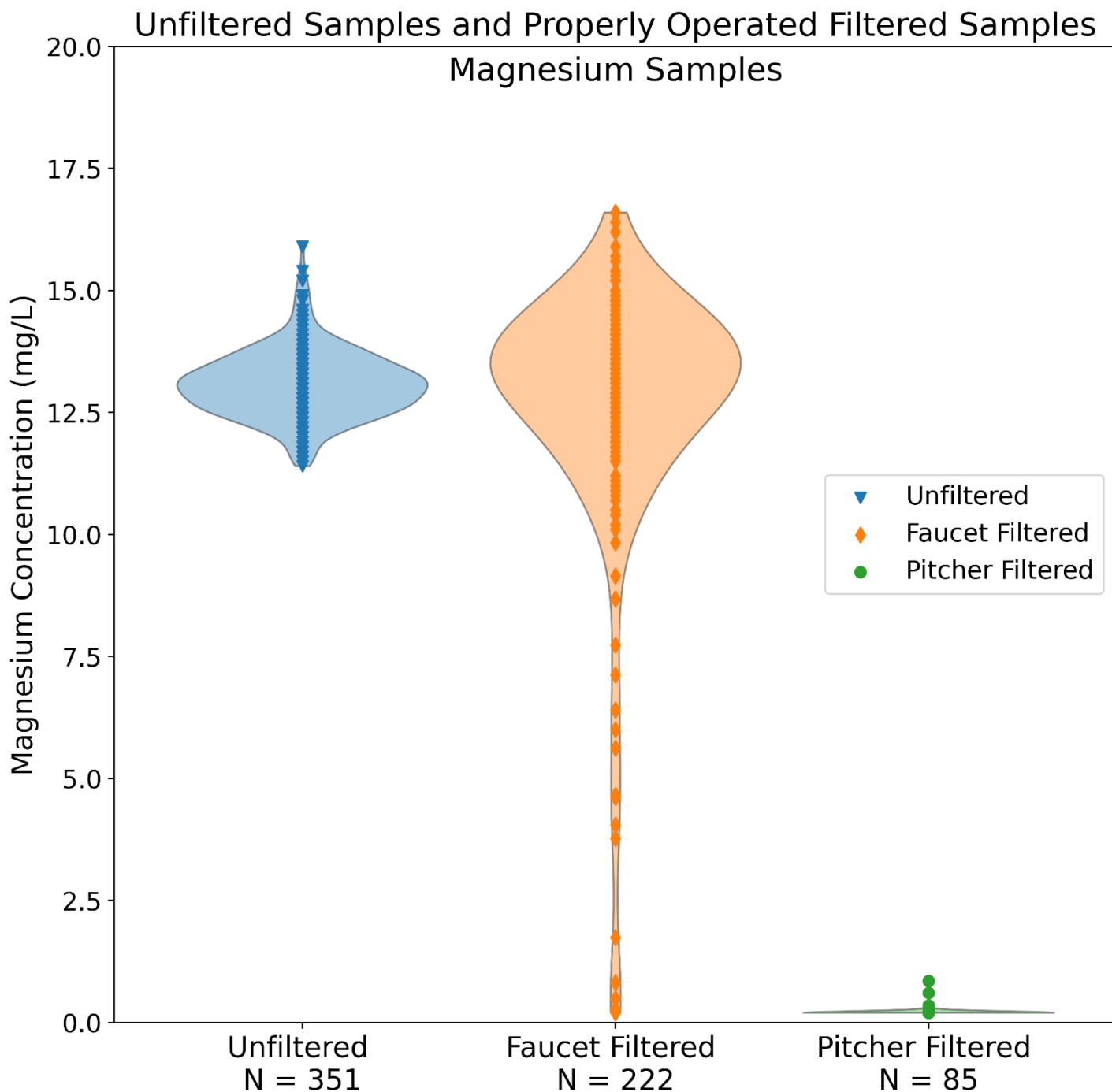


Figure 19. Violin plots for magnesium concentrations for: unfiltered, faucet-mounted filtered, and pitcher filtered water. Samples BRL are plotted at the reporting limit of 0.2 mg/L.

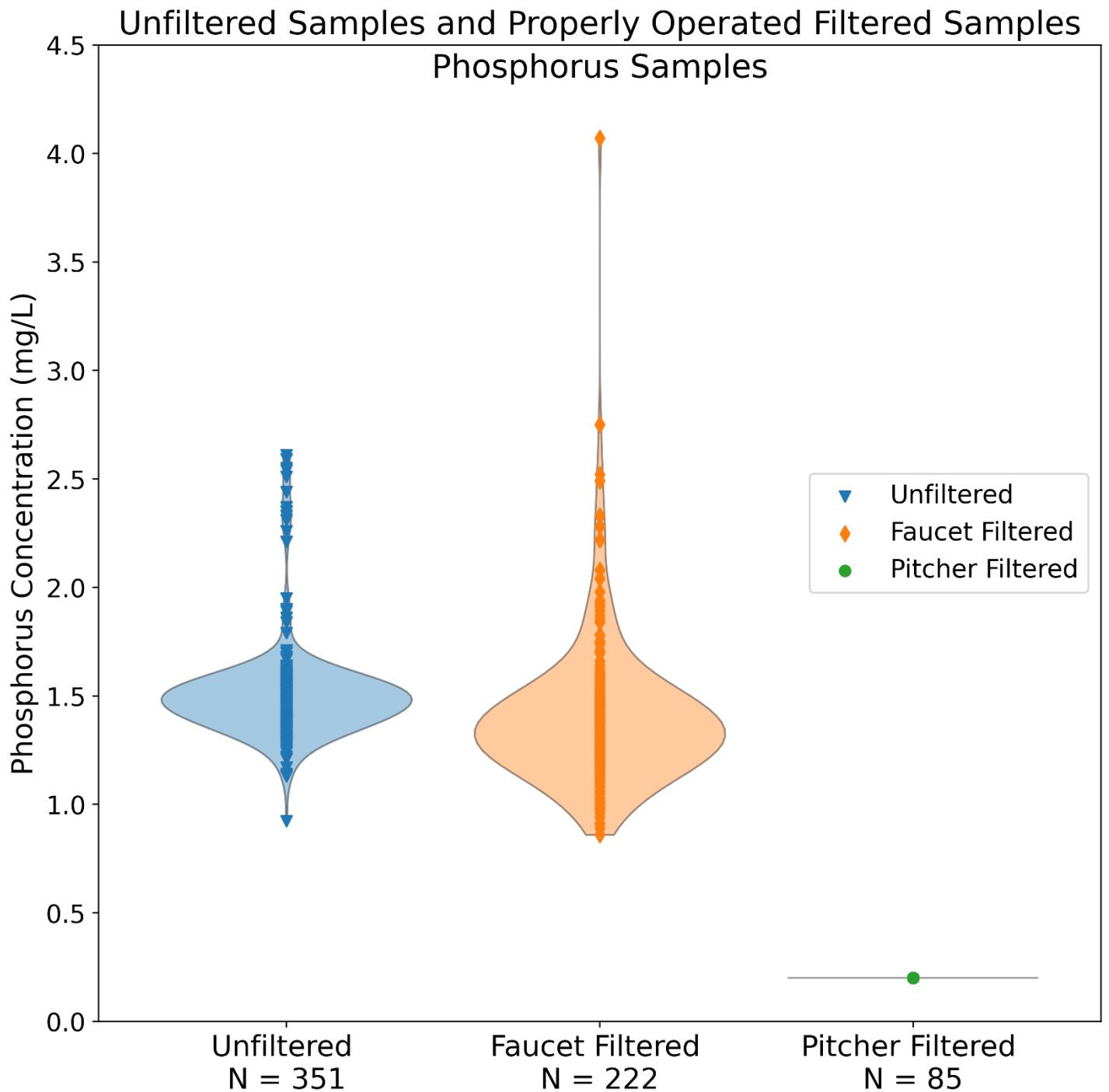


Figure 20. Violin plots for phosphorus concentrations for: unfiltered, faucet-mounted filtered, and pitcher filtered water. Samples BRL are plotted at the reporting limit of 0.2 mg/L.

3.5.4 Improperly Operated Filters

Amongst all the improperly operated water filters (-5FF, “e”, or “h”) there were only 5 samples with lead concentrations ≥ 0.5 ppb and only one sample (red light, hot water use, faucet-mounted water filter) where lead levels were observed in excess of the NSF/ANSI 53 lead certification at 5.8 ppb lead. It should also be noted that at the time of the study residents had been advised by the state of Michigan to use bottled water for consumptive purposes rather than water filters (MDHHS & EGLE, 2021), which may have contributed to the relatively high number of homes where filter cartridges had not been changed per manufacturer guidance. Although water filters were not typically being used for consumptive purposes due to the state guidance, if the filter is within its operational life and properly used the water filter should perform as certified.

Five-Second Flush Water Filter Results

At all faucet-mounted water filter site locations, the first five seconds of water while the water filter was in the “on” position was collected as a “5FF” sample. All of the 5FF samples collected, regardless of water filter light indicator color or whether or not hot water was run through the water filter, are considered improper use, as manufacturer instructions for the PUR[®] and Brita[®] faucet-mounted water filters instruct users to, prior to each use, run cold water for 5 seconds in filtered position to activate filter (Brita, 2019; PUR, 2022). Although this filtered water is not meant for consumption based on the manufacturer instructions, it is possible that residents could consume some of this water which is why a separate sample was collected.

A total of 180 “5FF” samples were collected, 151 of which had green/yellow indicator lights and 29 of which were malfunctioning, red light, or also associated with hot water use. All 180 samples were BRL for aluminum, cadmium, and tin (Table 10). For manganese and nickel, 179 samples were BRL. For lead and zinc, 178 samples were BRL (Table 10). Then for chromium, iron, and copper; 176, 175, and 168 samples respectively were BRL (Table 10).

For the other elements analyzed (calcium, magnesium, phosphorus, potassium, silica, and sodium) the majority of samples were found to have results above the reporting limits. Phosphorus, potassium, silica, and sodium were also all found to be higher in the “5FF” samples than in the background water quality samples collected in the sequential study. While none of these metals have a primary or secondary drinking water standard associated with them, it is worth noting that EPA does have a guidance level for sodium in drinking water of 20 mg/L for individuals restricted to a total sodium intake of 500 mg/day (USEPA, 2018a) and 116 samples fell above this level to a maximum of 1,300 mg/L. For individuals not on a sodium restricted diet EPA recommends drinking water sodium be reduced to 30-60 mg/L for taste concerns. The 95% confidence interval for sodium is 50-88 mg/L, indicating that the true mean of the 5-second flush population falls above EPA’s guidance level for sodium. Other sodium occurrences were observed in the pool of properly operated water filter samples, 71 samples were found to be ≥ 20 mg/L, all associated with a faucet-mounted water filter device. The faucet-mounted water filters appear to have the ability to add sodium to the water in excess of background levels which may be of concern for residents with a sodium restricted diet. In all of the unfiltered samples collected sodium was 17 mg/L or less, and in the background water quality samples it ranged from 13-16 mg/L.

Table 10. Summary of the filtered five-second flush results.

Five-second flush samples (N=180)						95% Confidence Interval	
Element	Instrumentation, Units	Percentage of Samples BRL ¹	Maximum Concentration	Average*	Standard Deviation*	Low*	High*
Lead (Pb)	ICP-MS ¹ , ppb	99%	2.66	178 samples BRL			
Copper (Cu)	ICP-MS, µg/L	93%	79	2.6	5.8	1.8	3.5
Zinc (Zn)	ICP-MS, µg/L	99%	169	178 samples BRL			
Aluminum (Al)	ICP-AES ² , mg/L	100%	BRL	180 samples BRL			
Cadmium (Cd)	ICP-AES, mg/L	100%	BRL	180 samples BRL			
Calcium (Ca)	ICP-AES, mg/L	8%	52	23.5	16.2	21.2	25.9
Chromium (Cr)	ICP-AES, mg/L	98%	12.9	176 samples BRL			
Iron (Fe)	ICP-AES, mg/L	97%	50	175 samples BRL			
Magnesium (Mg)	ICP-AES, mg/L	7%	20	11.0	5.6	10.1	11.8
Manganese (Mn)	ICP-AES, mg/L	99%	0.725	179 samples BRL			
Nickel (Ni)	ICP-AES, mg/L	99%	0.653	179 samples BRL			
Phosphorus (P)	ICP-AES, mg/L	0%	42	3.2	5.4	2.4	4.0
Potassium (K)	ICP-AES, mg/L	1%	1100	47.9	126.9	29.3	66.4
Silica (Si as SiO ₂)	ICP-AES, mg/L	0%	81	31.35	13.25	29.42	33.29
Sodium (Na)	ICP-AES, mg/L	0%	1300	69.9	129.9	50.9	88.9
Tin (Sn)	ICP-AES, mg/L	100%	BRL	180 samples BRL			

*Samples BRL are represented with the analyte reporting limit in these calculations.

¹ Below Reporting Limit

²Inductively coupled plasma-mass spectrometry

³Inductively coupled plasma-atomic emission spectroscopy

3.6 Sequential Study Results

Sequential profile datasets were collected from 26 Benton Harbor locations (Appendix D. Sequential Metal Profiles by Location). There are two profile plots presented for each location in the Appendix. One plot contains the lead profile results and the fully flushed lead value, whereas the other plot contains other metals of interest above the reporting limit along with repeated lead profile results (for ease of reference). Lead data associated with the sequential profile sites has been previously released in a March 2022 data report and is included here for completeness (USEPA, 2022c).

The value of sequential profile sampling is that the volume of each water sample can be translated to plumbing components and pipe length, which can be used to identify the location and source of metals in the drinking water associated with the service line and premise plumbing. A sequential profile should be interpreted relatively, where increases and decreases in metal concentrations could be associated with the presence and absence of various plumbing materials. Concentrations of metals do not immediately drop to BRL when the water sampled transitions from one material to the next; instead, there can be a more gradual shift in concentrations depending on the length and type of plumbing material (Lytle, Formal, Cahalan, Muhlen, & Triantafyllidou, 2021). Increased concentrations of zinc and iron can be indicative of galvanized iron plumbing, whereas increased copper concentrations can be indicative of copper plumbing. LSLs are often denoted by a parabolic curve, where lead levels increase to a maximum and then decrease.

3.6.1 Sequential Profiles for Lead

Benton Harbor metal profiles varied widely and reflected the unique plumbing configurations and make-up of materials within the home (premise) plumbing and service lines. Table 11 contains plumbing material information compiled during the course of the study. For the determination of service line materials EPA relied on the Abonmarche materials inventory. Premise plumbing materials listed in Table 11, when observed, were all from EPA sampler input.

Additionally, Table 11 contains the fully flushed lead concentration observed at each location. Fully flushed samples can include low levels of metals picked up as running water moves through the service line and plumbing, so they can be used as a means of LSL identification when the study is properly set up, sampling a pool of control and known LSL houses (Hensley, Bosscher, Triantafyllidou, & Lytle, 2021; Michael R. Schock, Darren A. Lytle, Ryan R. James, Vivek Lal, & Min Tang, 2021). Sequentially sampled homes were targeted based on the presence of an LSL or previous high concentrations of lead; therefore, there was not a representative non-LSL group to appropriately compare for the purposes of LSL identification. However, an analysis of materials and lead concentrations revealed that the average fully flushed lead concentration for LSLs on the utility-side was 2.3 ppb (BRLs included in that average at the reporting limit of 0.5 ppb). There were four fully flushed samples which were BRL for lead: two locations have partial LSLs and two are confirmed non-LSL locations. More data collection would be necessary to use fully flushed sampling as an identification method in Benton Harbor, particularly the inclusion of sites that have never had an LSL.

Table 11. Plumbing Materials from Sequentially Sampled Locations.

Location	Premise Plumbing Materials	Service Line Materials		Fully Flushed Pb (ppb)
		Customer-Side	Utility-Side	
2312	Galvanized Iron	Galvanized Iron	Lead	BRL ¹
2710	Galvanized Iron	Galvanized Iron	Lead	4.62
2715	Galvanized Iron	Copper	Lead	1.94
2753	PVC ²	Galvanized Iron	Lead	3.6
2765	Copper, Galvanized Iron, PVC	Galvanized Iron	Lead	1.98
3057	Galvanized Iron	Galvanized Iron	Lead	3.63
3108	Copper, Galvanized Iron	Galvanized Iron	Lead	0.8
3119	PVC	Galvanized Iron	Lead	2.58
3150	Copper, Galvanized Iron	Copper	Copper	BRL
3174	Galvanized Iron	Galvanized Iron	Lead	1.75
3184	Galvanized Iron	Galvanized Iron	Lead	2.24
3225	Galvanized Iron, PVC	Galvanized Iron	Lead	2.43
3275	Not Observed	Copper	Lead	1.79
3276	Copper, Galvanized Iron, PVC	Galvanized Iron	Lead	1.21
3395	PEX ³ , PVC	Copper	Lead	1.06
3407	Copper, Galvanized Iron, PVC	Galvanized Iron	Lead	2.34
3446	Copper, Galvanized Iron	Copper	Lead	2.89
3492	Galvanized Iron	Galvanized Iron	Lead	BRL
4348	Galvanized Iron, PVC	Galvanized Iron	Lead	0.83
4518	Galvanized Iron	Copper	Copper	BRL
4579	Galvanized Iron	Galvanized Iron	Lead	1.72
4613	Copper	Galvanized Iron	Lead	1.67
4615	Copper, Galvanized Iron	Galvanized Iron	Lead	2.48
4645	Copper, Galvanized Iron, PEX	Galvanized Iron	Lead	2.94
4730	Copper, Galvanized Iron	Galvanized Iron	Lead	8.65
4827	Galvanized Iron, PEX	Galvanized Iron	Lead	0.98

¹BRL- below reporting limit of 0.5 ppb.

²PVC- polyvinyl chloride

³PEX- cross-linked polyethylene

In the sequential profiles, lead sources were approximated from the location of the metal profile peaks. Three general metal profile trends were observed that were indicative of the following lead source(s): (1) faucet and associated adjacent connections, (2) premise plumbing (i.e., plumbing between the faucet and service line), and (3) service line. LSL sources were characterized by a lead peak only (no other metals) located later in the profile sequence at a cumulative water volume where the service line was expected. Examples include locations 3057 (lead peak at the 10th liter) and 2765 (8th liter) in Appendix D. Sequential Metal Profiles by Location. Faucet (i.e., brass, aerator particulate) lead source peaks contained lead as well as other metals, particularly copper and zinc, located within the initial 0.25 to 1 L profile volume (e.g., see locations 3225 and 2715 in Appendix D. Sequential Metal Profiles by Location). Lastly, premise plumbing lead contributions include galvanized pipe (steel coated in zinc oxide to prevent the iron from rusting, on which lead is known to

accumulate) (AWWARF-TZW, 1996; Clark et al., 2015; HDR, 2009; McFadden et al., 2011; Pieper et al., 2017; Sandvig et al., 2008), brass plumbing components (composed mostly of copper and zinc, but which could contain up to 8 percent lead if purchased prior to 2011), and leaded solder (USEPA, 2022d). These peaks contain lead as well as zinc, iron, and other metals (e.g., see locations 2765 for copper, zinc, and iron, 3184 for copper, manganese, zinc, iron, and nickel, and 4730 for copper, cadmium, manganese, zinc, and iron, Appendix D. Sequential Metal Profiles by Location). A complete and detailed home plumbing inventory would be useful in verifying approximations. Also, due to the variability of lead in water sampling and potential for incomplete stagnation (Lytle et al., 2021; Triantafyllidou et al., 2021), lead sources may be present even if a site has low lead concentrations in the sampling results.

The maximum peak (many profiles had more than one peak) lead concentration in the profiles ranged between about 3 to 391 ppb, and the median maximum concentration was 15 ppb (Figure 21). Three of the profiles had maximum lead concentrations below 5 ppb, two being sites that had full copper service lines (locations 3150 and 4518) and location 3492 which had a galvanized iron to an LSL. Maximum lead profile concentrations clustered around 1 to 3 L and 6 to 11 L (Figure 22), which shows that the water filter effectiveness study's attempt to target service line water at the 7th and 8th liters was a realistic approximation for the community. The minimum lead profile concentrations ranged between BRL (0.5 ppb) and 10.5 ppb. The weighted average lead concentration was determined by dividing the sum of the lead mass of all samples in a profile by the sum of water sample volume of all samples collected in the profile. The weighted average lead concentrations across the entire profile ranged between 0.6 ppb and 31 ppb, and the median weighted average value was 6.3 ppb (Figure 21) reflecting the location of different lead sources in the drinking water in the premise plumbing and service line materials. The first draw 1L equivalent is calculated from each individual profile using Equation 2. First draw 1L equivalent concentrations ranged between 1.9 ppb and 188 ppb, and the median was 5.6 ppb lead.

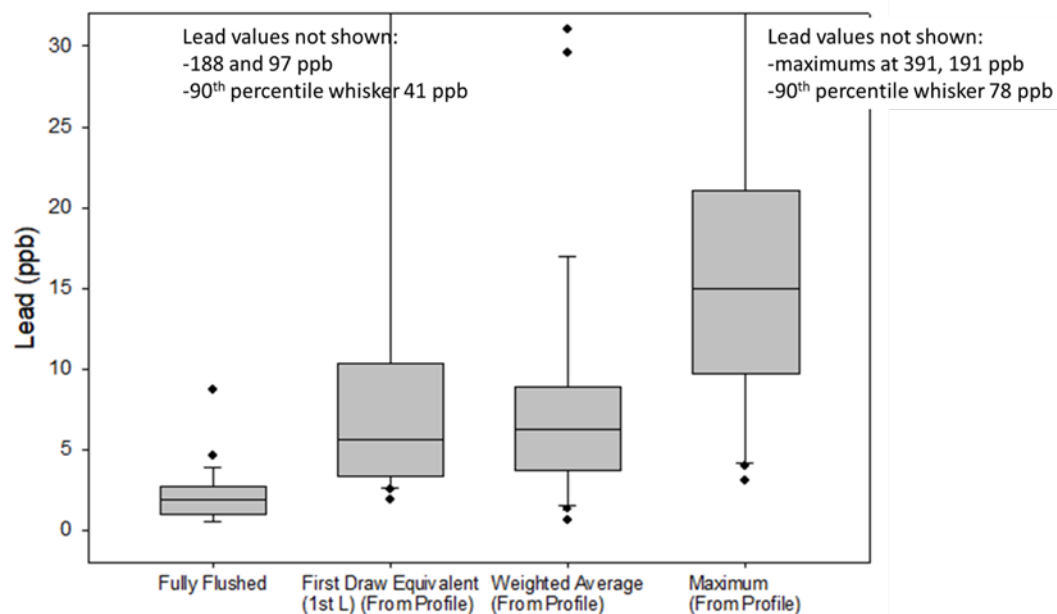


Figure 21. Summary of profile data (26 profiles). Boxes represent the median and 25th and 75th percentiles. Error bars (whiskers) are displayed at the 10th and 90th percentiles. Dots are data that fall outside of the 10th and 90th percentiles.

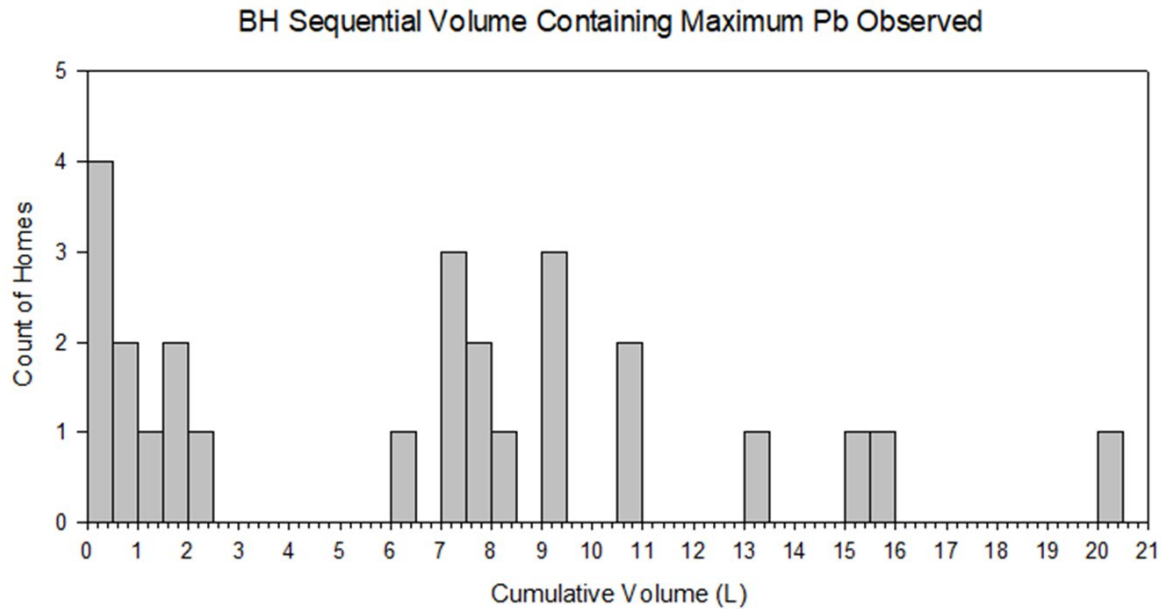


Figure 22. Location (Liter, L) where maximum lead concentration appears in profile.

Equation 2. First draw 1 L equivalent from smaller volume sequential samples.

$$\frac{\left(SS01 \text{ mg} \frac{Pb}{L} \times 0.125L \right) + \left(SS02 \text{ mg} \frac{Pb}{L} \times 0.125L \right) + \left(SS03 \text{ mg} \frac{Pb}{L} \times 0.5L \right) + \left(SS04 \text{ mg} \frac{Pb}{L} \times 0.250L \right)}{1L}$$

3.6.2 Other Metals

The other metals analyzed in the sequential study samples helped to shed light on the various plumbing configurations in the community. Overall, the additional metals seemed to corroborate the service line determinations and premise plumbing materials noted by the samplers (Table 11).

The second graph presented for each location in Appendix D. Sequential Metal Profiles by Location contains other metals that were analyzed during the sequential sampling study. These profiles further emphasize the prevalence of galvanized piping in this sample set as all 26 profiles have signatures of galvanized iron piping (zinc and/or iron concentrations). The maximums for both lead and zinc in the profiles are generally offset from one another; however, there does appear to be lead concentrations persisting in sections of the profile where zinc is at its highest concentrations. Lead levels associated with zinc maximums not associated with the first liter of water generally range from 1-25 ppb lead, with an average around 6 ppb lead. For two locations, the additional metals data helped to clarify the available premise plumbing materials information. Location 3119's lead data indicates that there are premise plumbing components other than plastic in the residence such as galvanized iron or copper (due to some low concentrations of iron, zinc, and copper). More clarity of plumbing materials was brought to location 3275 (originally not observed) with data suggesting a mix of galvanized iron and copper premise plumbing.

3.7 Particulate Study Results

Lead data associated with the particulate filtrations has been previously released in a March 2022 data report and is included here for completeness (USEPA, 2022c).

3.7.1 Sample Filtrations

Particle size fractionations by filtration (0.45 μm and 0.2 μm filtrations, and ultrafiltration) were performed on water samples that targeted volumes of water with previous high lead concentrations in 16 of the sequential profile sets (locations). Early in the study, a lead field analyzer test kit (Kemio™, from Palintest, United Kingdom) was used to screen these targeted volumes, and filtrations were not performed unless a sample tested ≥ 9.5 ppb lead. While the field analyzer remained in use, the trigger level for filtrations was removed for samples collected on and after 11/23/21 (after review of preliminary ICP-MS lead data that indicated the field analyzer was reading some lead sample concentrations low).

Lead concentrations in the unfiltered targeted water samples (-PC##-TM) ranged between 5 and 133 ppb (median concentration was 14 ppb), and there was little difference between the amount of lead passing different filter sizes (0.45 μm , 0.2 μm , ultrafilter) in any of the samples (Table 12). Most filtration concentrations were within ± 1 ppb of each other, indicating that the majority of lead particulate was $> 0.45 \mu\text{m}$. One exception is location 3184, with an ultrafiltered lead concentration approximately 4 ppb greater than the 0.45 μm and 0.2 μm syringe filtrations, indicating a higher proportion of soluble lead in that sample. If lead particulate would have had a range of particle sizes, different lead concentrations would be seen in the different size filtrations; instead, the “soluble” lead concentration shown by the ultrafiltration result was very similar to that seen in the 0.45 μm and 0.2 μm filtrations. If particles $< 0.2 \mu\text{m}$ were present within the samples the ultrafiltration lead concentrations would be lower than what was observed in the 0.2 μm and 0.45 μm filtrations. The fraction of lead in the particulate form based on ultrafiltered lead results ranged between 15 and 95% (median 37%) (Table 12). Lead particle size fractions indicated by filter fractionization analyses are not necessarily reflective of individual lead particle sizes. Particle-particle interactions, particle interactions with filter surfaces, and other factors can impact filter fractionization observations. For example, particles can clump together during the filtration process and act (in regard to the filtrations) as a larger particle than each of the particles may be as individuals. Due to that uncertainty the presence of particles was evaluated by two other means, the effectiveness of the certified drinking water filters and electron microscopy (detailed below).

Table 12. Lead concentrations by particle size filtrations.

Sample Location	Sample Date	Lead Concentrations (ppb)					Percent (%)	
		Targeted Water Sample (-PC##-TM)	0.20 µm Filtration	0.45 µm Filtration	Ultrafiltered	Total Particulate (Targeted Sample - Ultrafiltered)	Particulate Lead	Soluble Lead
BH2710	11/18/2021	17.1	12.6	13.1	12.8	4.3	25	75
BH2715	12/1/2021	13.1	8.6	8.8	8.1	5.0	38	62
BH2765	11/30/2021	20.6	17.0	17.3	16.8	3.8	18	82
BH3057	11/16/2021	13.4	5.4	5.8	4.7	8.7	65	35
BH3119	11/12/2021	29.7	11.3	10.6	11.1	18.6	63	37
BH3174	12/3/2021	4.9	1.4	1.3	1.7	3.3	67	33
BH3184	11/15/2021	16.4	8.0	8.5	12.4	4.0	24	76
BH3225	12/16/2021	12.6	10.8	10.6	10.7	1.9	15	85
BH3275	11/30/2021	11.4	0.9	0.7	0.6	10.8	95	5
BH3407	11/18/2021	18.5	12.2	12.3	11.8	6.7	36	64
BH3446	12/6/2021	133.0	6.6	6.7	6.9	126.1	95	5
BH4579	11/12/2021	14.6	10.1	10.2	10.2	4.4	30	70
BH4613	11/18/2021	4.6	3.6	3.5	3.1	1.5	33	67
BH4615	11/9/2021	13.6	2.7	No sample	2.5	11.2	82	18
BH4730	12/8/2021	24.2	3.1	3.3	3.0	21.2	88	12
BH4827	12/7/2021	9.4	6.1	6.0	7.0	2.4	26	74

Zinc was the other common metal in the filtrations ranging from 11 µg/L to 949 µg/L in the targeted water samples (-PC##-TM), and only one of the 16 samples was BRL (location 4613). For locations 3446 and 4730, 50% or more of the zinc was particulate; in the 13 other locations with zinc above the reporting limit, zinc was mainly soluble. Low total metal concentrations of copper (2-6 µg/L) were generally observed in the unfiltered targeted water (-PC##-TM) samples and filtrations with two exceptions being locations 3275 and 3446 which had copper concentrations up to 33 ug/L and 93.5 µg/L, respectively, well below the health-based MCL Goal of 1.3 mg/L (USEPA, 40 CFR Part 141).

Iron and manganese concentrations were only observed in the targeted water (PC##-TM) samples of those locations where the targeted bottle was collected right after the first two 125 mL samples (locations 3275, 3446, and 4730). These metals are not in any of the filtrations collected from these locations indicating that the metals are associated with particulate >0.45 µm in size. Location 4730 also had 0.011 mg/L of cadmium that was associated with particulate. For locations 3446 and 4730, the premise plumbing contained some galvanized iron in addition to a known partial LSL, whereas the premise plumbing was not observed for location 3275. The targeted water (PC##-TM) samples for all other locations that had filtrations was at the 5th liter or beyond; therefore, the prevalence of iron/manganese-rich particulate in the first liter with various premise plumbing materials cannot be completely assessed. Total manganese and iron were found above the reporting limits in some houses in the sequential profile results (see section 3.6.2) and above Secondary MCLs (see section 3.8).

3.7.2 Electron Microscopy Particulate Characterization

Particles trapped on the ultrafilter from sixteen residences were analyzed by SEM, TEM, EDS and XRD. The XRD analysis concluded that sufficient concentrations of crystalline particles were not present to generate diffraction patterns, aside from the pattern produced by the ultrafilter substrate material itself. Thus, particles with a crystalline structure were not present in great enough quantities in the sampled water or the particles present had no crystalline structure (X-ray amorphous) and would not be detected by this method. The electron microscopy analyses did identify particles in every sample, and at least one sample (SEM or TEM) from each of the 16 residences had a detection for lead. Lead particles were detected more frequently in the SEM analysis. In the cases where there was not a lead detect in the SEM analyses, there was a lead detect for the sample in the TEM analysis.

This electron microscopy analysis is not a complete characterization of all the particles present in Benton Harbor drinking water as the analysts were focused on finding lead-rich material, although non-lead material was also imaged in the process. Particularly in the SEM, this means searching for brighter particles while in back scatter detection (BSD) mode. A variety of particles (non-lead and lead) were observed, and when lead was detected, it was as a minor to trace component of the EDS analysis, with other elements such as oxygen, calcium, phosphorus, and aluminum being predominant. In the 32 samples analyzed (one SEM stub and one TEM grid per location) and over 200 images collected, particles could be classified into categories. These categories are based on visual features observed via electron microscopy in the particulate samples. Non-lead particles were classified into eight categories (Figure 23), and lead-containing particles into six categories (Figure 24). Five of the six categories for the lead-containing particles overlapped with those of the non-lead particles.

3.7.3 Non-Lead Containing Particles

Several categories of the non-lead containing particles overlapped with particle categories where lead was detected including mats of semi-rounded hexagonal clustered particles (Figure 23A), chains of semi-rounded hexagonal particles (Figure 23B), conglomerates (Figure 23H), needle-like particles (Figure 23D), and single particles (Figure 23E). Particle categories unique to non-lead particles include rounded and oblong (Figure 23C), ribbon-like (Figure 23F), and blocky discrete particles (Figure 23G). Oxygen, calcium, aluminum, and phosphorus were commonly detected elements in these non-lead particles. Although no lead was detected, there were other potential elements of interest identified such as: zinc, titanium, iron, manganese, chromium, nickel, and tin. For example, the sphere imaged in Figure 23E was comprised mainly of titanium, oxygen, and aluminum with a trace of silica.

3.7.4 Lead Containing Particles

The most commonly observed categories for lead-containing particles were mats of semi-rounded hexagonal clustered particles and mats of matrix material with embedded clusters of particles (Figure 24A and Figure 24E respectively). Although the ultrafiltration process likely contributed to the observation of this particle feature in the SEM imaging, particles imaged in the TEM were collected prior to filtration and show that mats of particles are present. Both of these categories of particles were found to be mainly composed of oxygen, calcium, phosphorus, and aluminum. In Figure 24E, the matrix material (darker) also contained iron, silica, magnesium, zinc, manganese, chloride and a minor amount of lead, and the brighter particles included

iron, silica, magnesium, manganese, zinc, chloride, copper, and lead. The embedded clusters of particles were found to vary as semi-rounded hexagonal particles, irregularly shaped particles, needle-like, and were occasionally indistinctive (mass of bright material with no definite structure visible). Another commonly observed category were conglomerates (Figure 24F). These were irregularly shaped particles containing both angular and rounded embedded grains. Some conglomerates were found to have a mainly iron-rich matrix, while others were more silica-rich.

Less commonly observed categories were needle-like particles and single chains of semi-rounded hexagonal particles (Figure 24D and Figure 24B). For the needle-like particles the main elements observed were still oxygen, aluminum, calcium, and phosphorus, but iron was also frequently detected. Single, discrete lead-containing nanoparticles (<100 nm or <0.1 μm) were not widely found or common. Single nanoparticles were identified but differ greatly from those characterized by ORD in the Newark, NJ, Pequannock drinking water system and were not consistently found in all of the samples analyzed (Figure 24C). Lead is also not the main element comprising these nanoparticles (as it was in Newark, NJ); some appear to be rich in oxygen, iron, aluminum, and phosphorus, while others contain mainly oxygen, calcium, silica, and phosphorus. No discrete single nanoparticles exhibit euhedral crystals, as were observed in Newark, NJ, and instead have irregular edges and shapes (Lytle et al., 2020).

Location 3446 had the highest lead concentration by ICP-MS analysis of the PC##-TM water sample associated with the sequential sampling portion of the study, at 133 ppb total lead. While many lead-containing particles were found in this sample by both SEM and TEM, no discrete <100 nm particles were identified. Instead, all lead-containing particulate was associated with a matrix or agglomerated particles. In one agglomeration multiple particle categories are visible, although the main category for the image would be mats of matrix material with embedded clusters of particles (Figure 25). In Figure 25, chains/agglomerations of semi-rounded hexagonal particles are visible, along with needle-like particles. However, all of the lead-containing particles are associated with a matrix material (duller material surrounding the bright particle clusters).

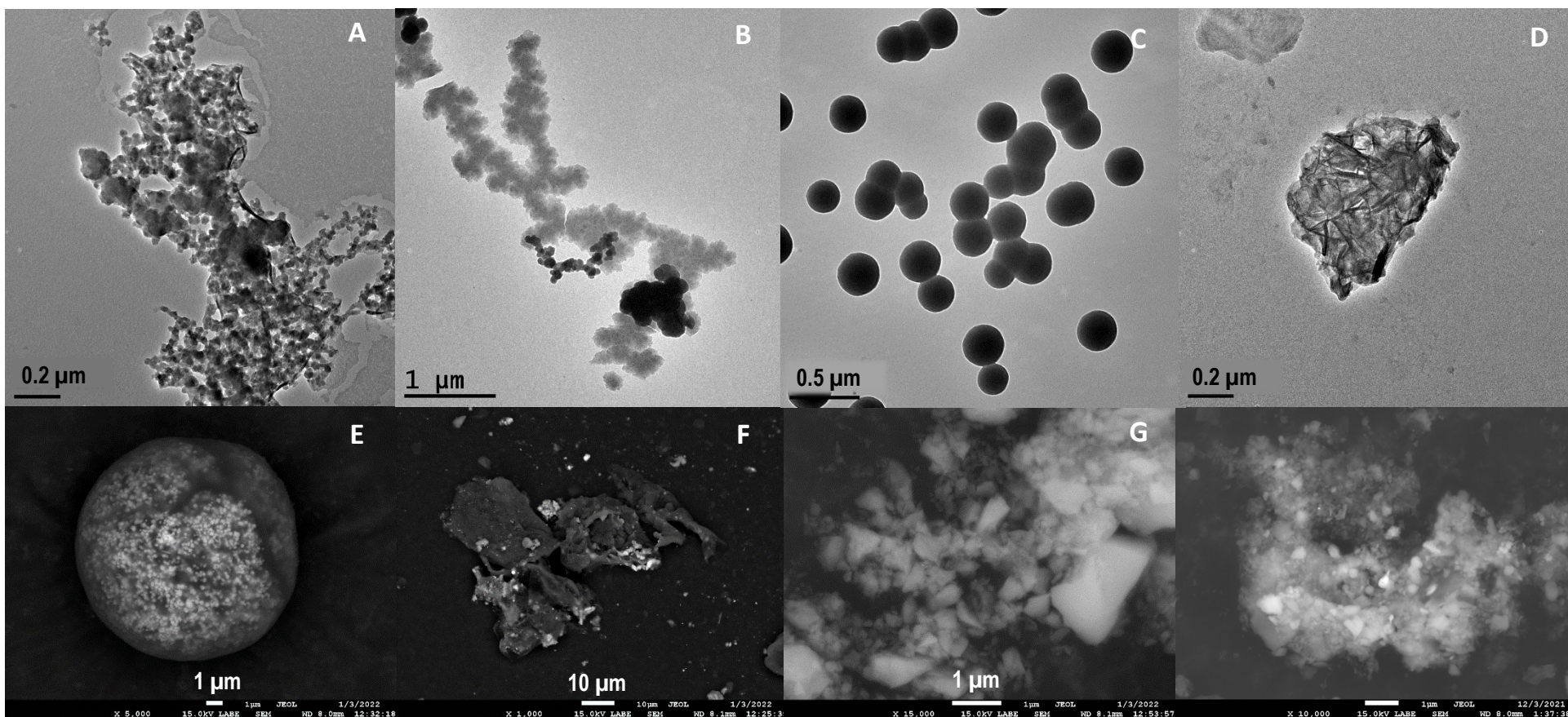


Figure 23. Non-lead containing particles. Images A-D collected on the TEM at 200 kV. Images E-H collected on the SEM in back scatter detection mode at 15 kV and a working distance of 8 mm.

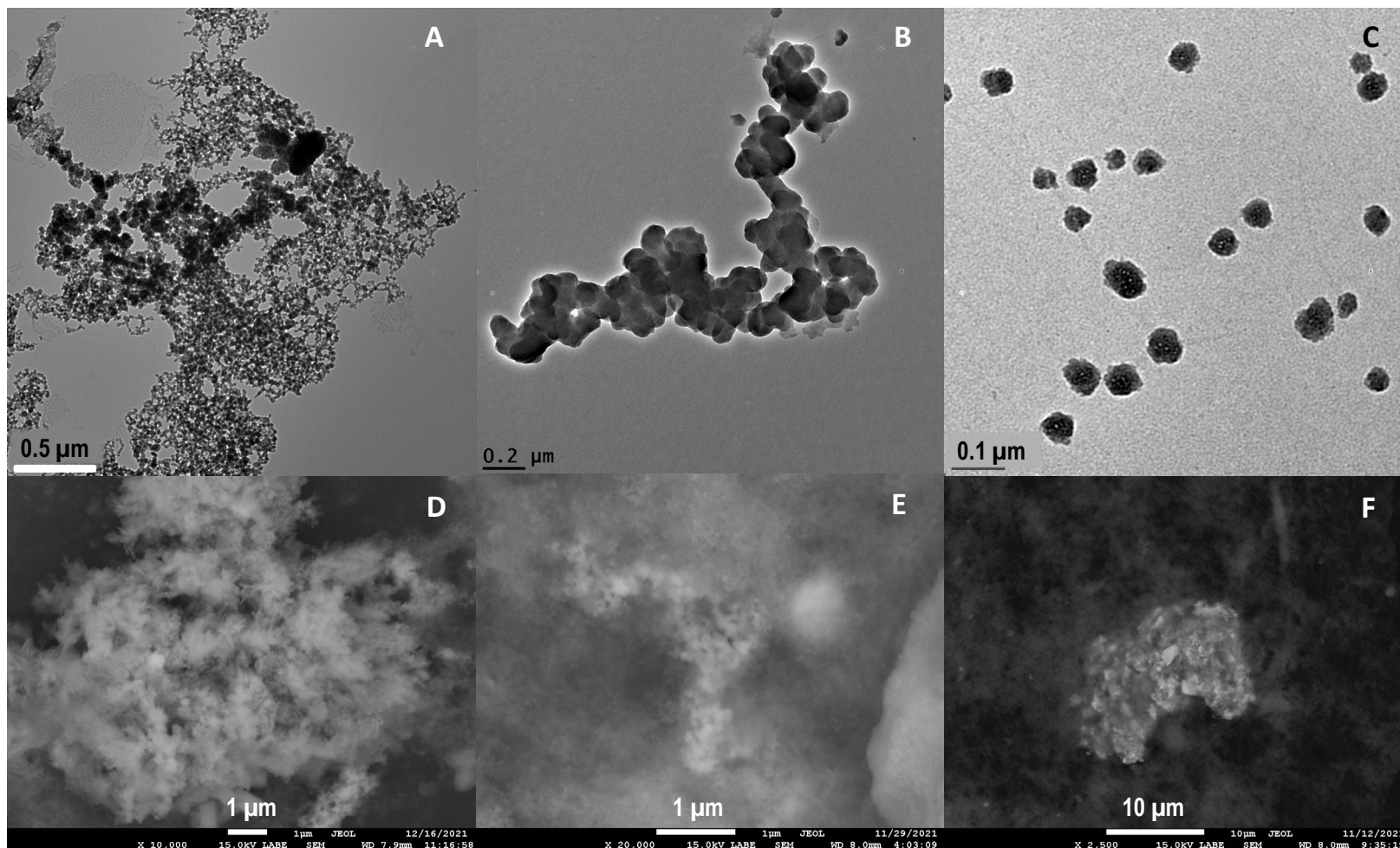


Figure 24. Lead-containing particles. Images A, B, and C collected on the TEM at 200 kV. Images D, E, and F collected on the SEM in back scatter detection mode at 15 kV and a working distance of 8 mm.

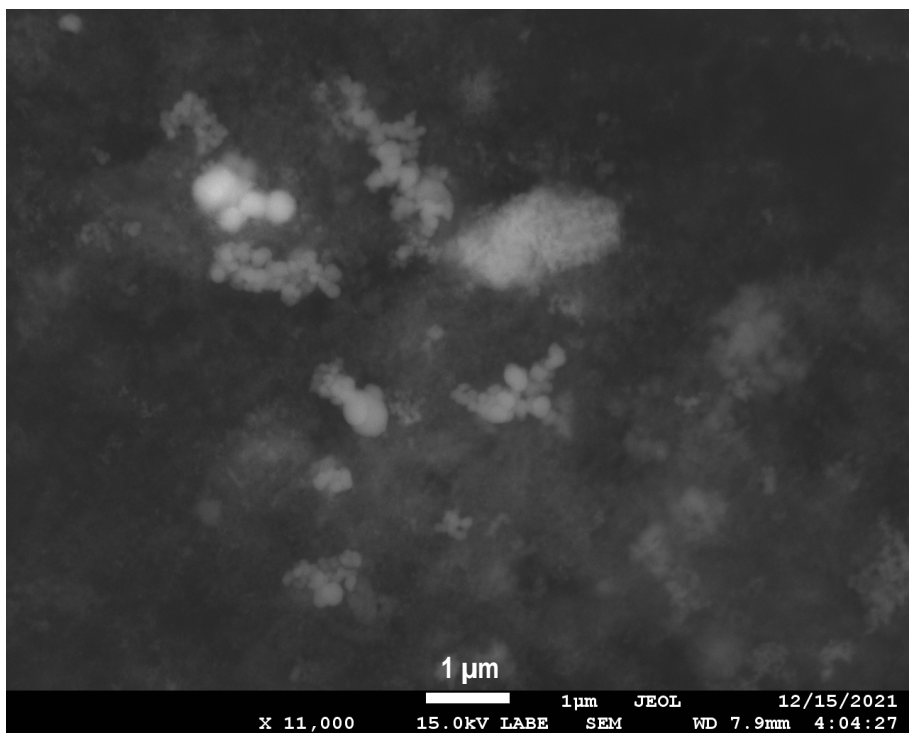


Figure 25. Lead-containing particles from location 3446. Image collected in back scatter detection mode on the SEM at 15 kV and a working distance of 8 mm.

3.8 Other Metals of Concern

Out of all the study samples collected in Benton Harbor between November and December 2021, a small subset were found to exceed portions of the National Primary and Secondary Drinking Water Regulations for elements measured other than lead (Table 13). For the National Primary Drinking Water Regulations, five samples (representing two locations) were found to have cadmium ≥ 0.005 mg/L, the cadmium MCL, and one sample was found to have chromium ≥ 0.1 mg/L, the chromium MCL. For the Secondary Regulation, thirteen samples (representing 6 locations) had iron ≥ 0.3 mg/L, the iron secondary MCL, and four samples (representing 2 locations) had aluminum ≥ 0.5 mg/L, the aluminum secondary MCL. However, additional samples may have exceeded the aluminum secondary standard because the reporting limit for aluminum is well above the secondary MCL at 0.5 mg/L.

There were also four samples (representing 3 locations) that had manganese greater than the Secondary MCL for manganese at 0.05 mg/L. It should be noted that there is a life-time health advisory in place for manganese in drinking water at 0.3 mg/L, meaning that there are potential health effects that can be associated with manganese levels at or above 0.3 mg/L. Manganese was not a ubiquitous contaminant in the water samples collected from Benton Harbor or frequently occurring, with only 23 samples above the reporting limit across all samples. Further, the one sample with manganese above the health advisory was a 5-second flush sample (BH4588-5FF01), which is water that is not meant, per manufacturer's instructions, to be consumed.

Sample BH4588-5FF01 was found to have multiple high concentrations, including Secondary MCL exceedances for chromium, iron, and manganese along with health advisory exceedances for manganese and nickel in Table 13. This same sample also had lead at 2.7 ppb, copper at 78.6 $\mu\text{g/L}$, and sodium at 91.6 mg/L. As it is a five-second flush sample, this water is not meant for human consumption per the manufacturer's recommendation. Further, given the high iron concentrations (highest sample measured in the entire study, next highest is 3.4 mg/L) it is likely representative of a particle captured in the sample. A particle would be unlikely to have made it through the water filter cartridge; however, it potentially could have come off of the faucet or have splashed up onto the water filter and was rinsed off into the sample bottle.

After receipt of these metals results, EPA coordinated with the state of Michigan to contact each home with metals result(s) exceeding an MCL or Life-Time Health Advisory. EPA notified the residents of the results via phone call in April 2022 and their final results letter in May 2022. MDHHS intended to follow-up with each home to evaluate sources and mitigation measures.

Table 13. Samples exceeding primary and secondary drinking water maximum contaminant level (MCLs) regulations and life-time health advisory levels.

Samples Exceeding the Primary Cadmium MCL of 0.005 mg/L	
Sample ID	Cadmium Concentration (mg/L)
BH2710-SS02	0.006
BH4730-PC03-TM	0.011
BH4730-SS01	0.008
BH4730-SS02	0.026
BH4730-SS04	0.008
Samples Exceeding the Primary Chromium MCL of 0.1 mg/L	
Sample ID	Chromium Concentration (mg/L)
BH4588-5FF01	12.9
Samples Exceeding the Secondary Iron MCL of 0.3 mg/L	
Sample ID	Iron Concentration (mg/L)
BH3014-UF03	0.42
BH3108-SS01	0.60
BH3108-SS02	1.2
BH3446-PC03-TM	0.58
BH3446-SS01	2.1
BH3446-SS02	3.4
BH3446-SS04	0.83
BH3472-UF03	1.7
BH4588-5FF01	50
BH4730-PC03-TM	0.72
BH4730-SS02	0.76
BH4730-SS04	0.42
BH4730-SS05	0.32
Samples Exceeding the Secondary Manganese MCL of 0.05 mg/L	
Sample ID	Manganese Concentration (mg/L)
BH3446-SS01	0.162
BH3446-SS02	0.232
BH4588-5FF01	0.725 (Exceeds Health Advisory Life-Time Level of 0.3 mg/L)
BH4730-SS02	0.106
Samples Exceeding the Secondary Aluminum MCL of 0.05 mg/L	

Sample ID	Aluminum Concentration (mg/L)
BH3446-PC03-TM	0.71
BH3446-SS01	6.9
BH3446-SS02	3.2
BH4730-SS02	1.1
Samples Exceeding the Life-Time Health Advisory for Nickel at 0.1 mg/L	
Sample ID	Nickel Concentration (mg/L)
BH4588-5FF01	0.65

4.0 Conclusion

All properly operating water filter water samples were found to be below the NSF/ANSI 53 and bottled water certification (21 C.F.R. § 165.110) requirements of 5 ppb lead (FDA). Despite EPA efforts to challenge water filters by targeting LSL locations and efforts in the latter portion of the study to increase stagnation time, lead concentrations in associated unfiltered water samples were often found to be low in the locations sampled, with 79% of unfiltered water samples containing <5 ppb lead. Statistical analysis indicated that in the water filter effectiveness study, there was no difference in lead levels with longer stagnation times or the targeted service line samples in this community. However, higher lead levels were observed in stagnated samples at many sequential sampling locations.

Multiple peaks of lead were noted in many of the locations profiled, indicating more than one significant source of lead to household drinking water. There appeared to be two relative clusters where the highest lead levels in the profile samples appeared. One cluster was in the premise plumbing near the tap (1st-3rd liter), and another appeared in the volumes likely representing the service line in the range of the 6th to 11th liter. Additional elemental analyses allowed for the evaluation of other plumbing materials present within the premise plumbing and further identified galvanized iron piping as a prevalent material in Benton Harbor residences. It was also found that concentrations of lead (1-25 ppb) were associated with sections of the plumbing profiles where zinc concentrations were observed and where galvanized iron piping was suspected. Lead particulate was identified at all sixteen locations where particulate samples were collected, along with other non-leaded particles. Nanoparticulate lead was not common and when identified occurred as irregularly shaped particles in which lead was not the main element. Appearances of nanoparticulate in Benton Harbor are different from what ORD had observed in Newark, NJ.

The electron microscopy data coupled with the 100% success rate of all properly operating water filter samples collected in the community lends confidence that nanoparticulate lead is not a significant source of lead in drinking water in Benton Harbor. Properly operated and certified filters are working to reduce lead levels in this community's drinking water.

5.0 References

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Appendix A. Drinking Water Sampling Protocols for Benton Harbor Water Study, Version 2.5, 12/10/2021



Field Collection
Protocols_Revision_20

Appendix B. Benton Harbor, MI Filter Performance Screening and Assessment Study, Revision 0, 11/5/2021



Residential_Sampling
_QAPP_BH_Final.pdf

Appendix C. Total and Free Chlorine Results by Location

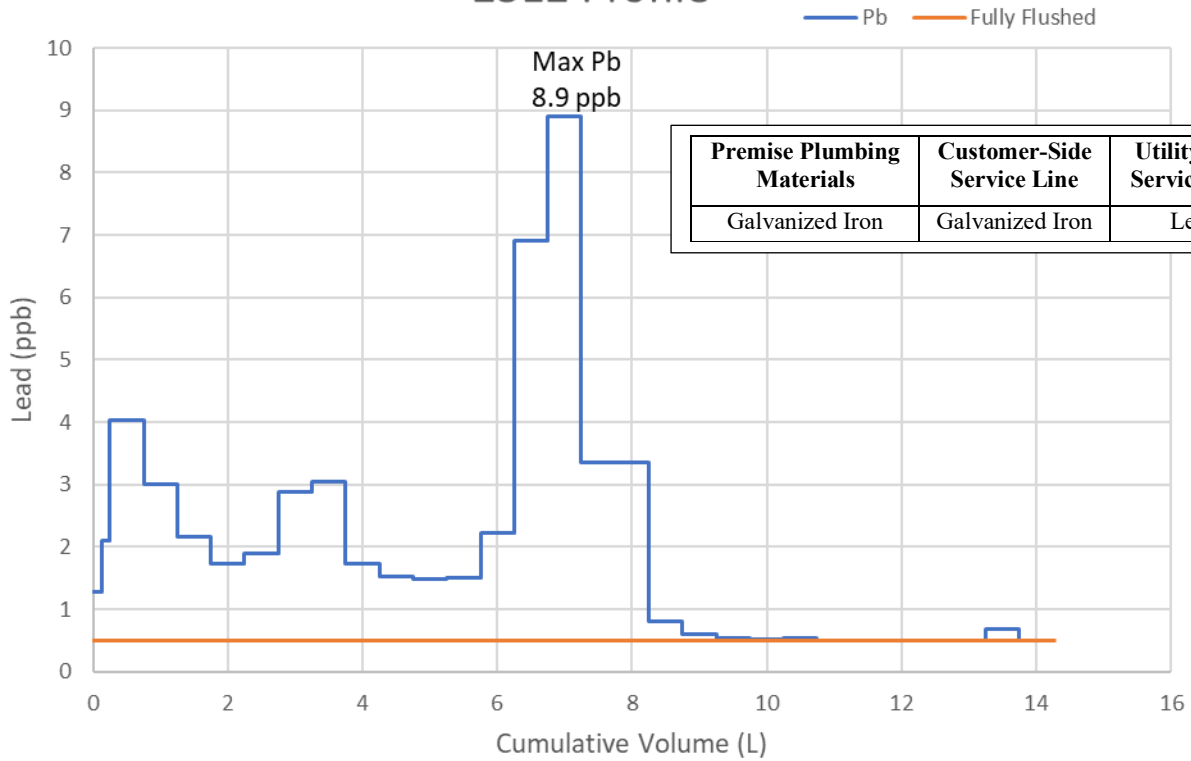


ChlorineResults_withD
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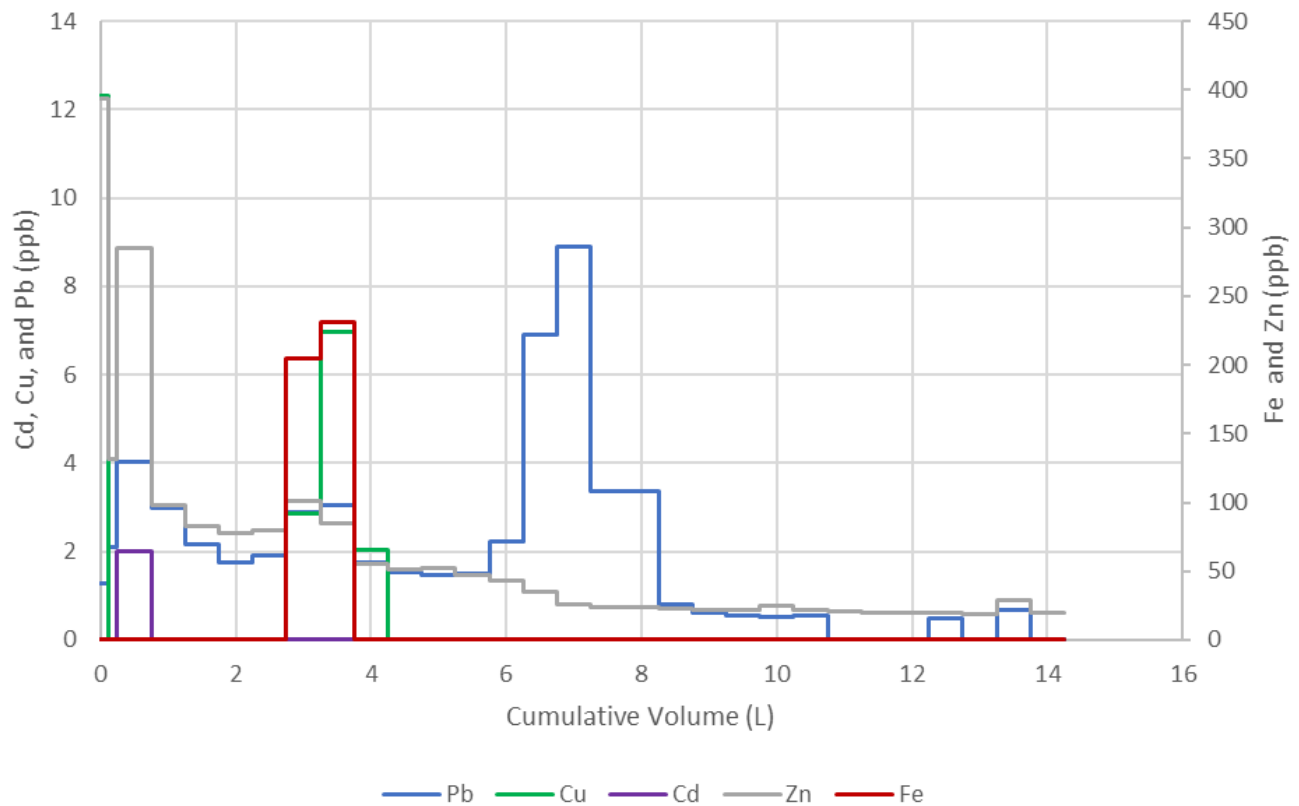
Appendix D. Sequential Metal Profiles by Location

For all the graphs presented in Appendix D, when concentrations were below the various reporting limits for the analytes “0”s were graphed. Additionally, if all samples in a profile have concentrations BRL for an analyte, that analyte will not be included on the graph. Elemental abbreviations on the graphs that follow: Cd- cadmium, Cr- chromium, Cu- copper, Fe- iron, Mn- manganese, Ni- nickel, Pb- lead, and Zn- zinc. All x-axes are “cumulative volume” in liters (L), while the y-axes show the concentrations of various elements in parts per billion (ppb).

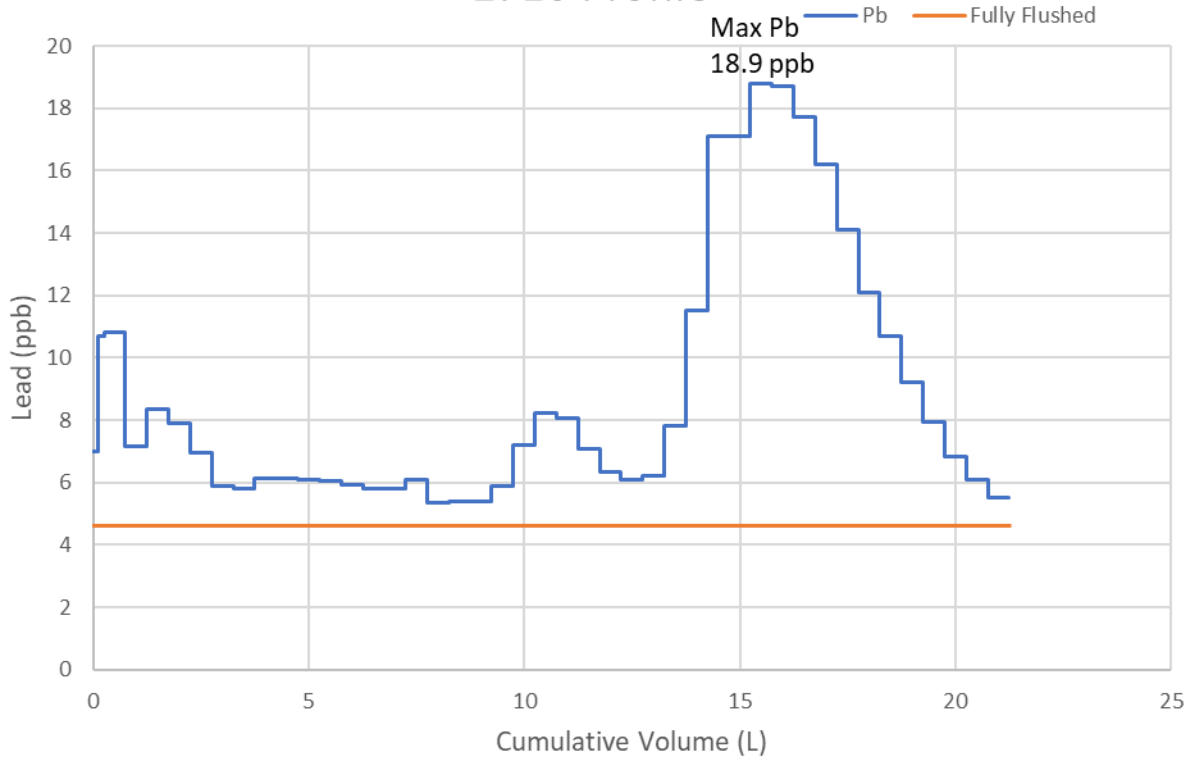
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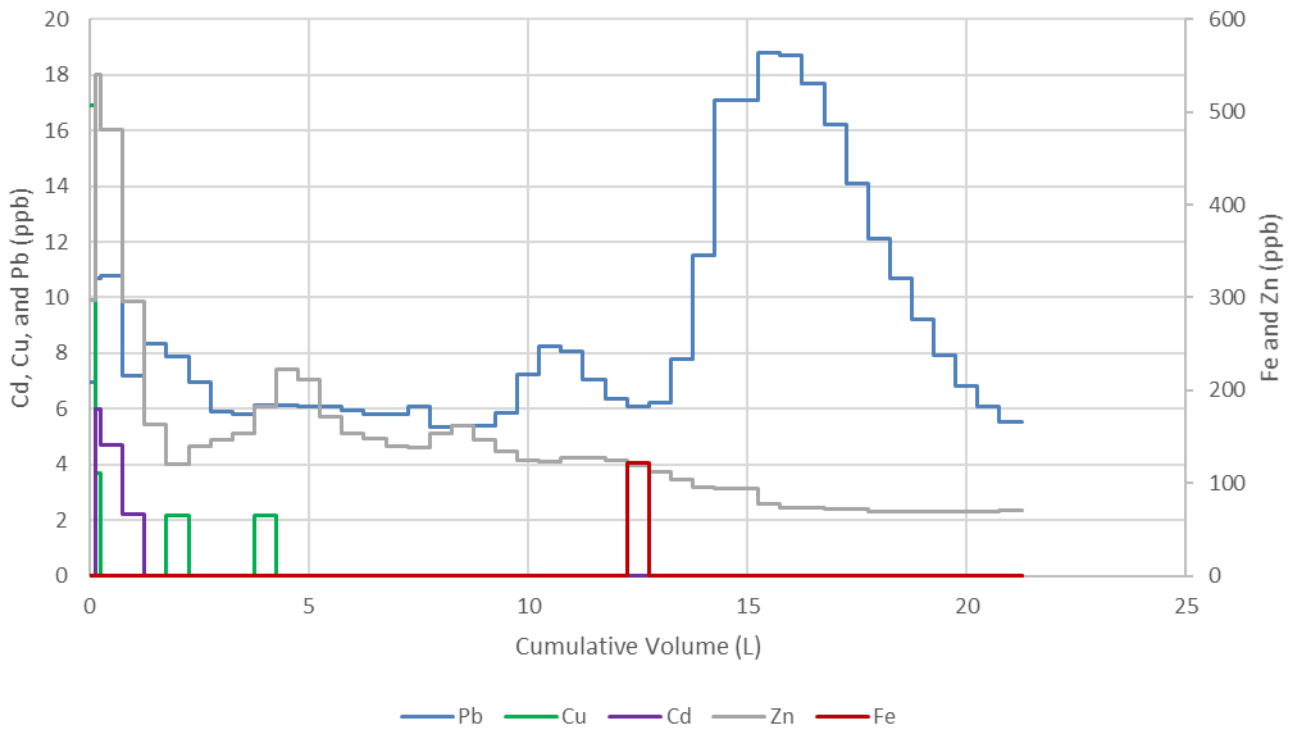
2312 Multiple Metals Profile



2710 Profile



2710 Multiple Metals Profile



Premise Plumbing Materials

Galvanized Iron

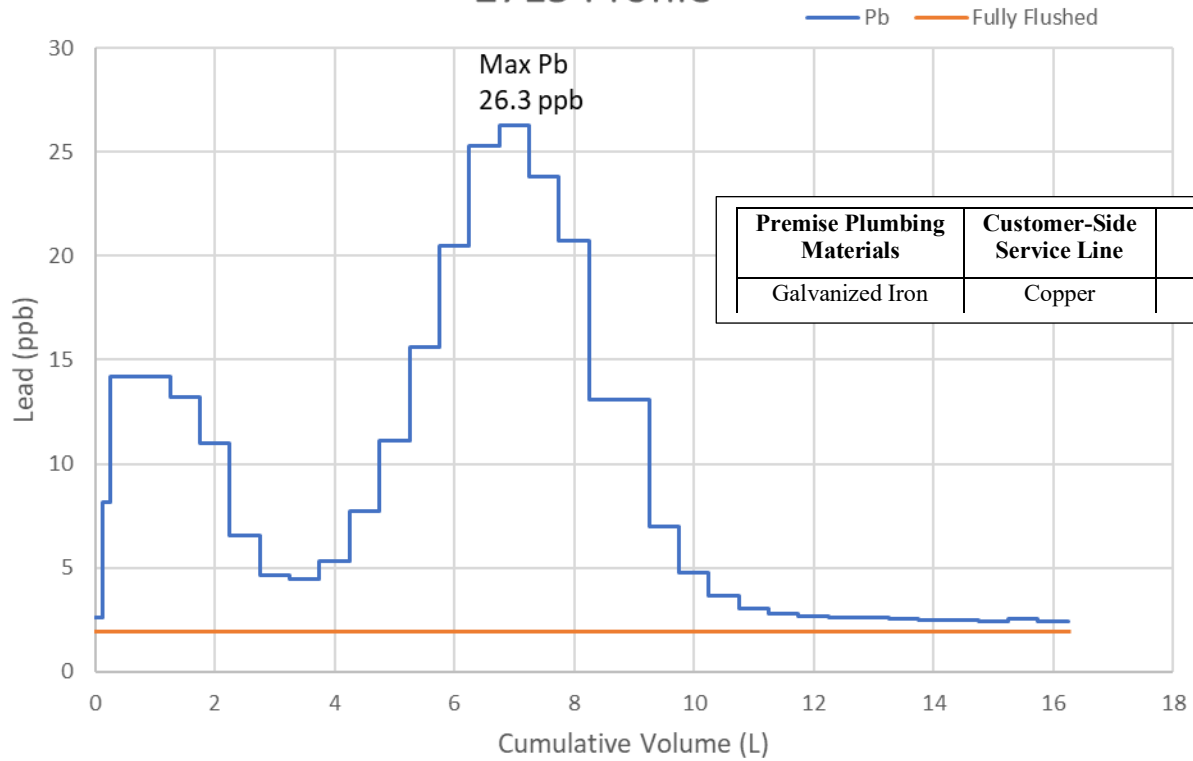
Customer-Side Service Line

Galvanized Iron

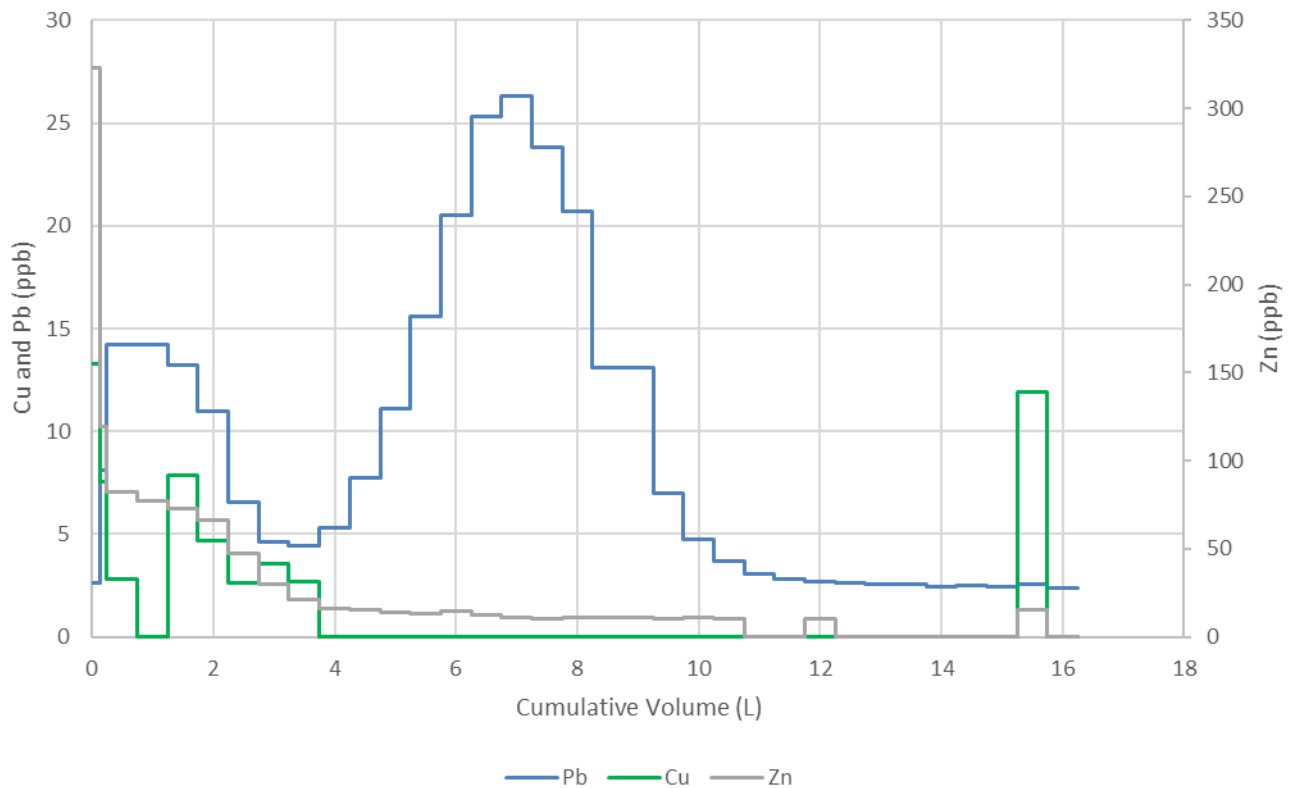
Utility-Side Service Line

Lead

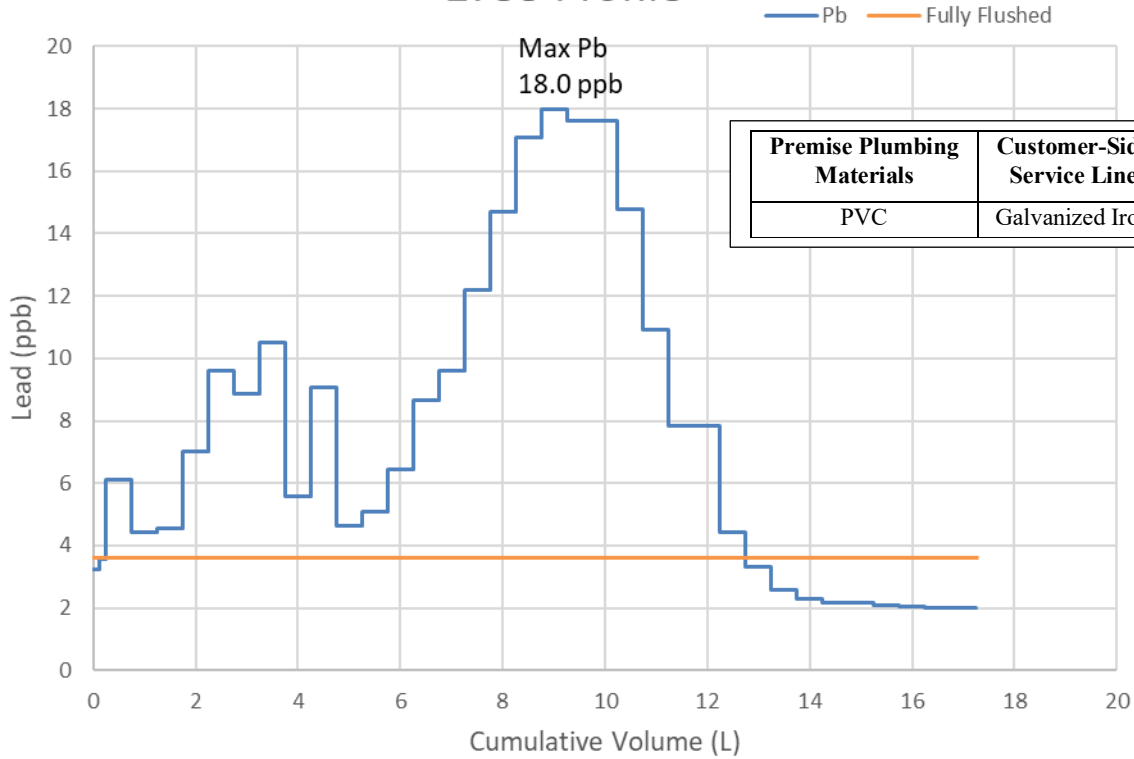
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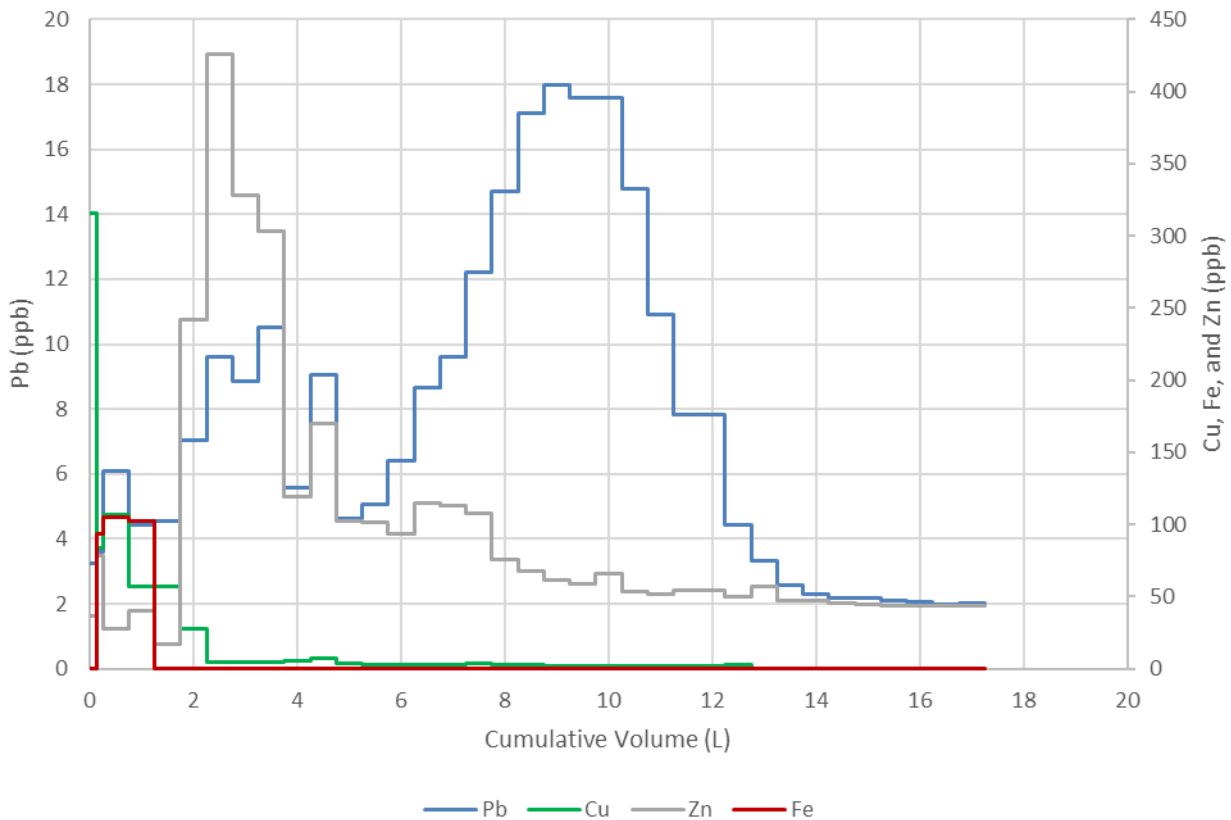
2715 Multiple Metals Profile



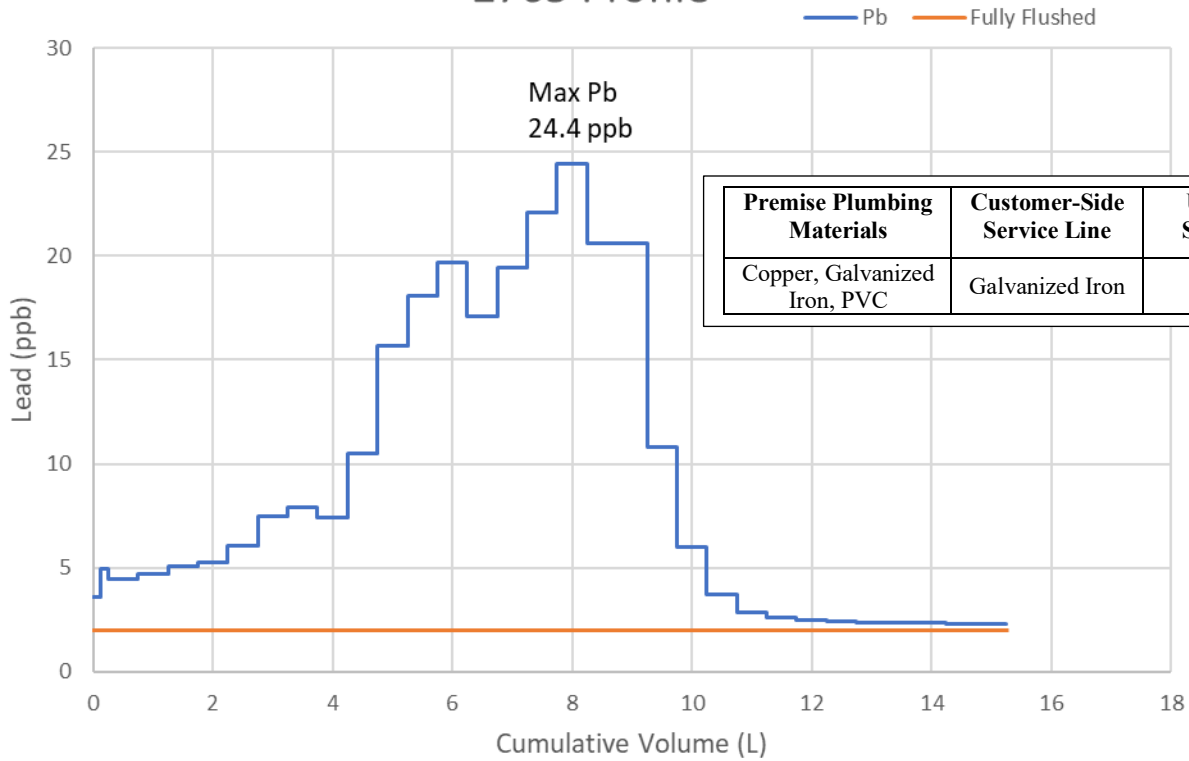
2753 Profile



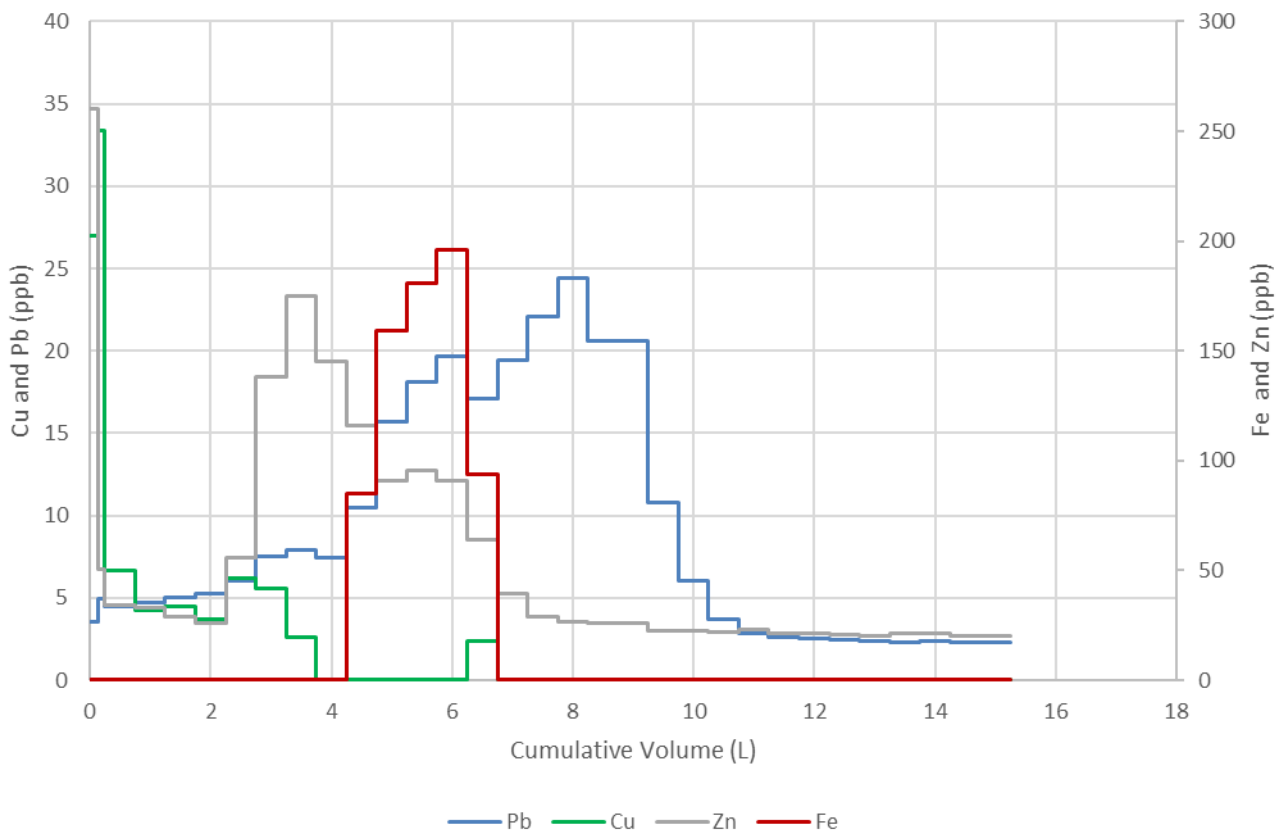
2753 Multiple Metals Profile



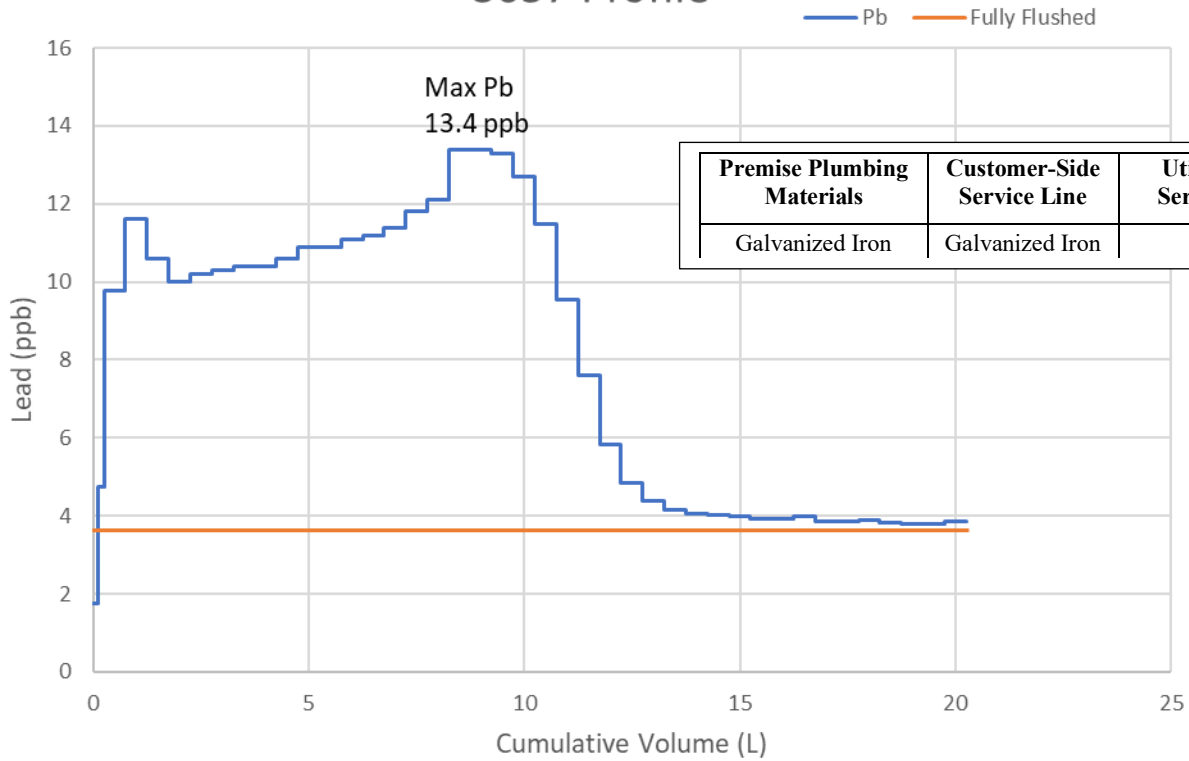
2765 Profile



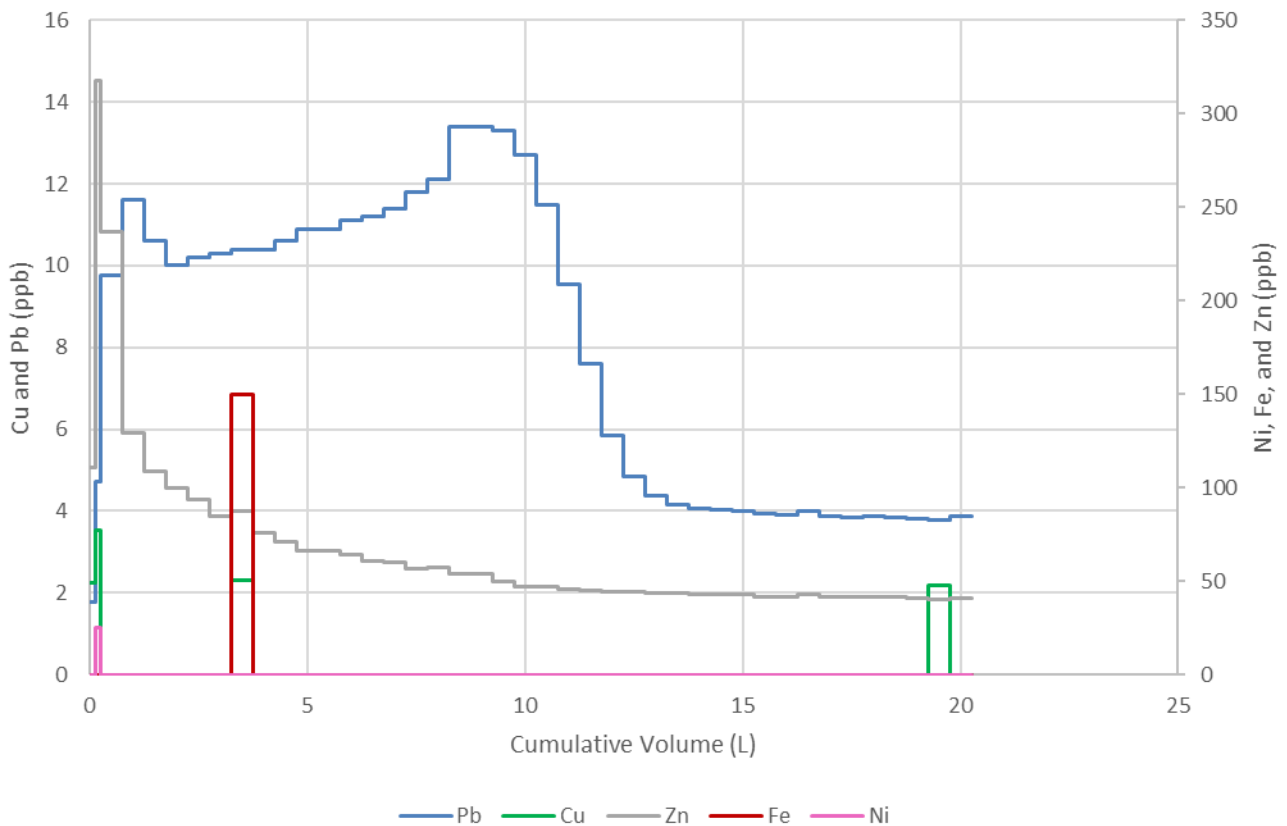
2765 Multiple Metals Profile



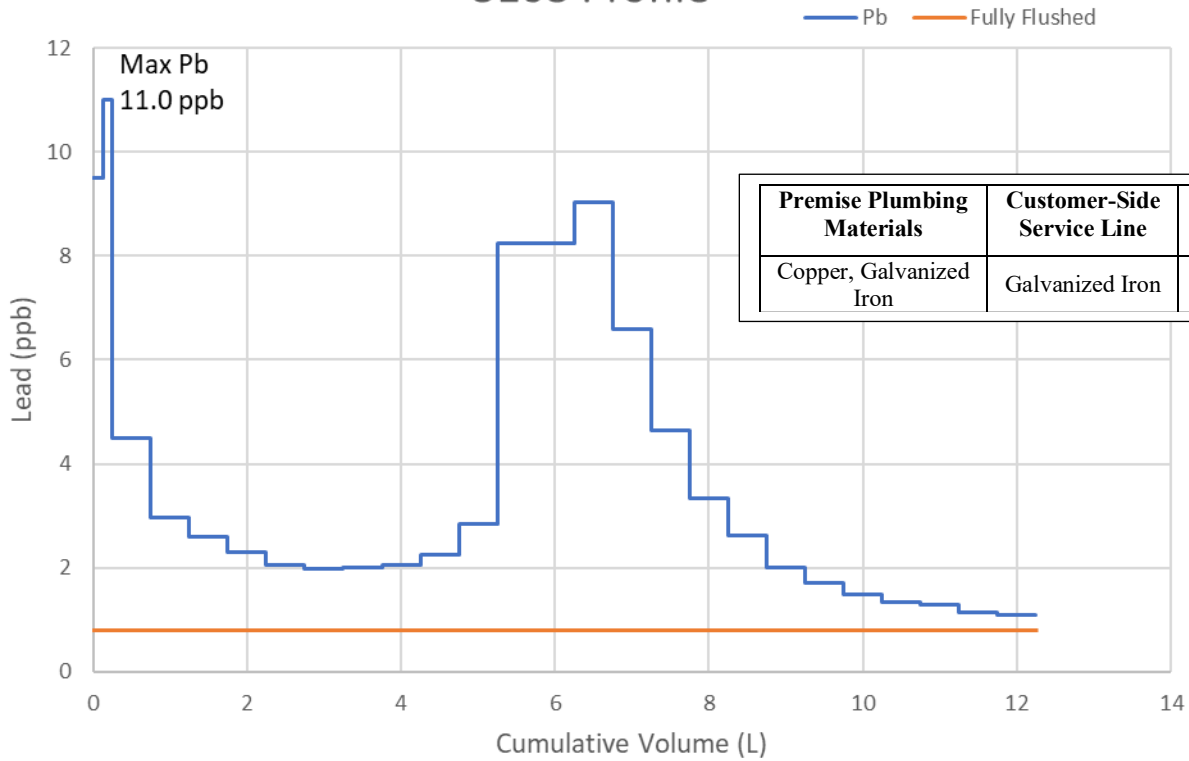
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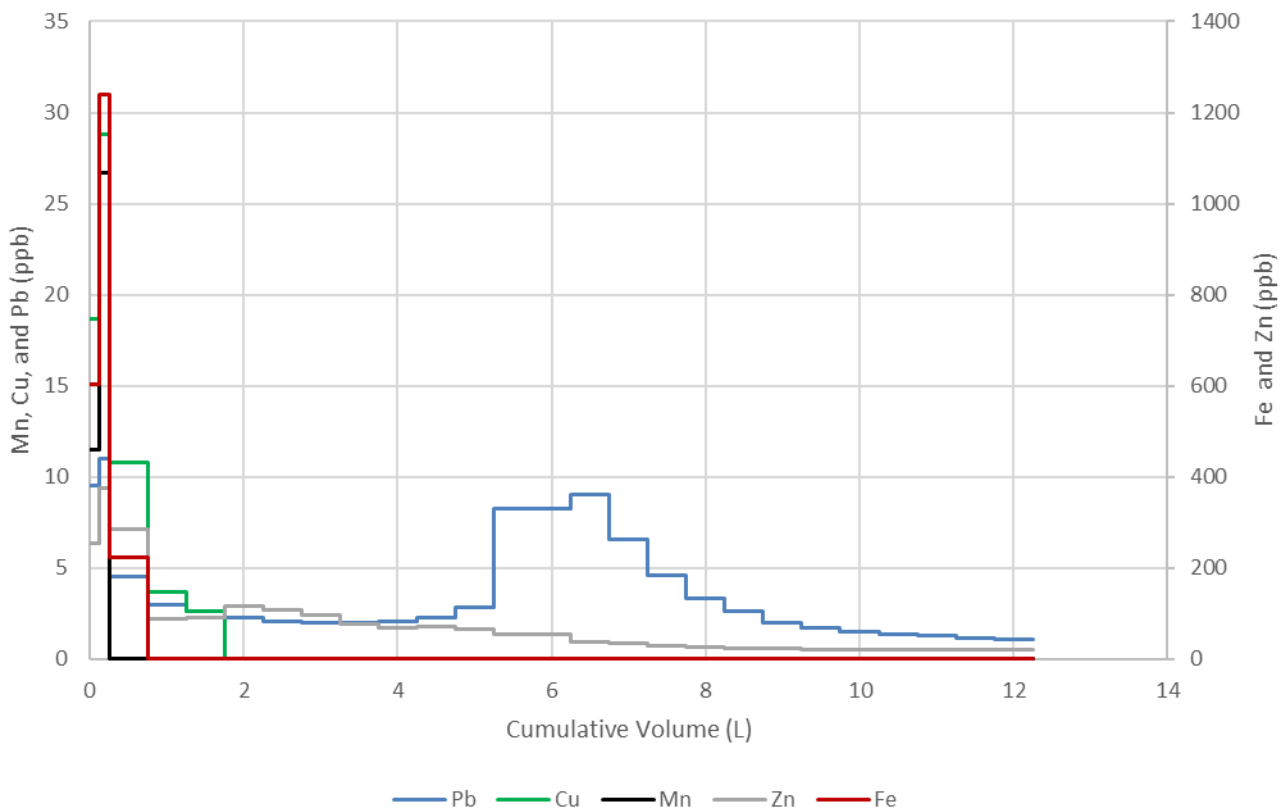
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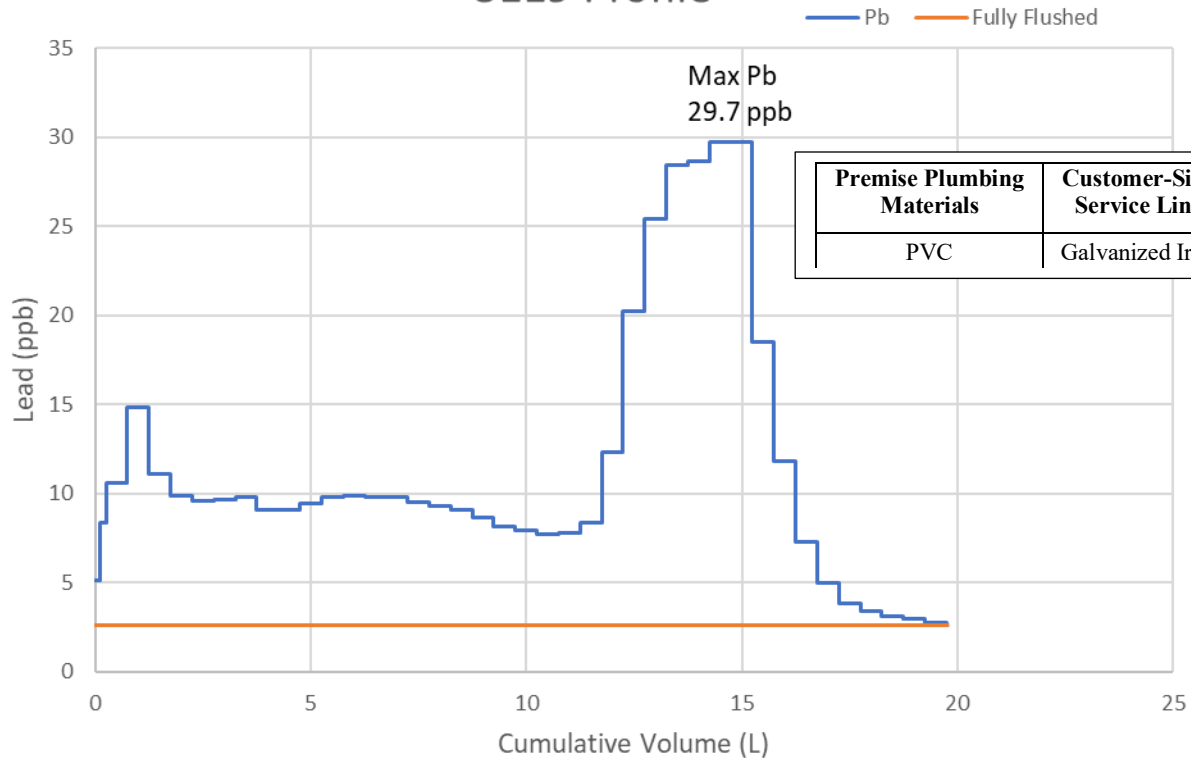
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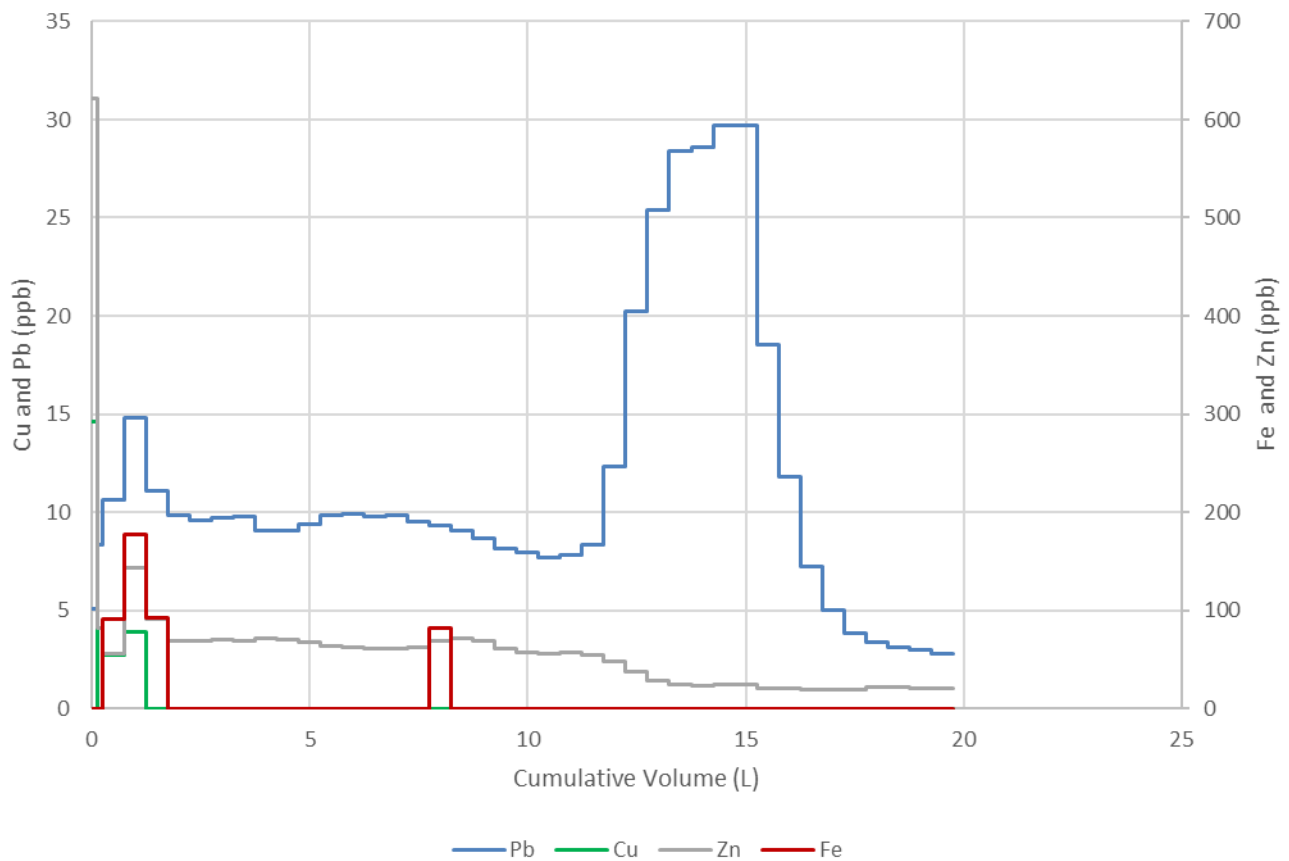
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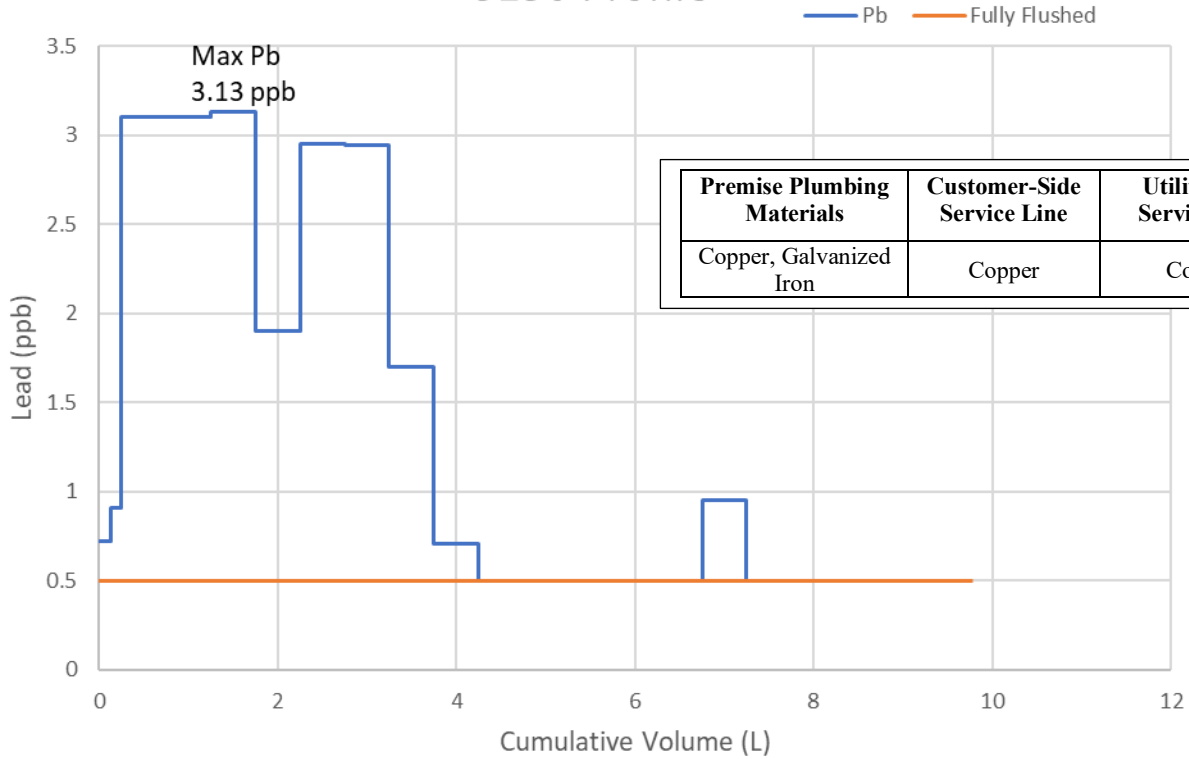
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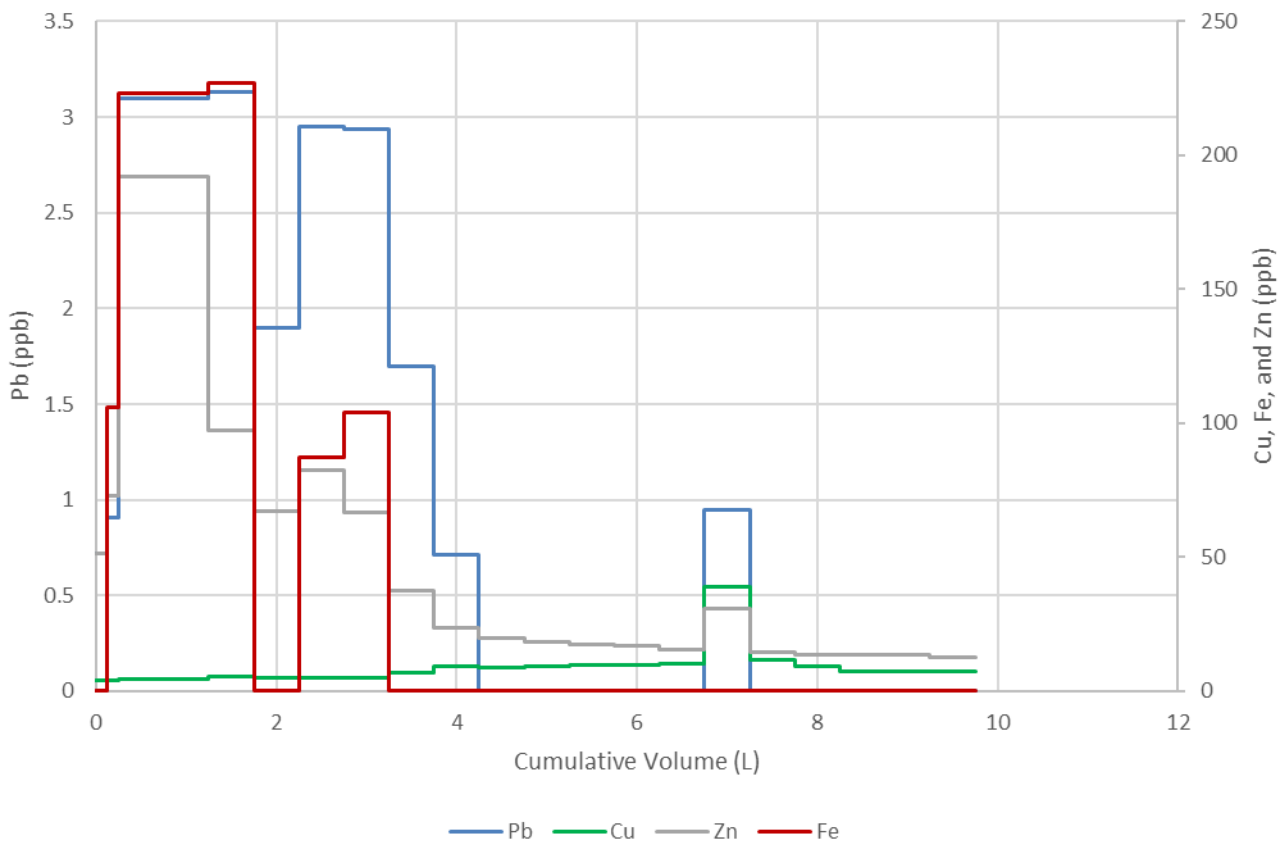
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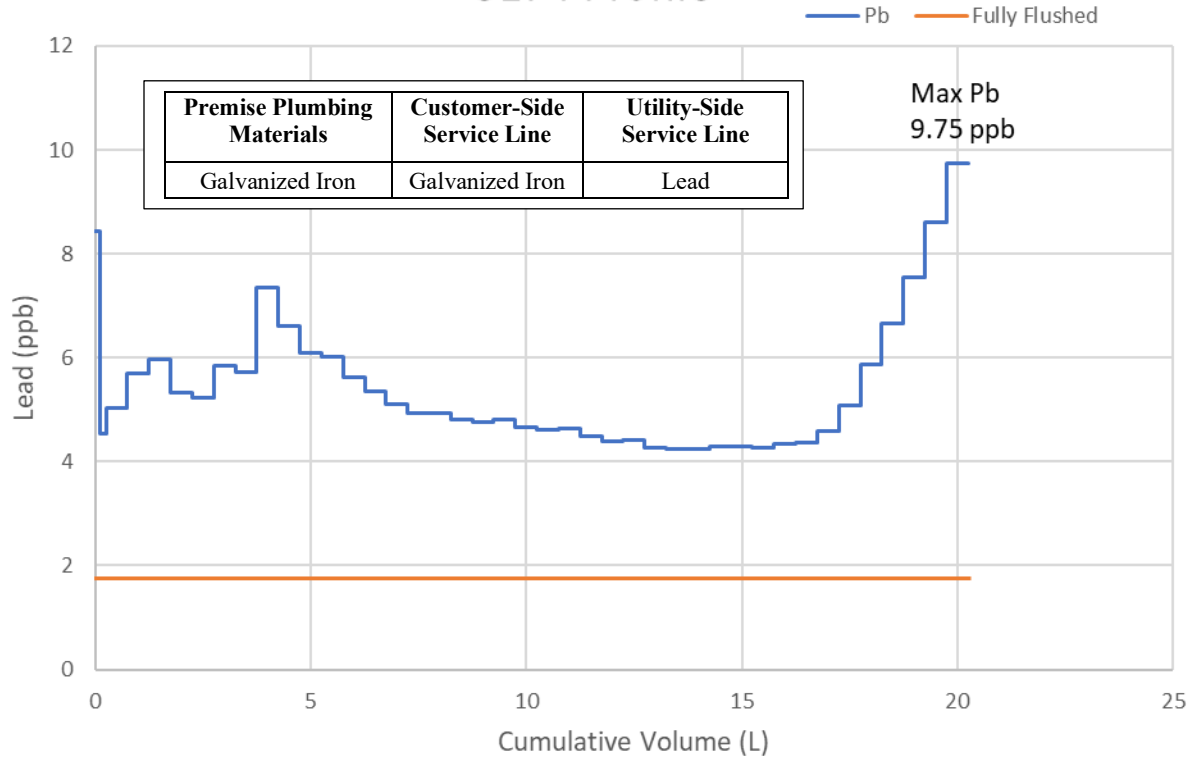
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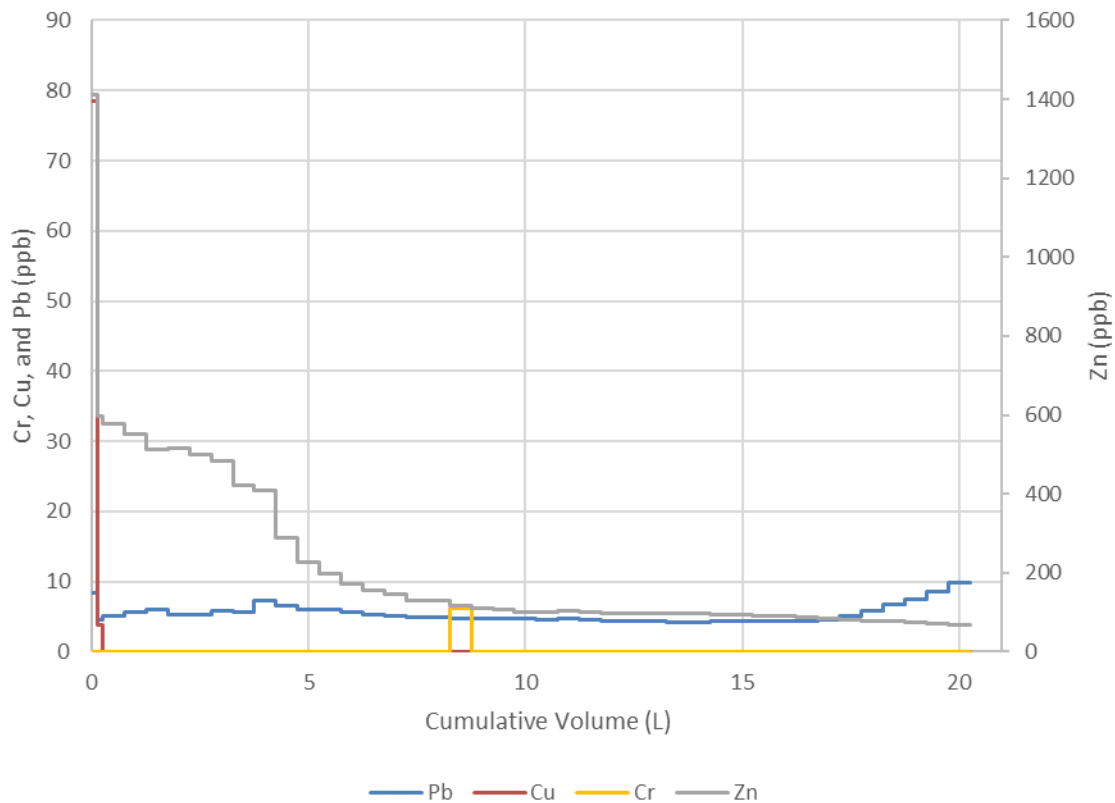
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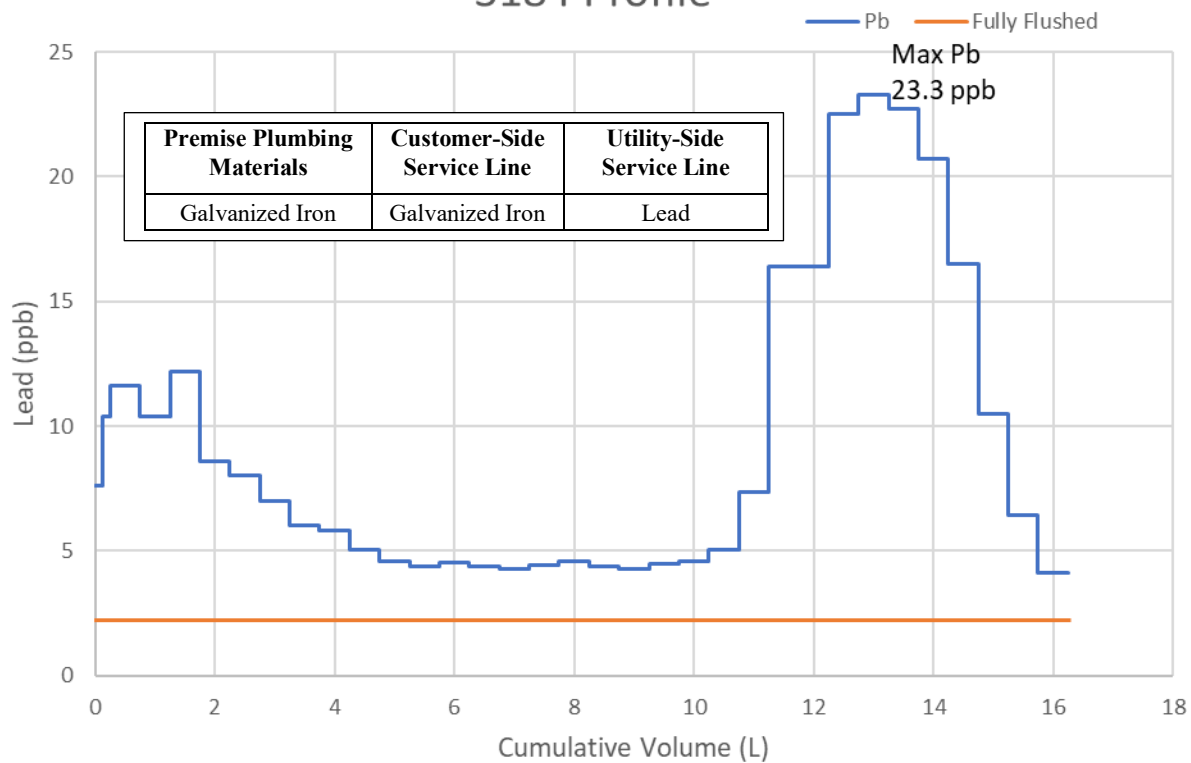
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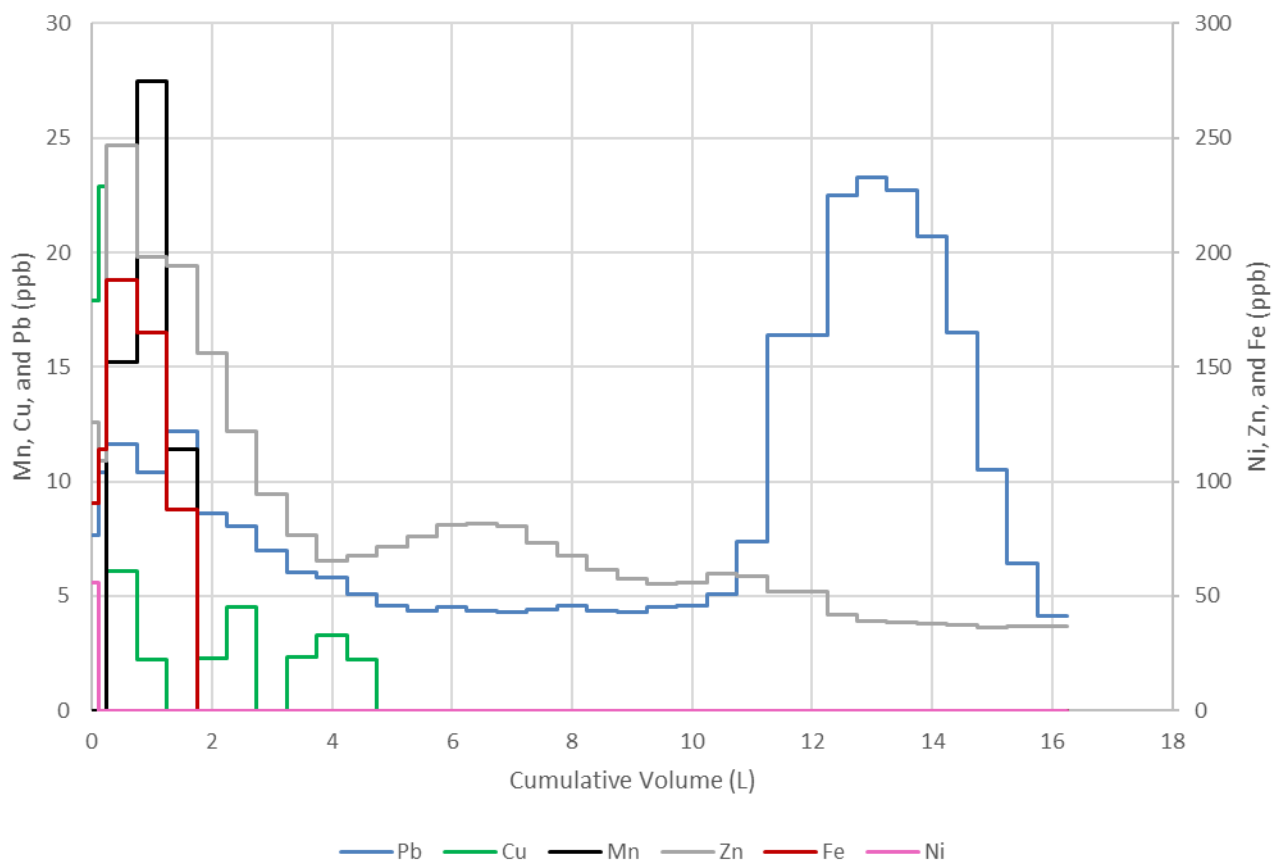
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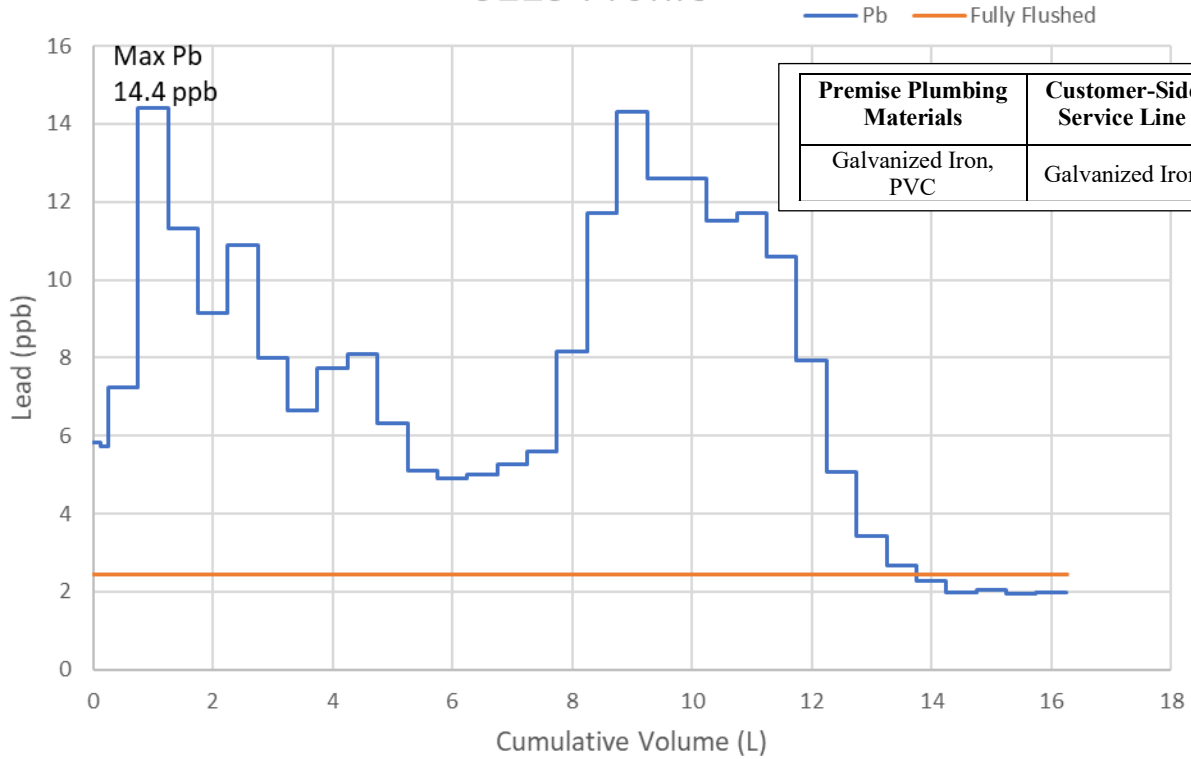
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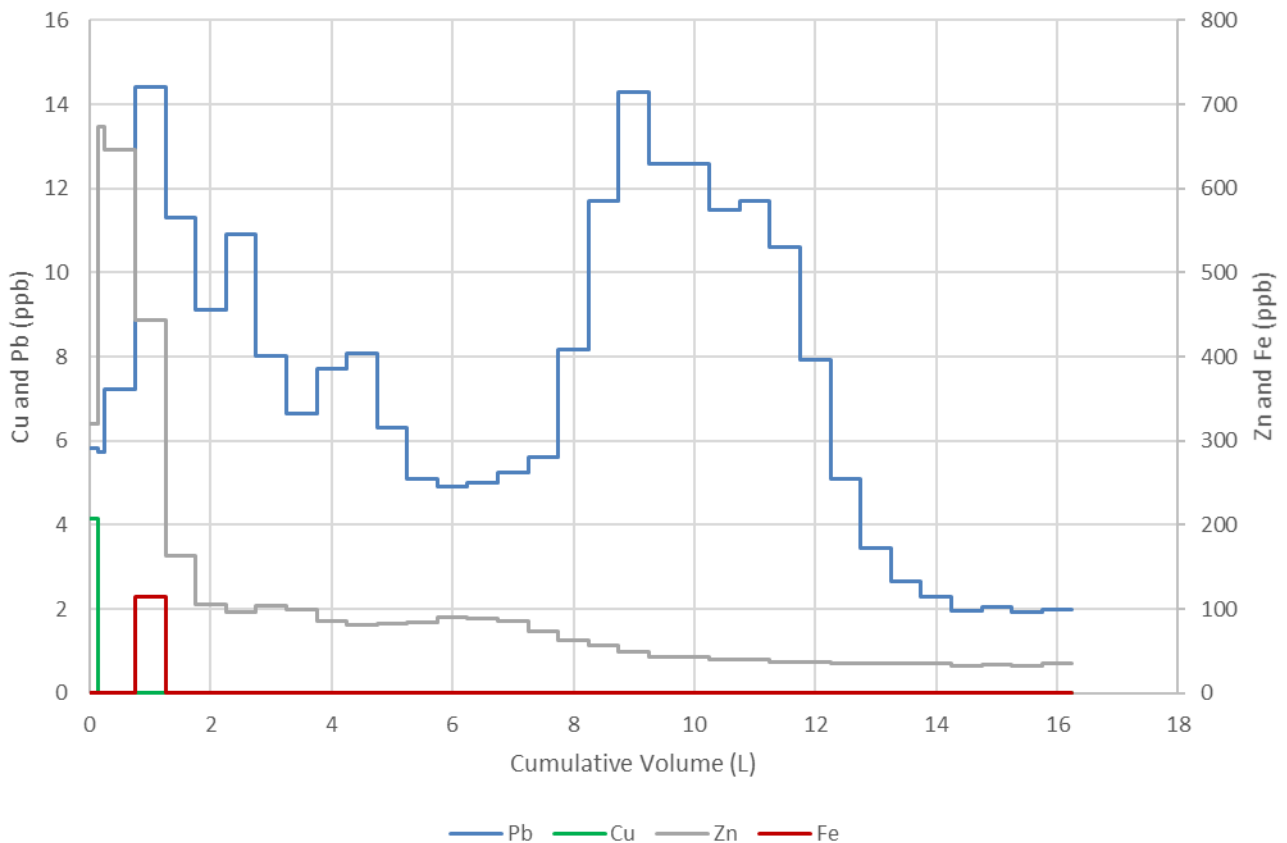
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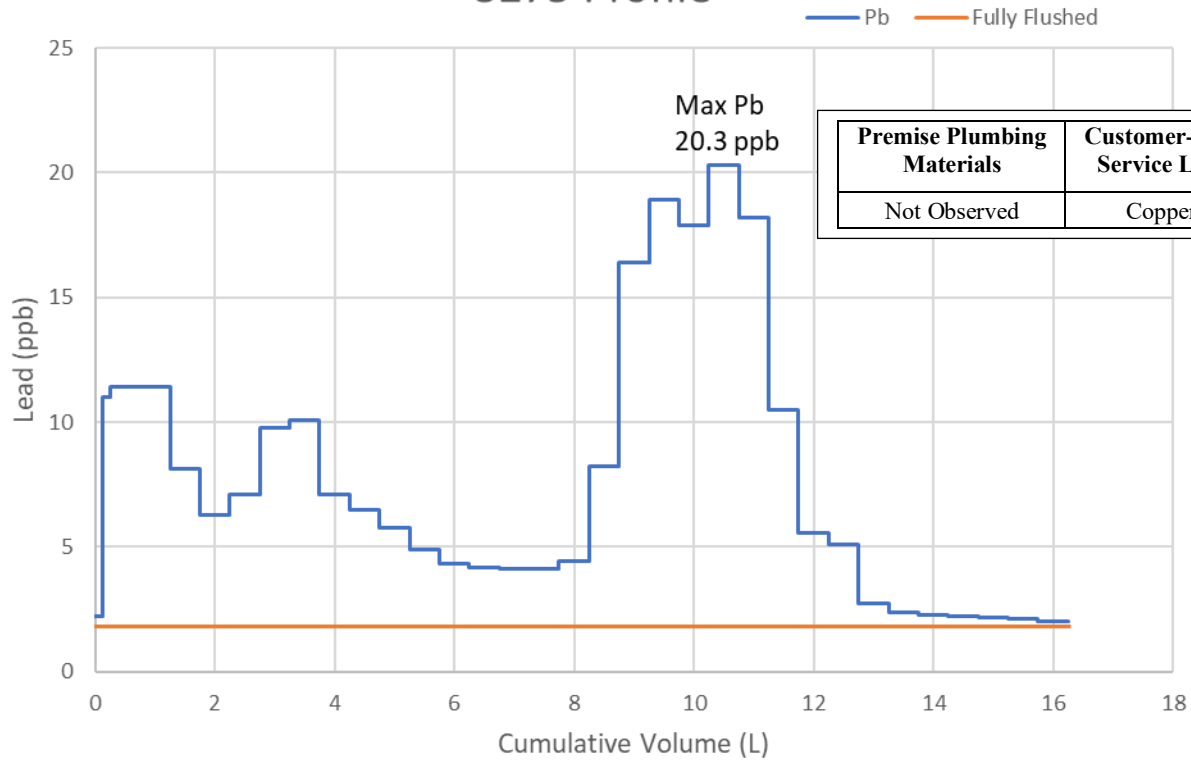
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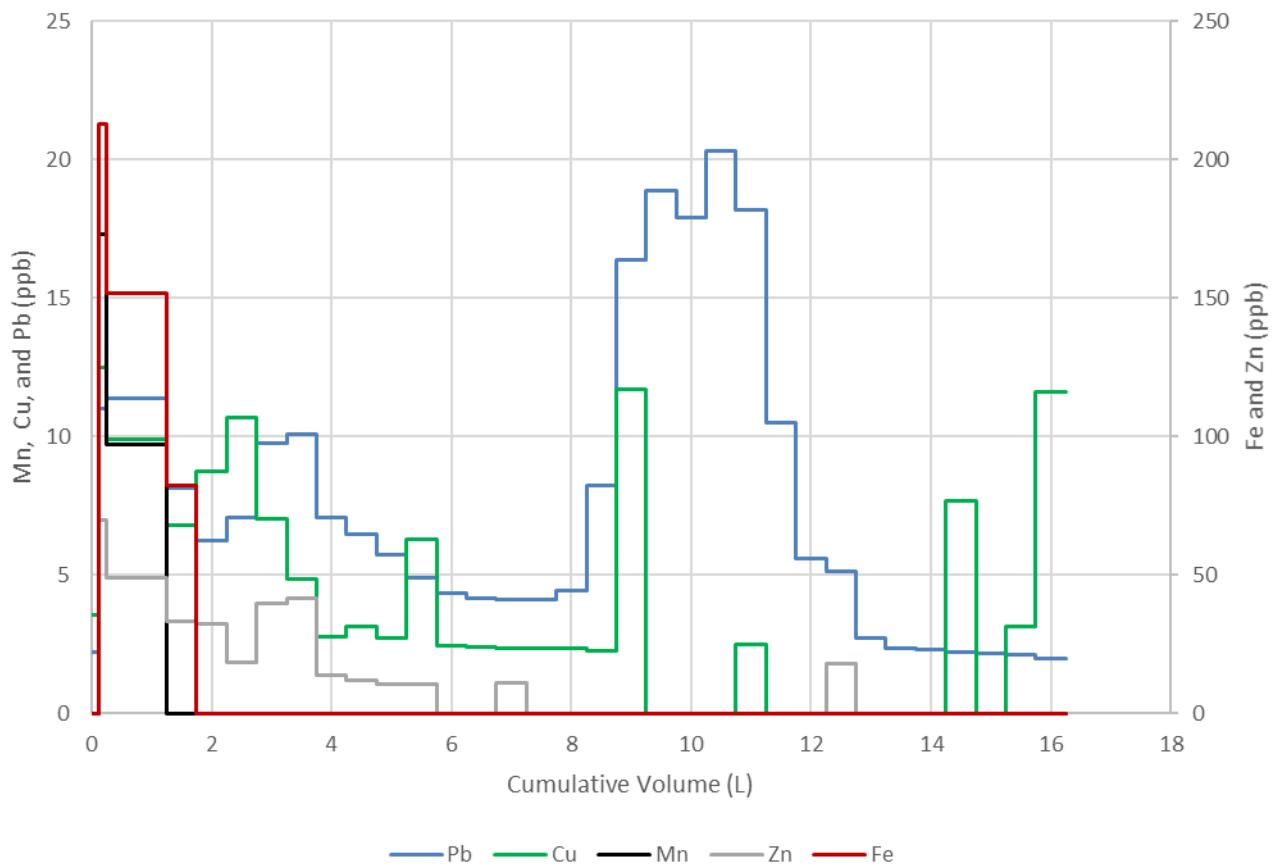
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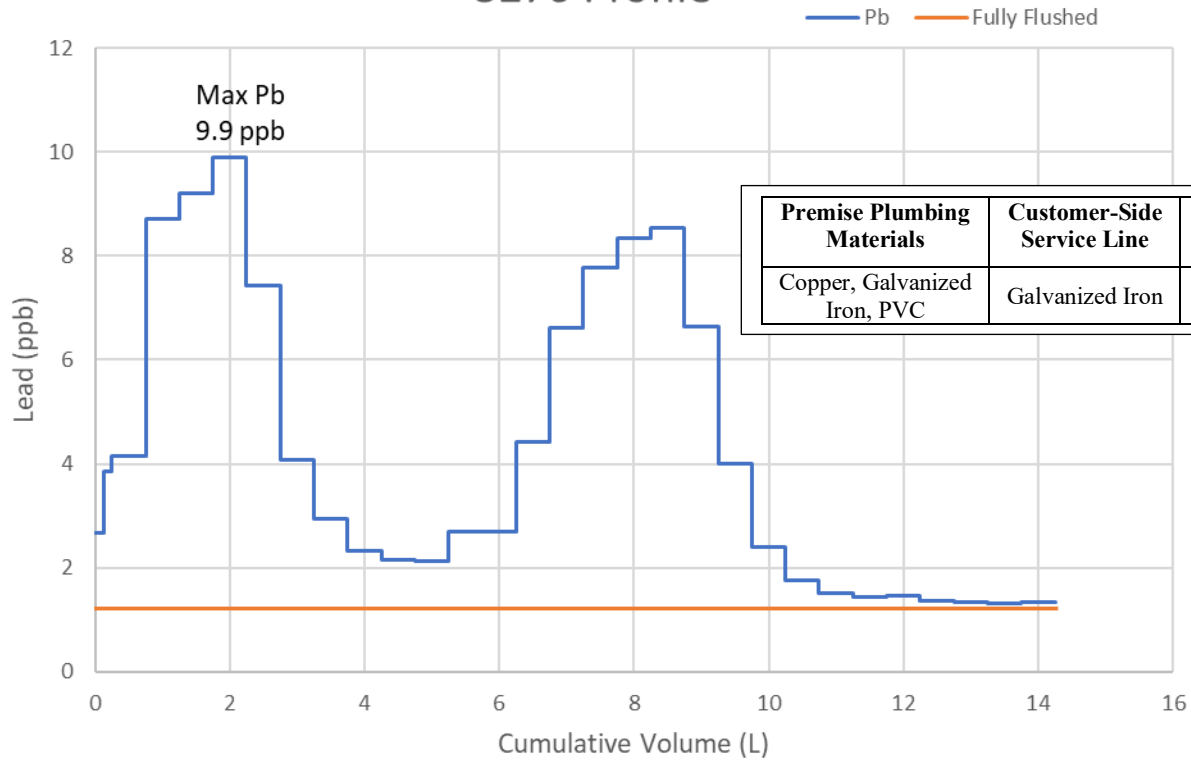
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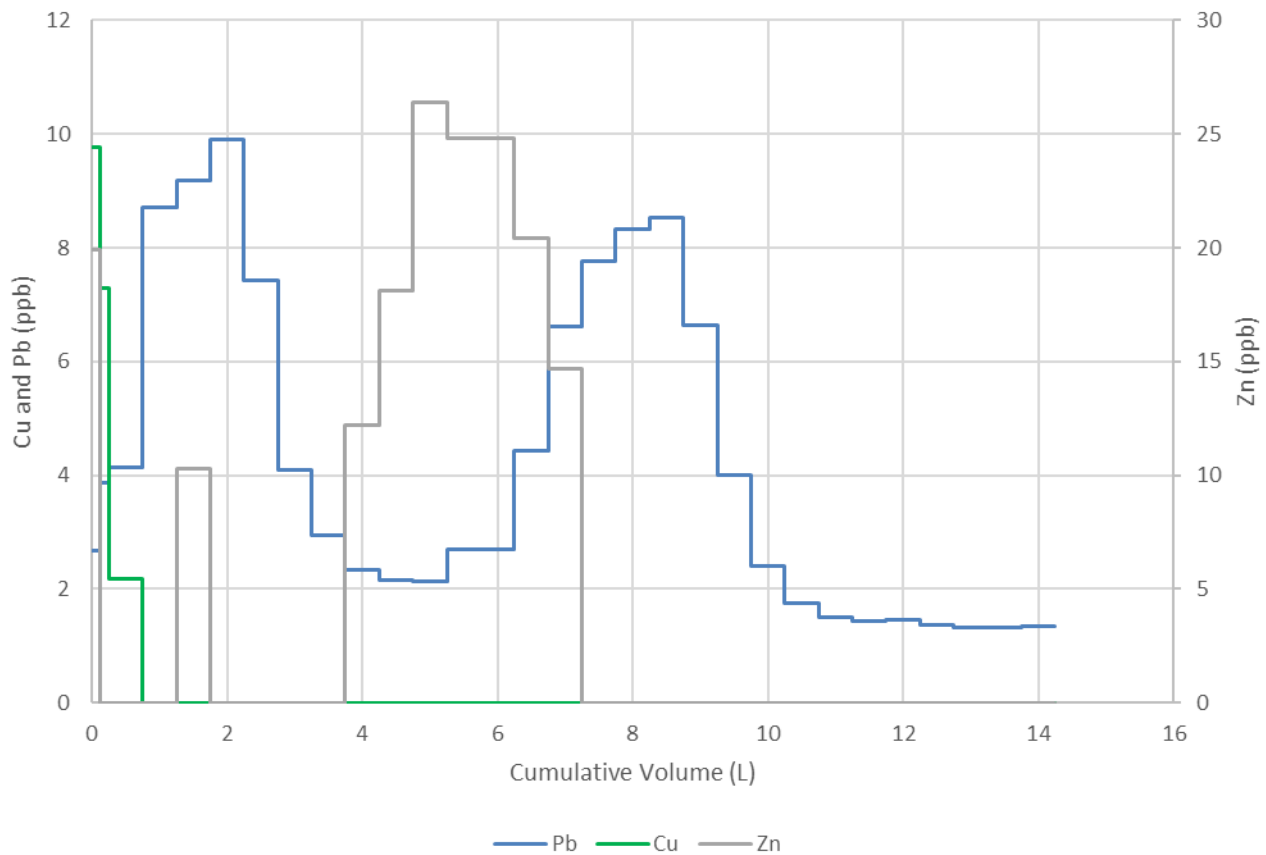
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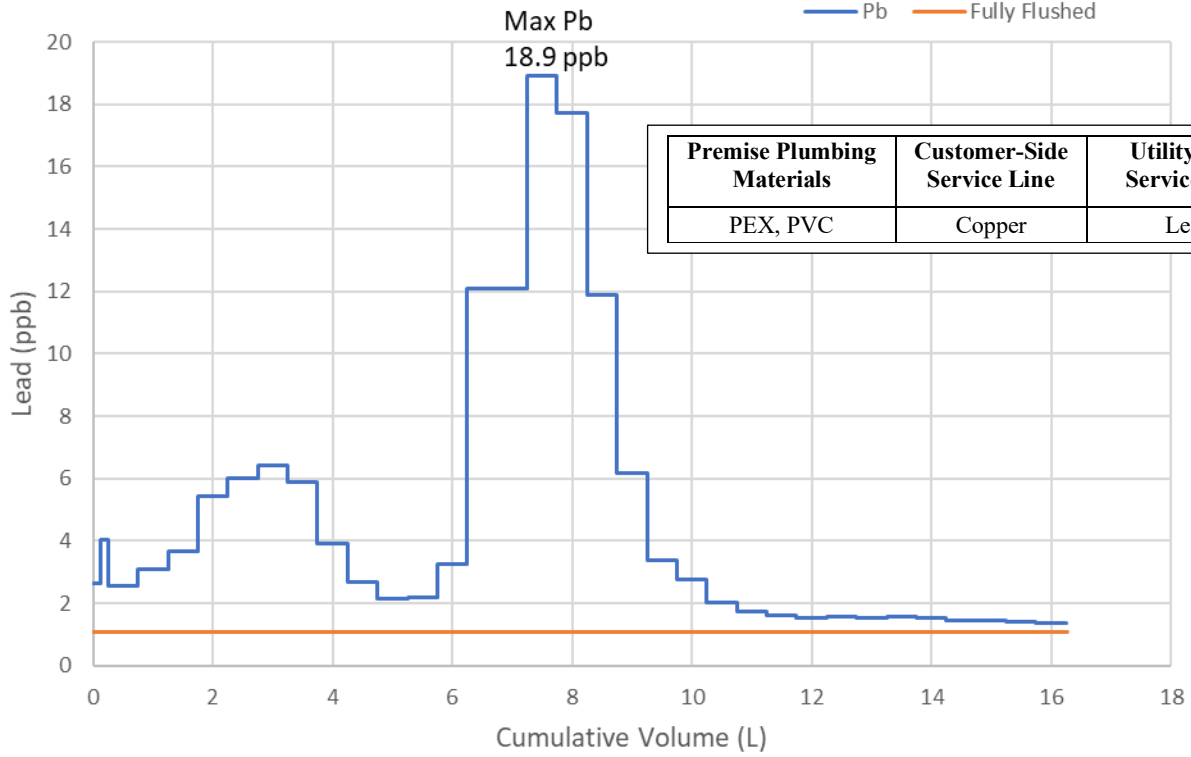
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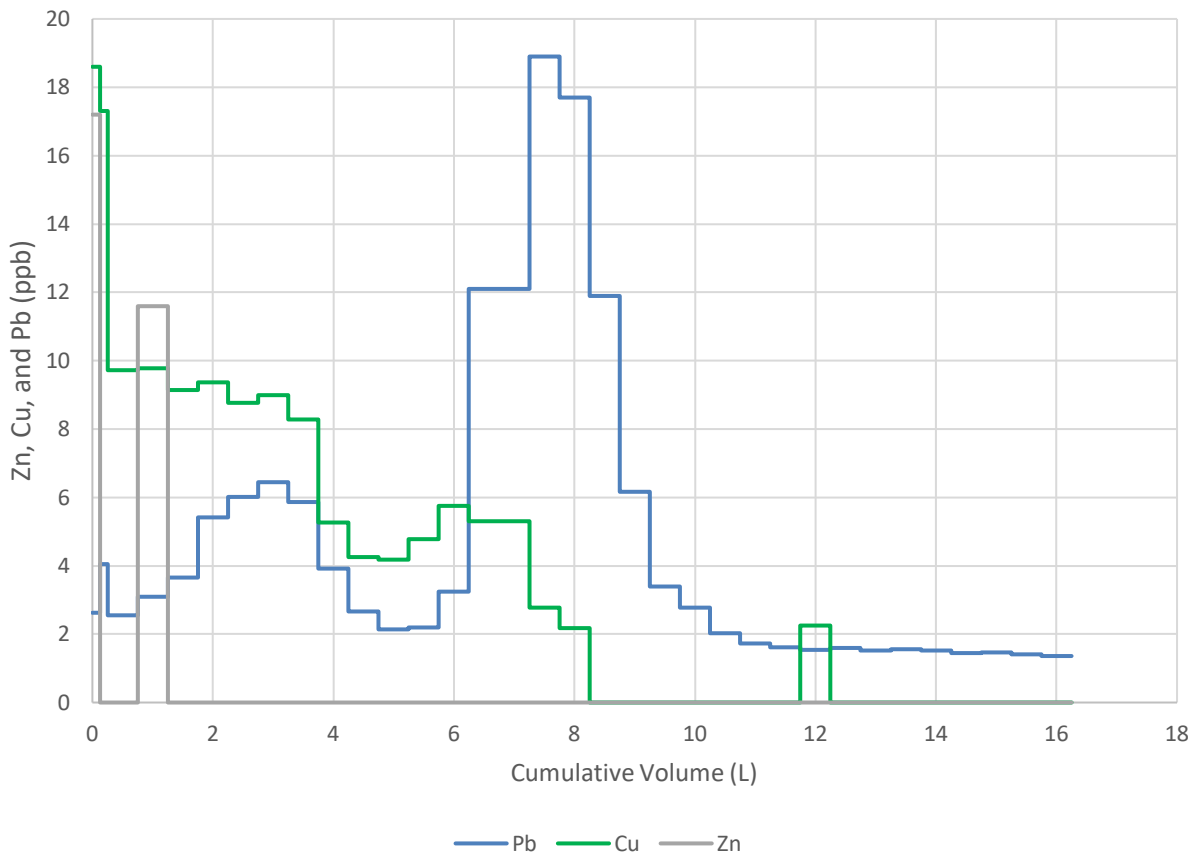
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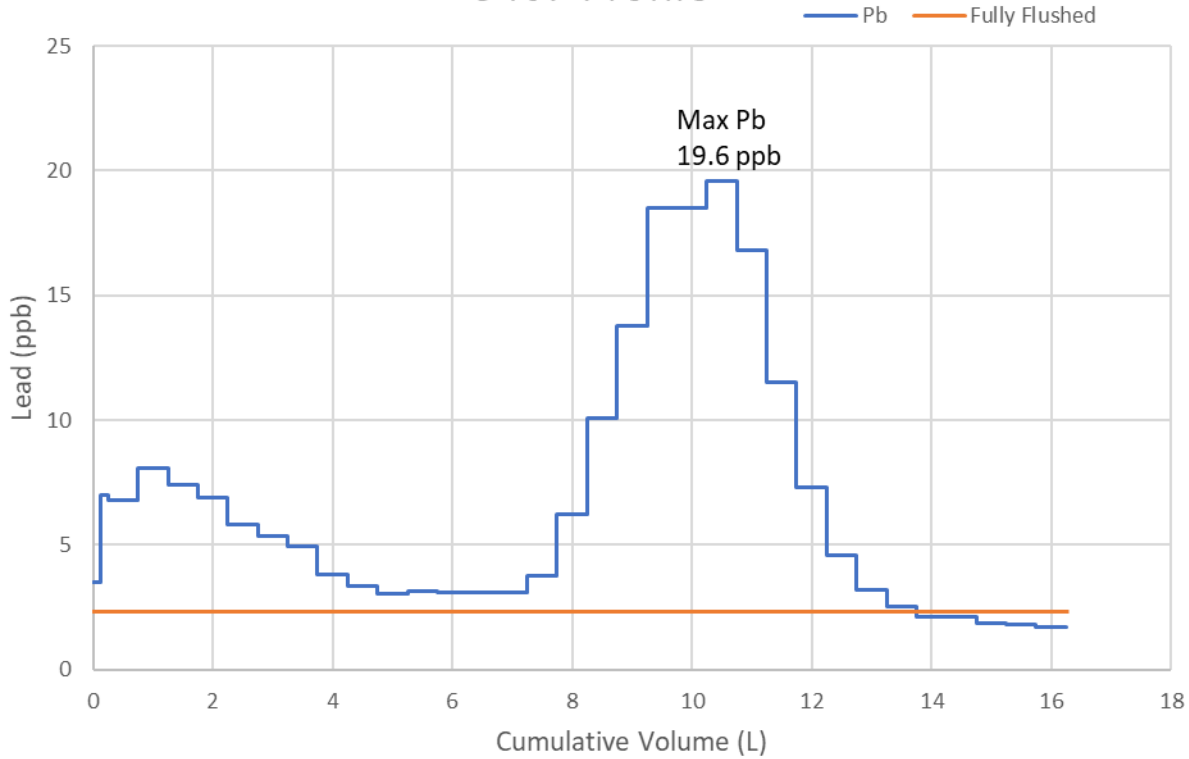
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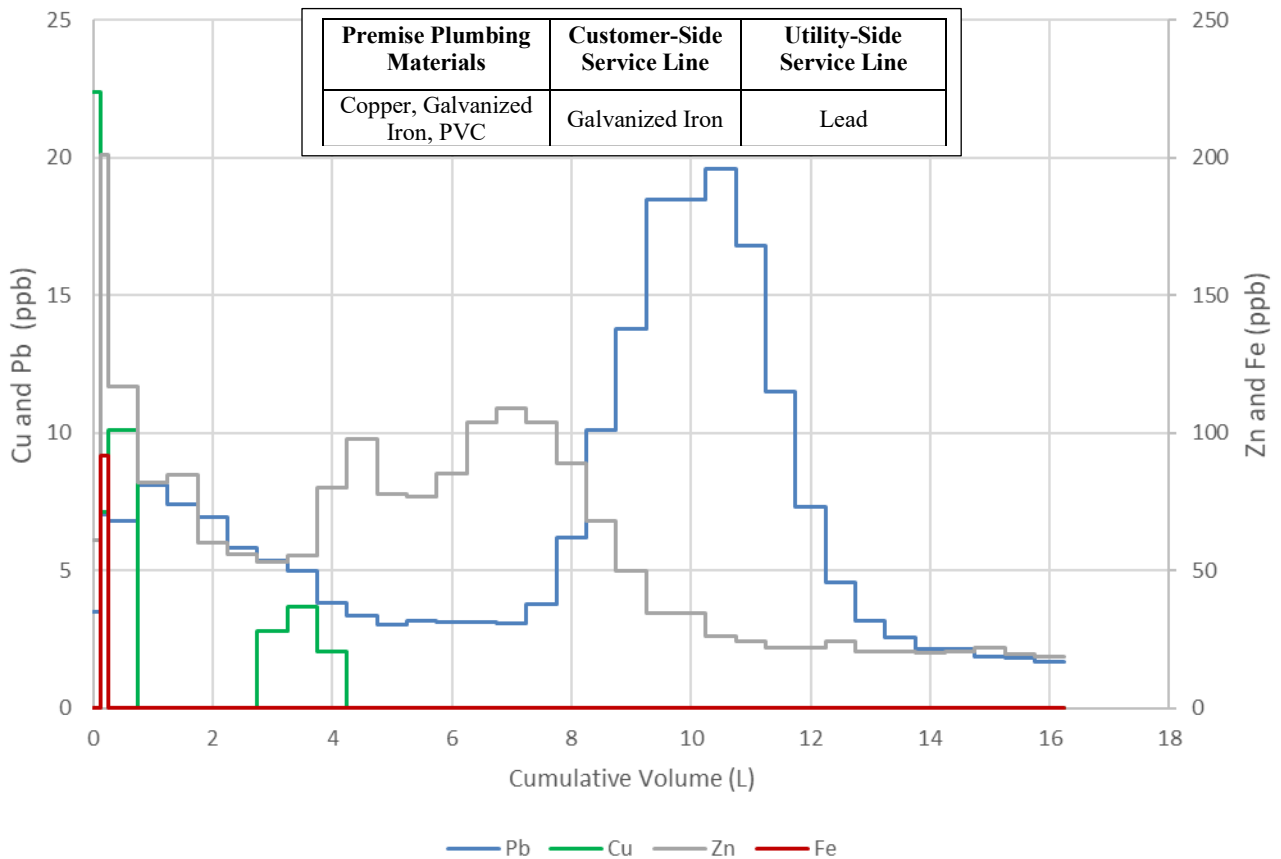
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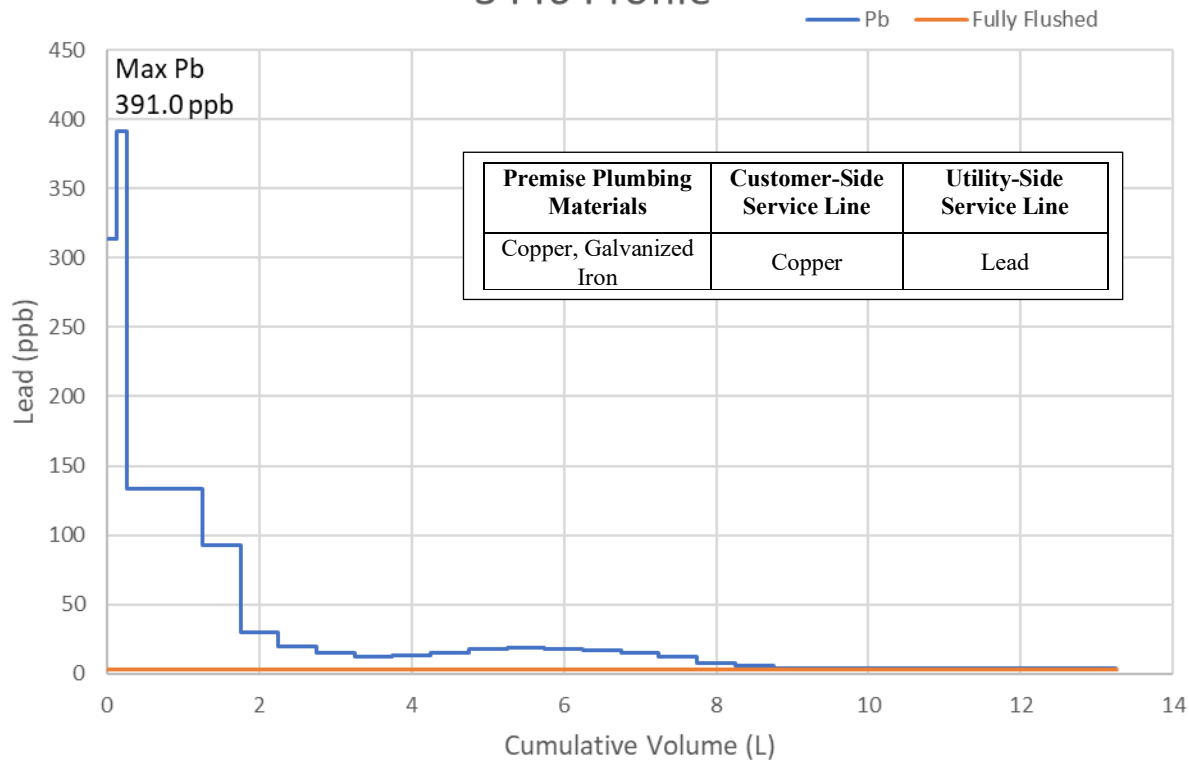
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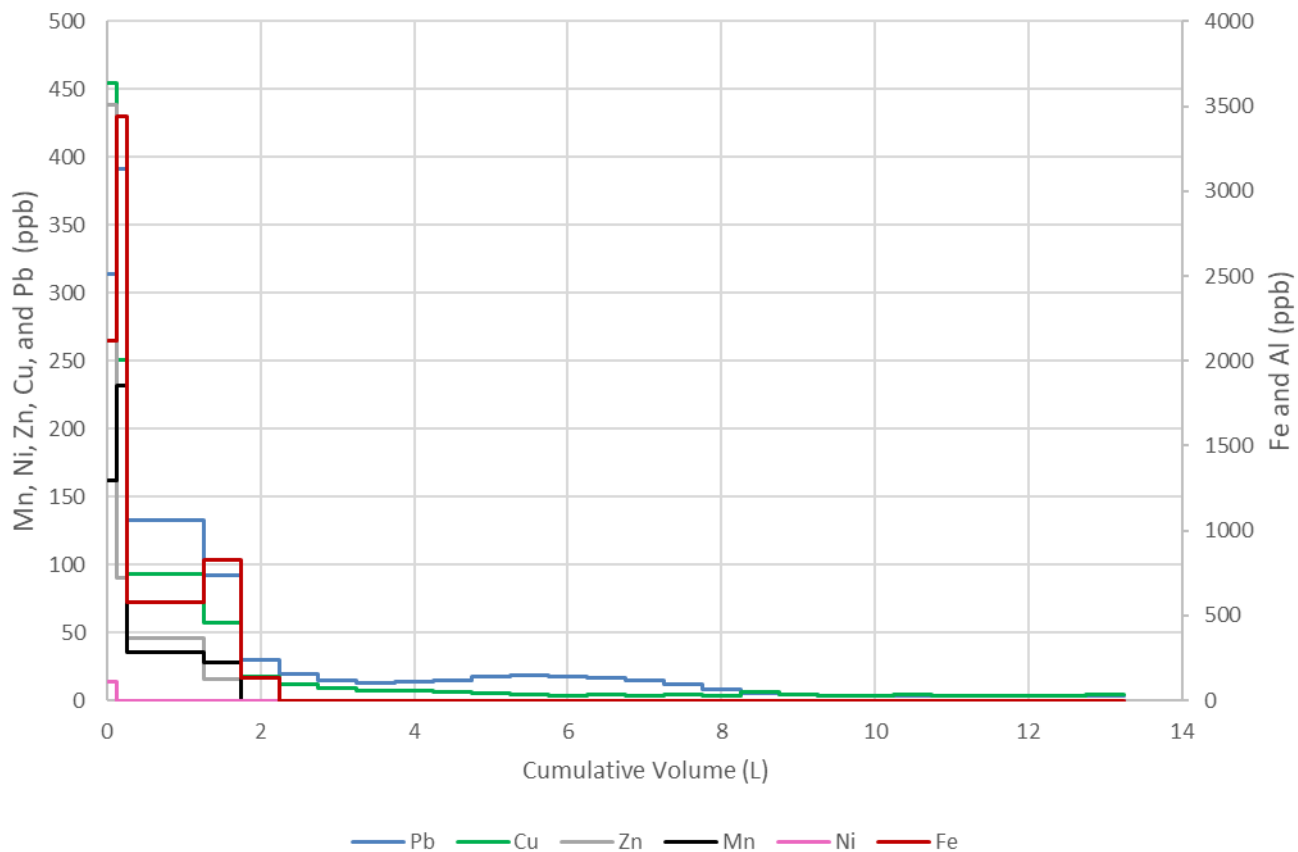
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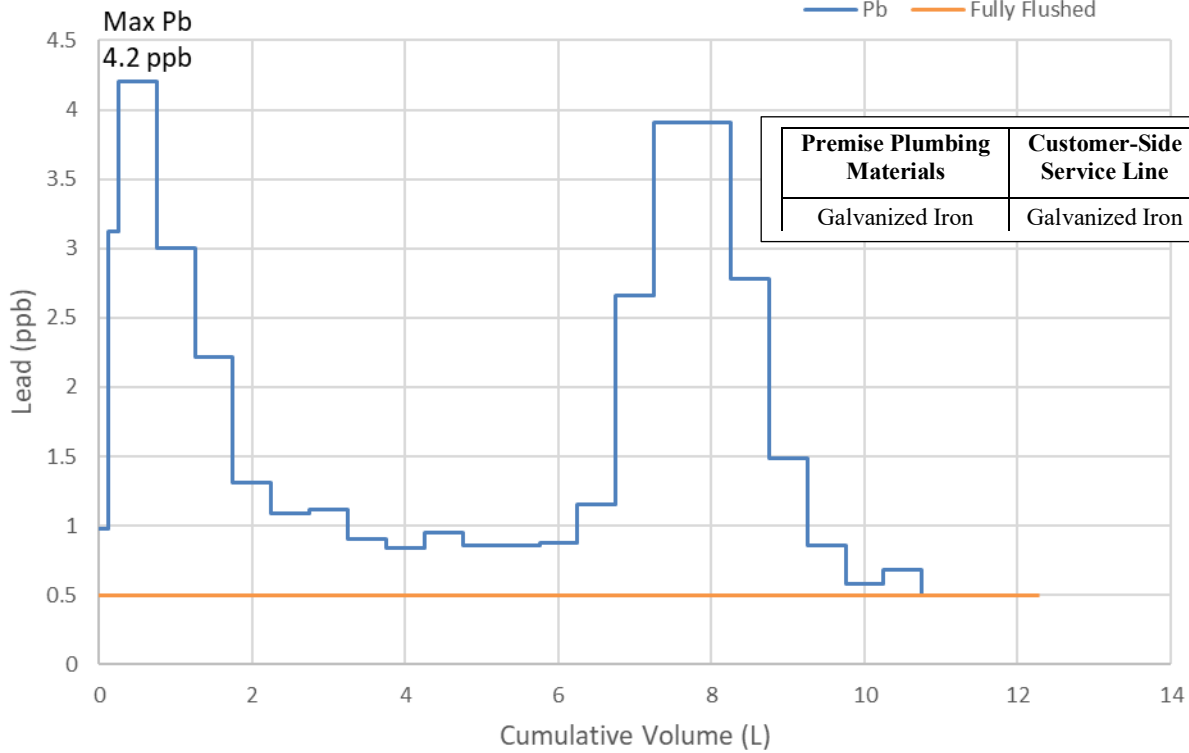
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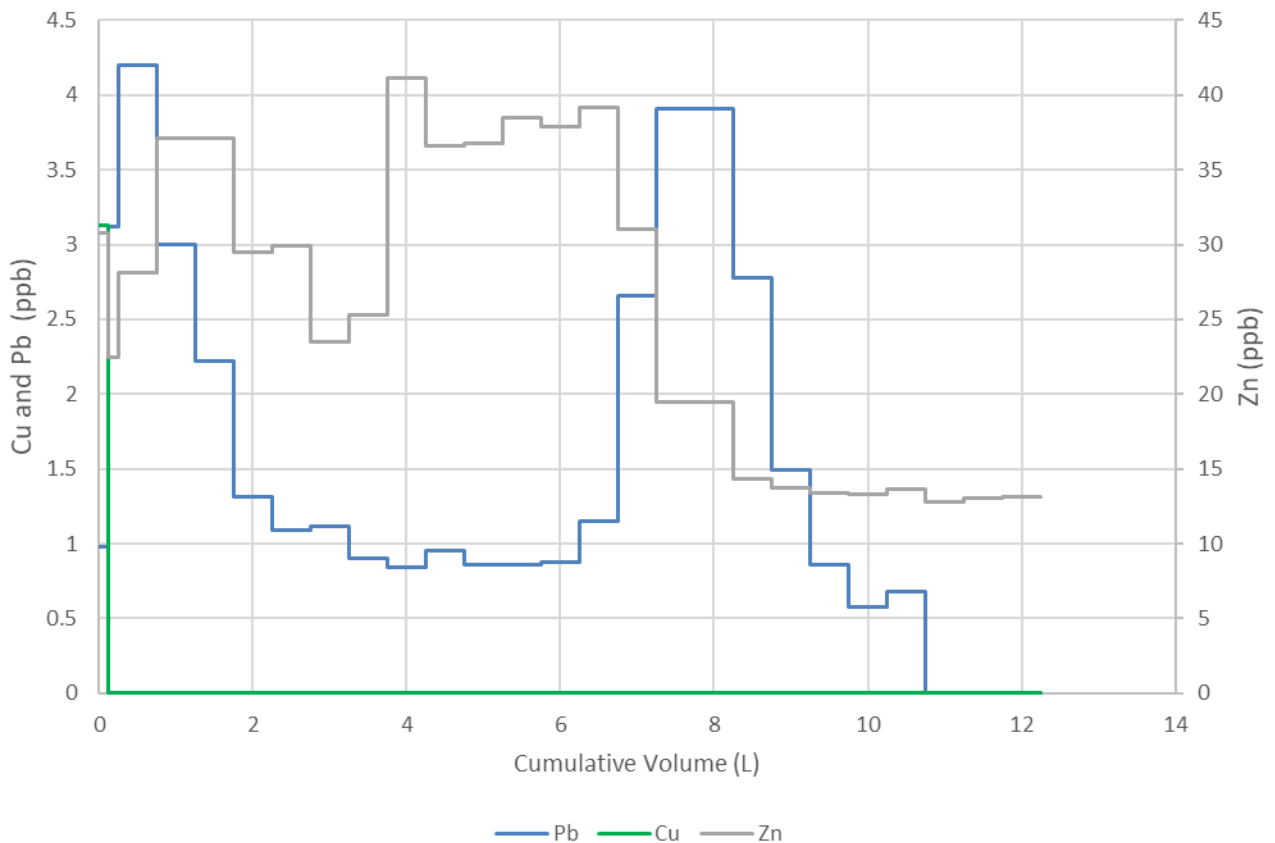
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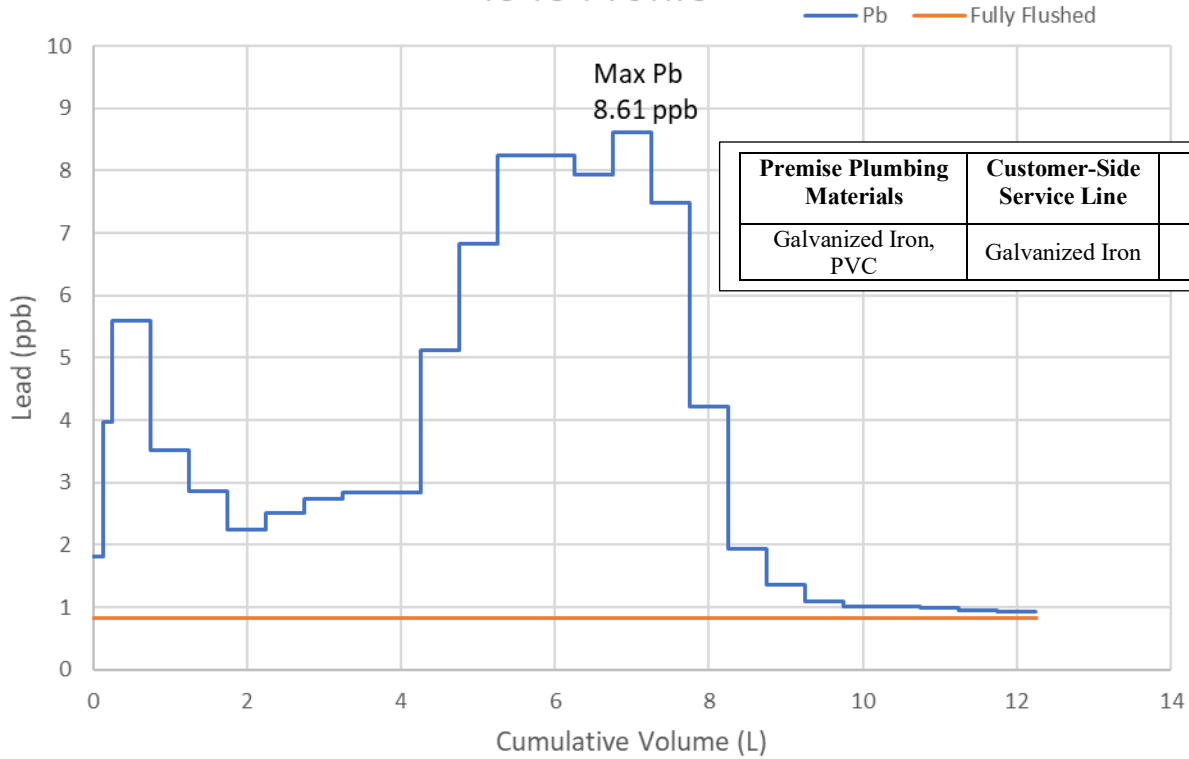
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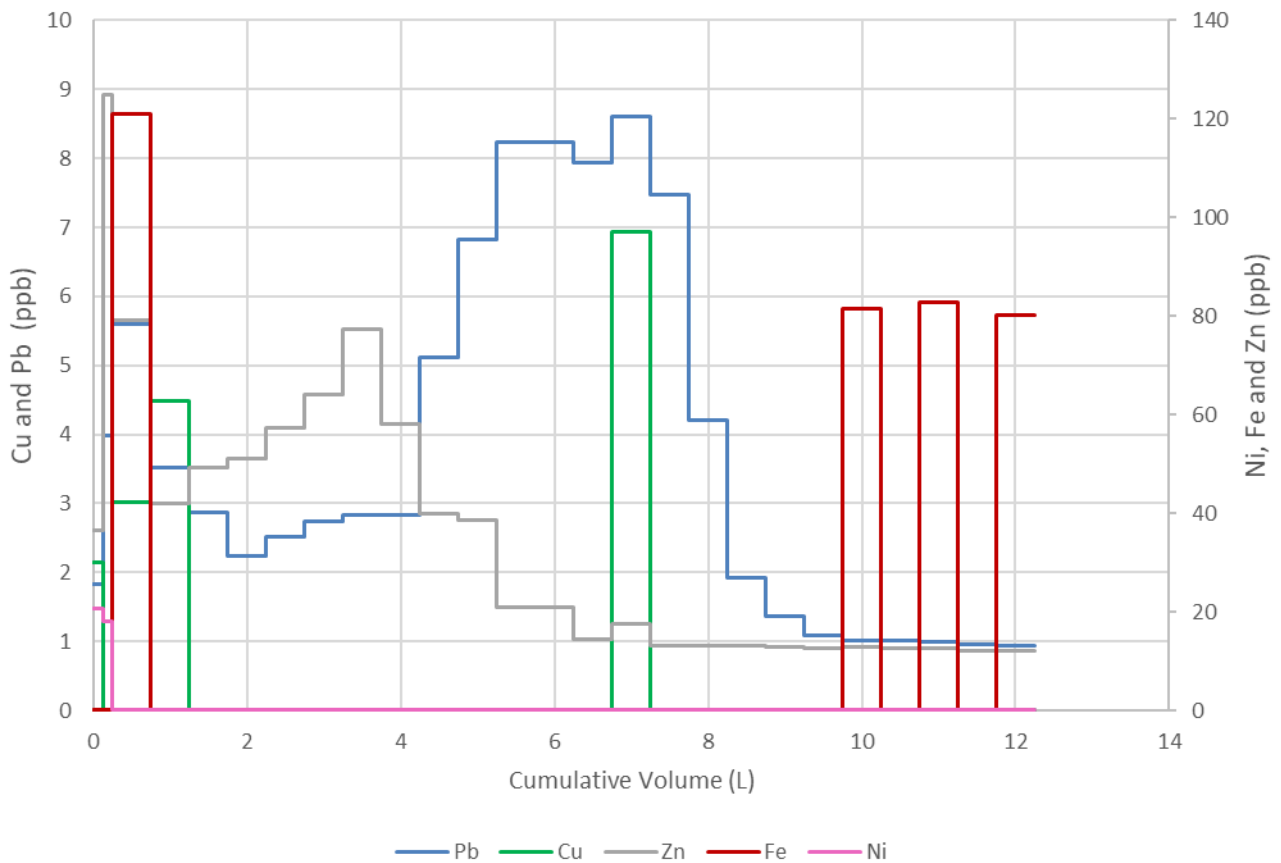
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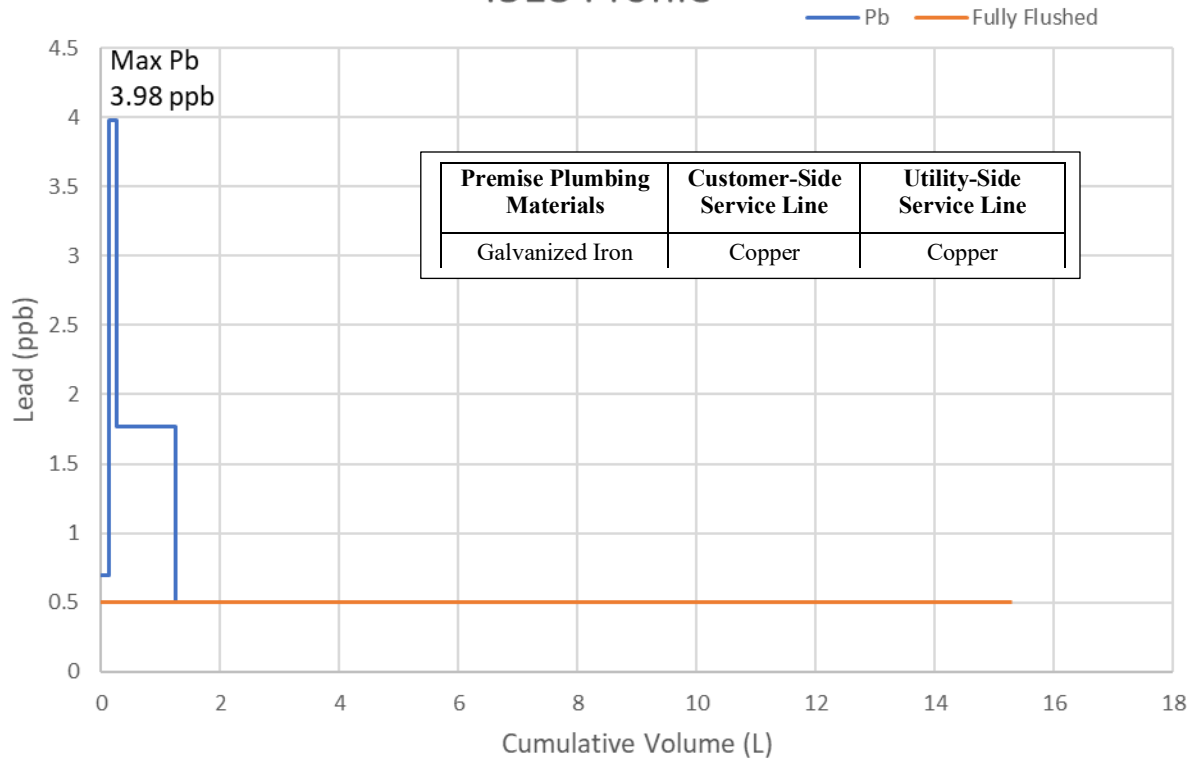
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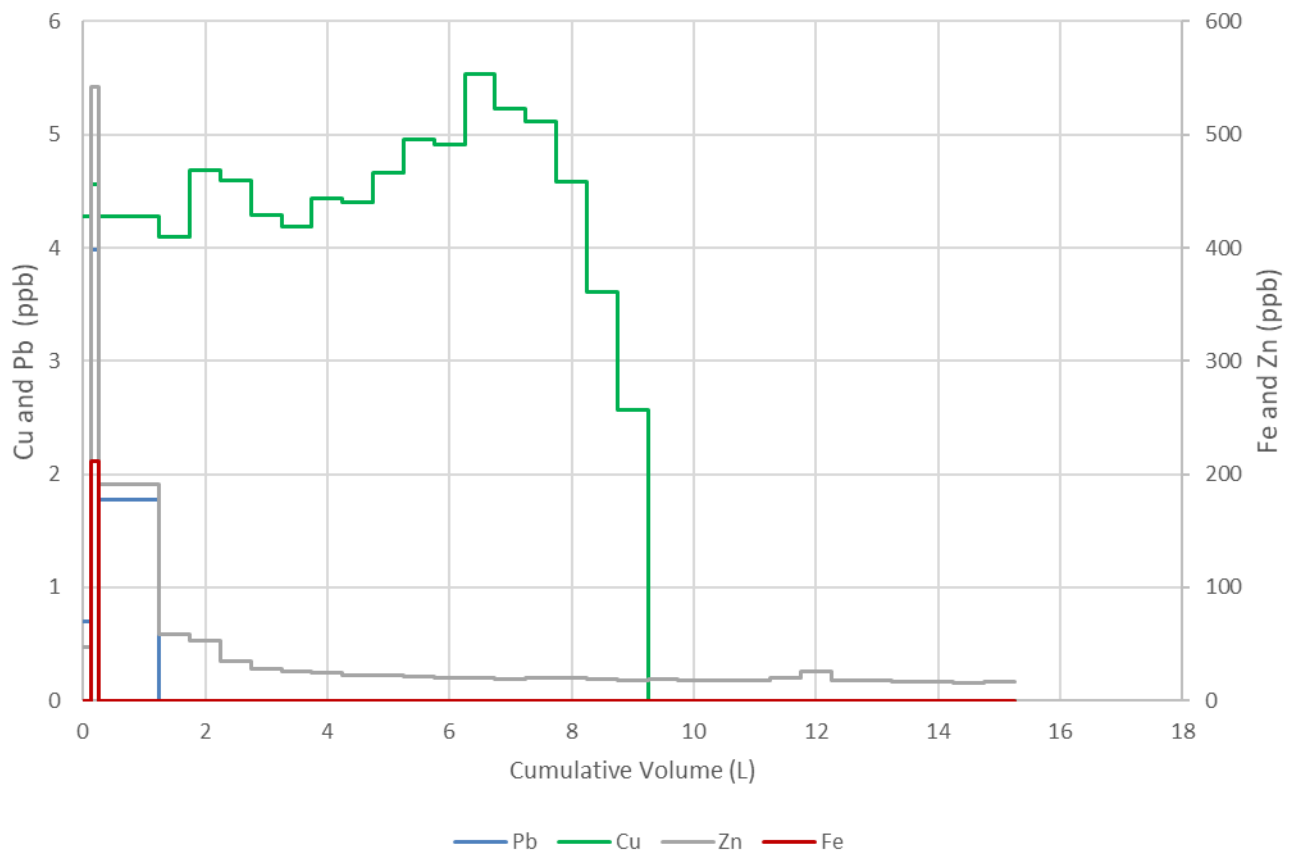
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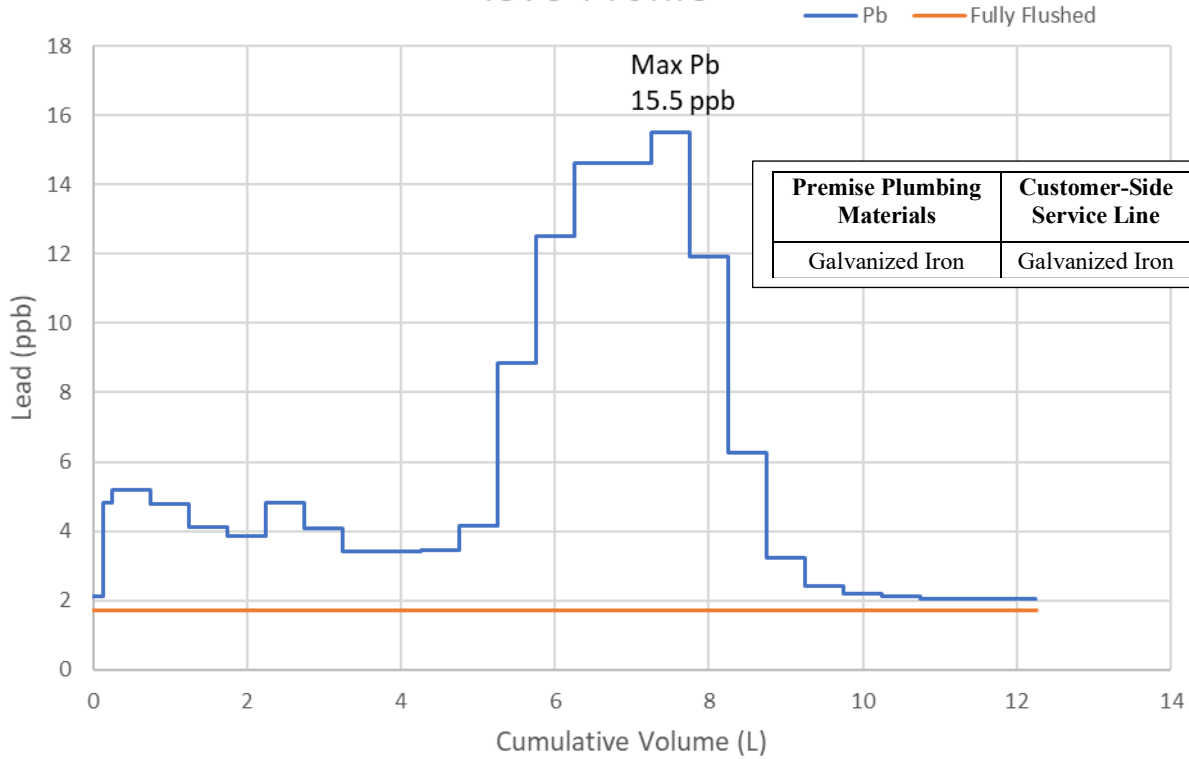
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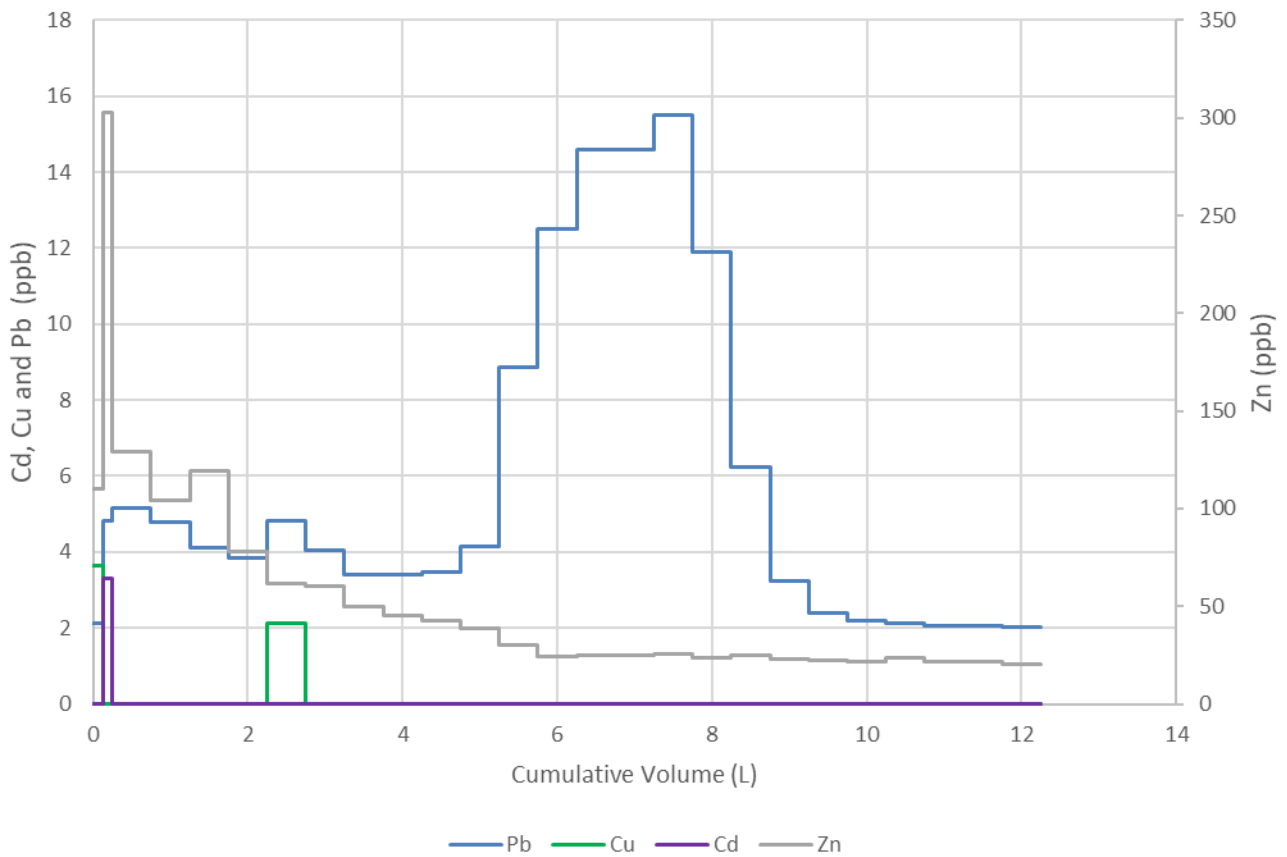
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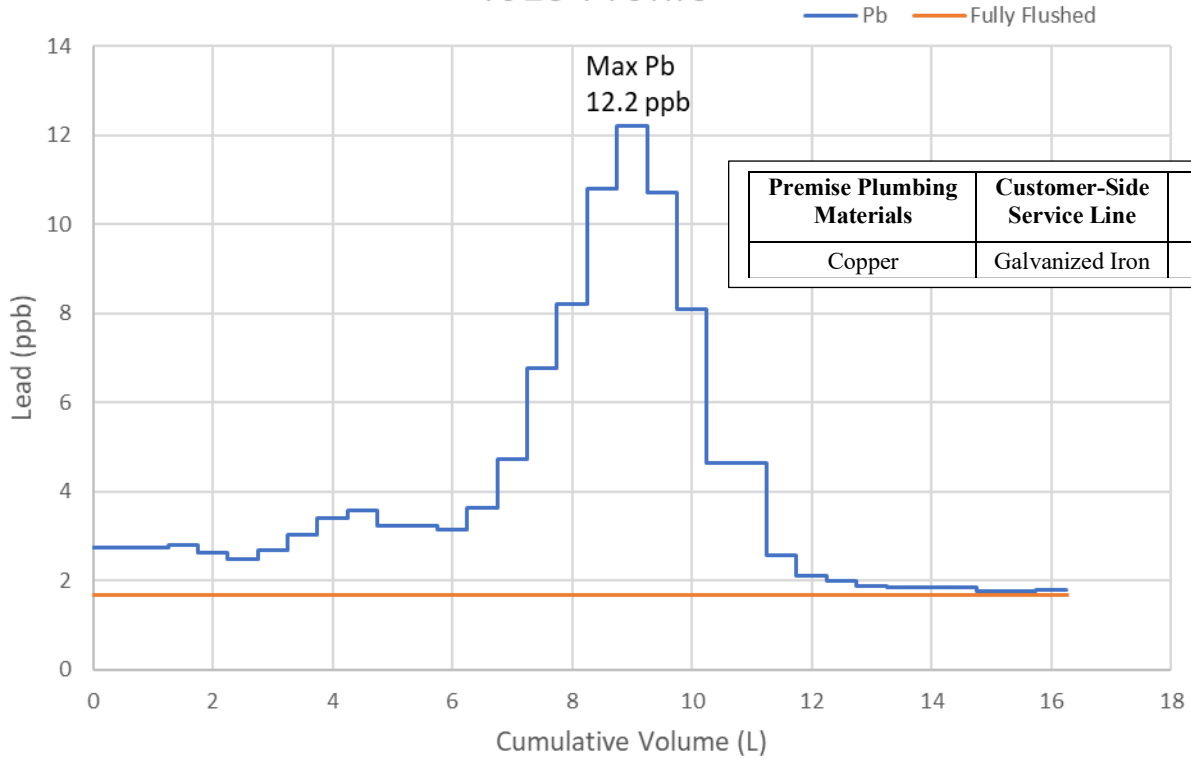
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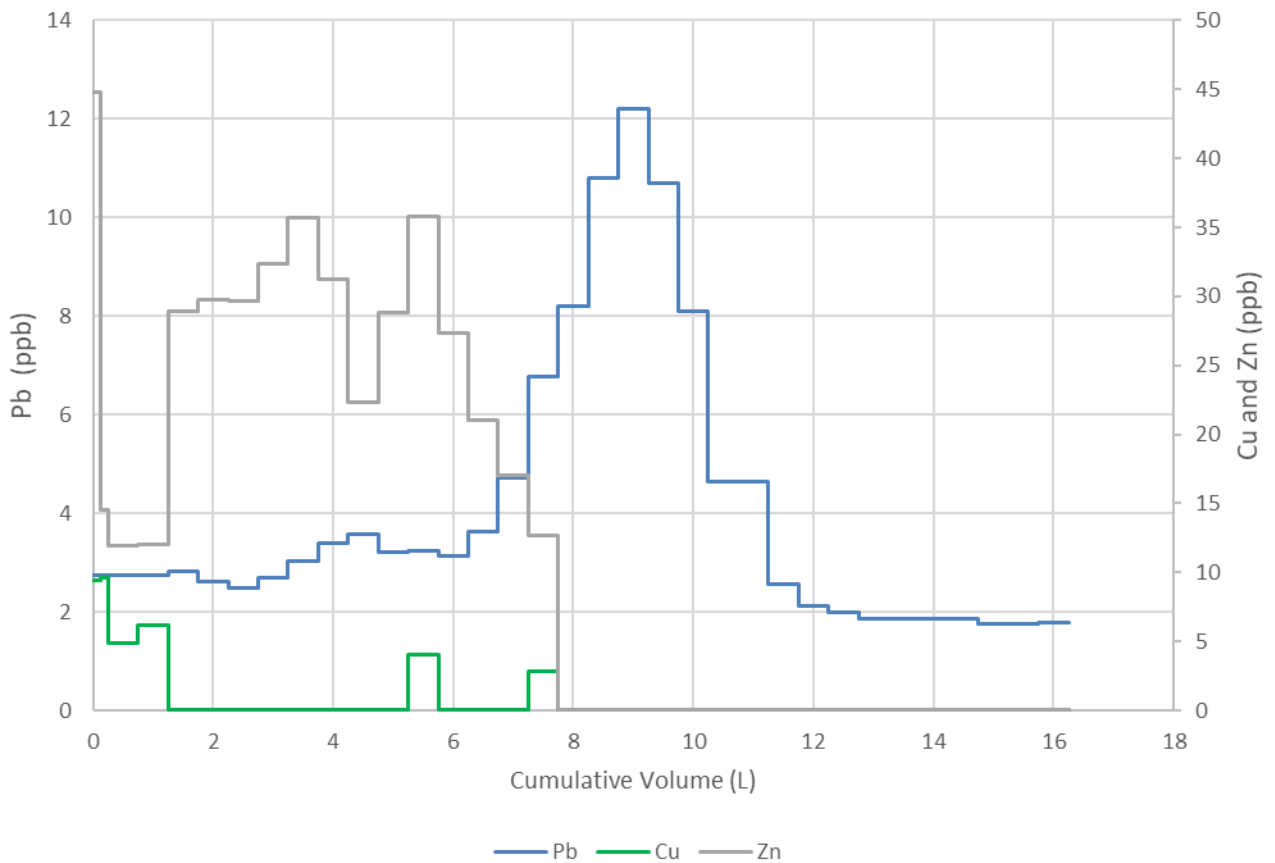
4579 Multiple Metals Profile



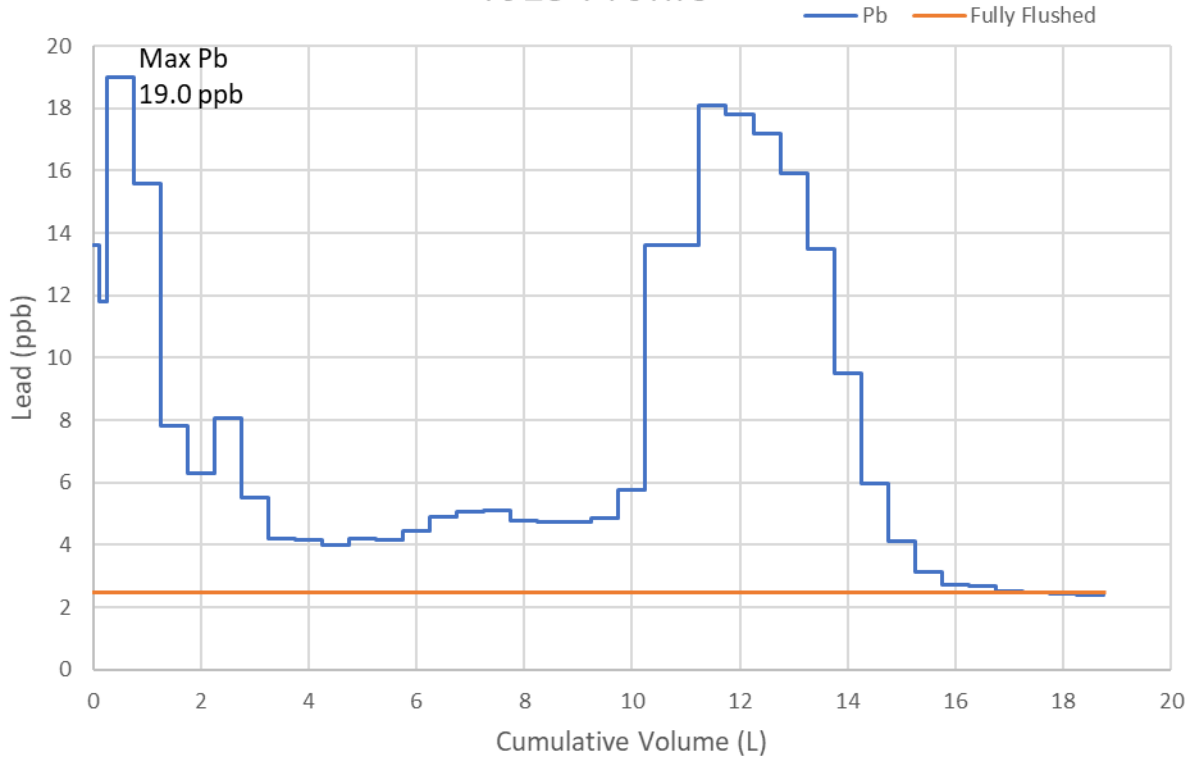
4613 Profile



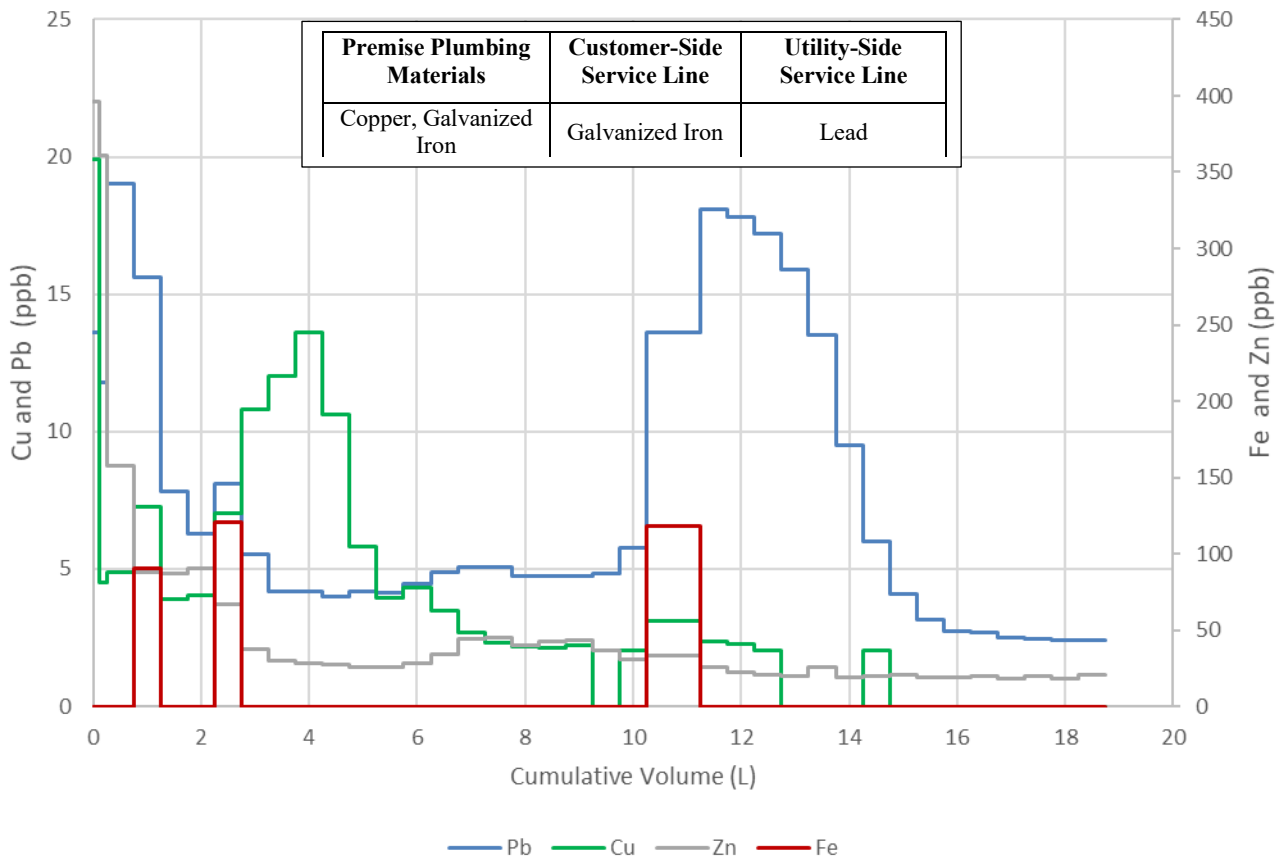
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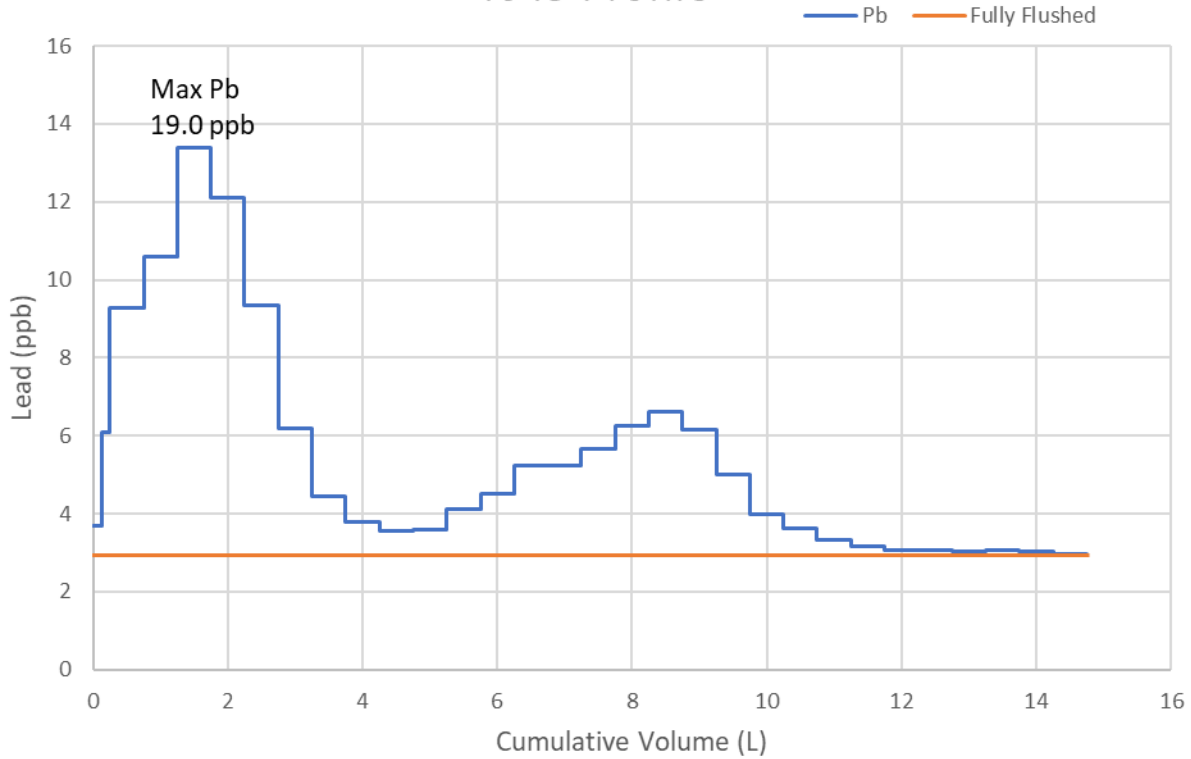
4615 Profile



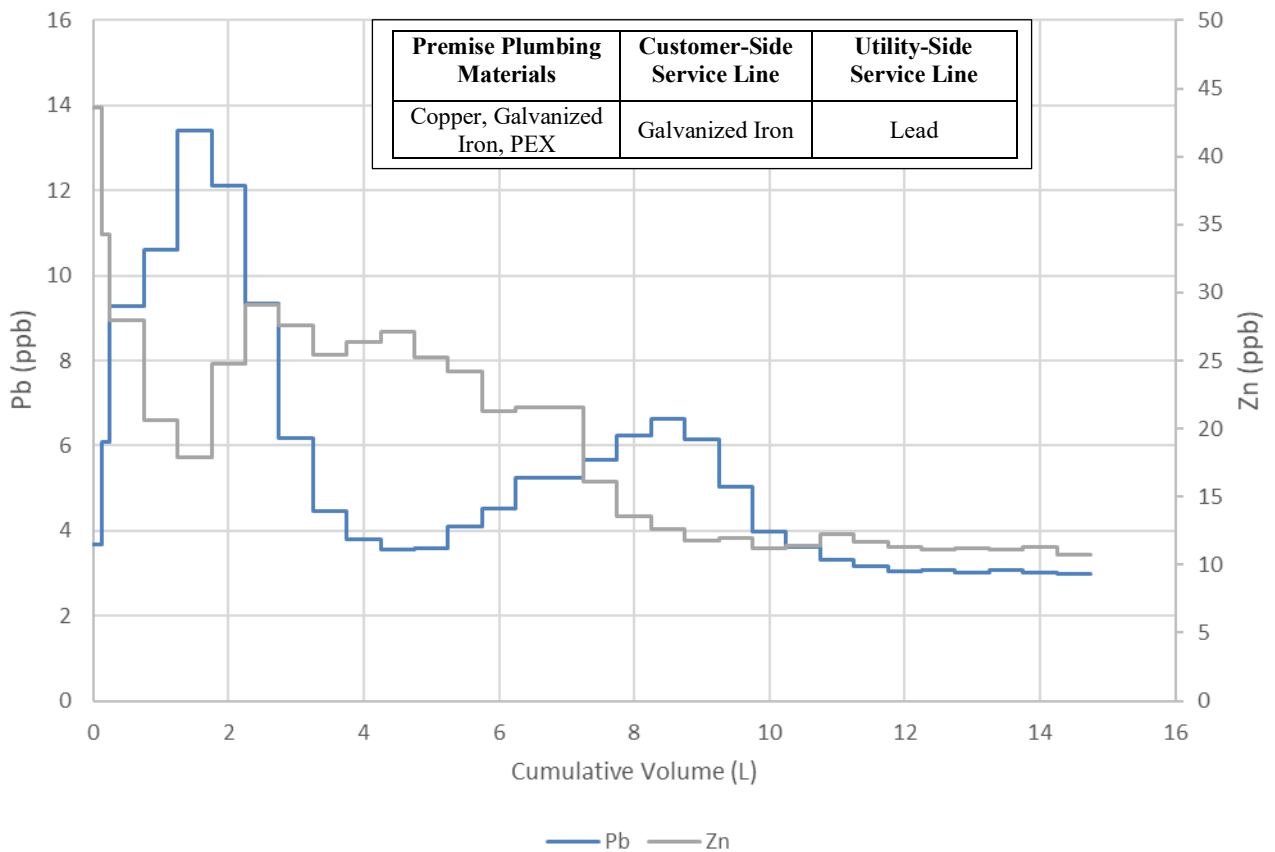
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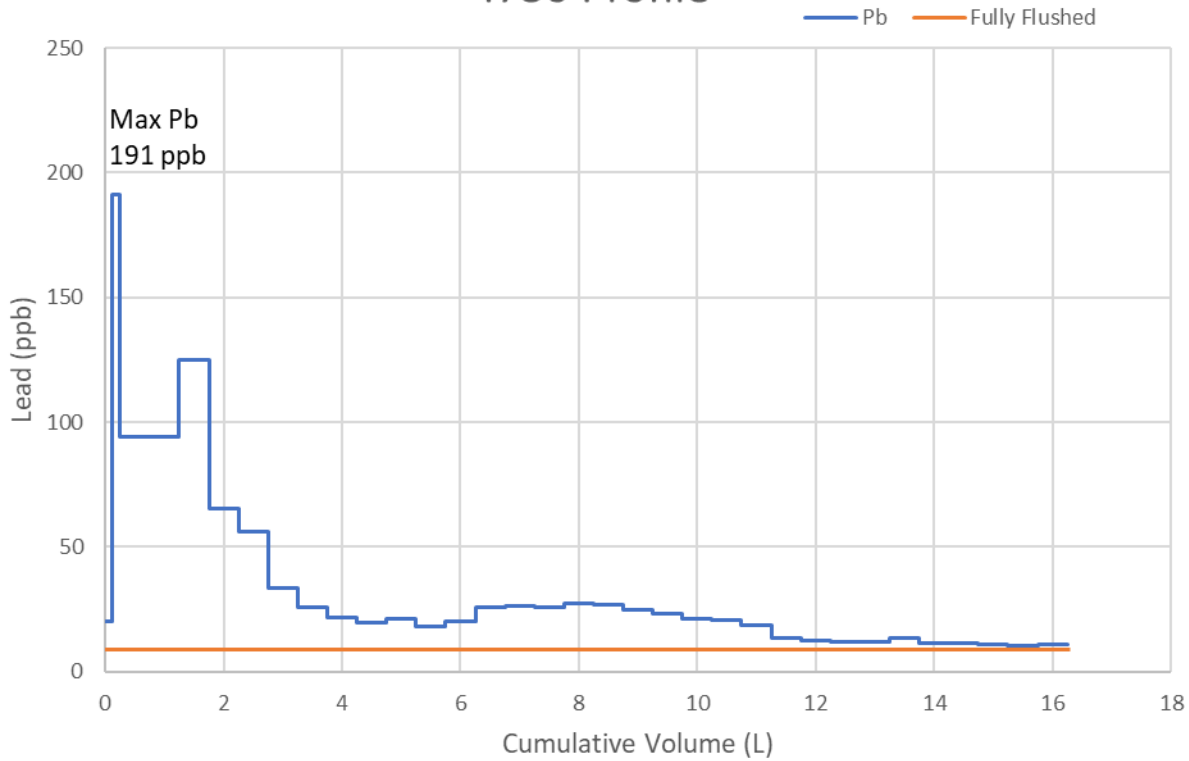
4645 Profile



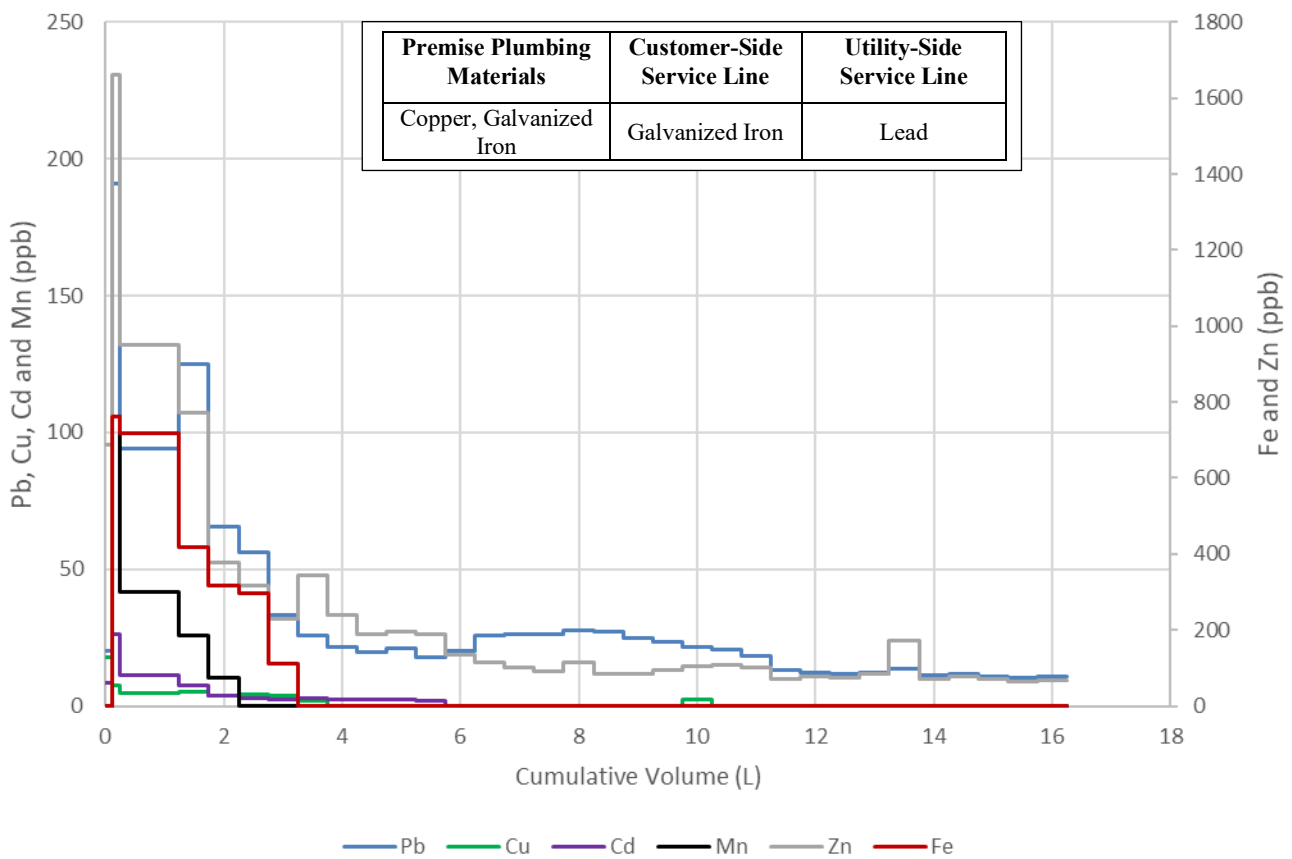
4645 Multiple Metals Profile



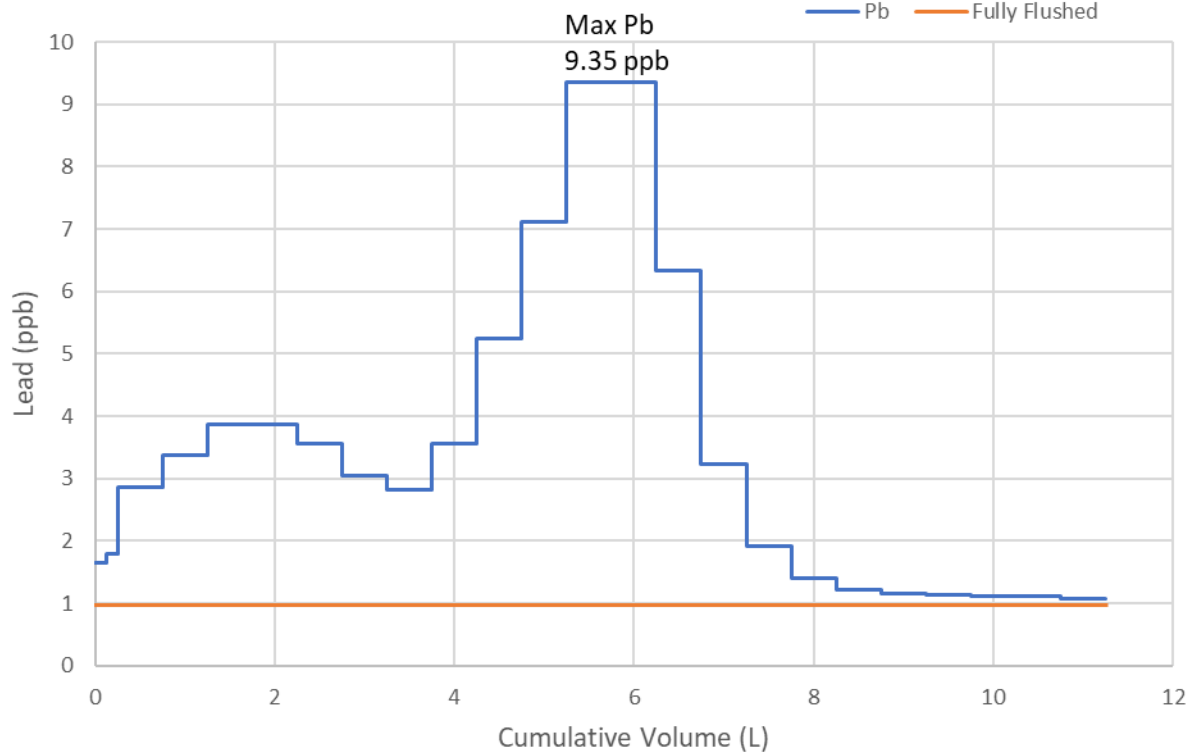
4730 Profile



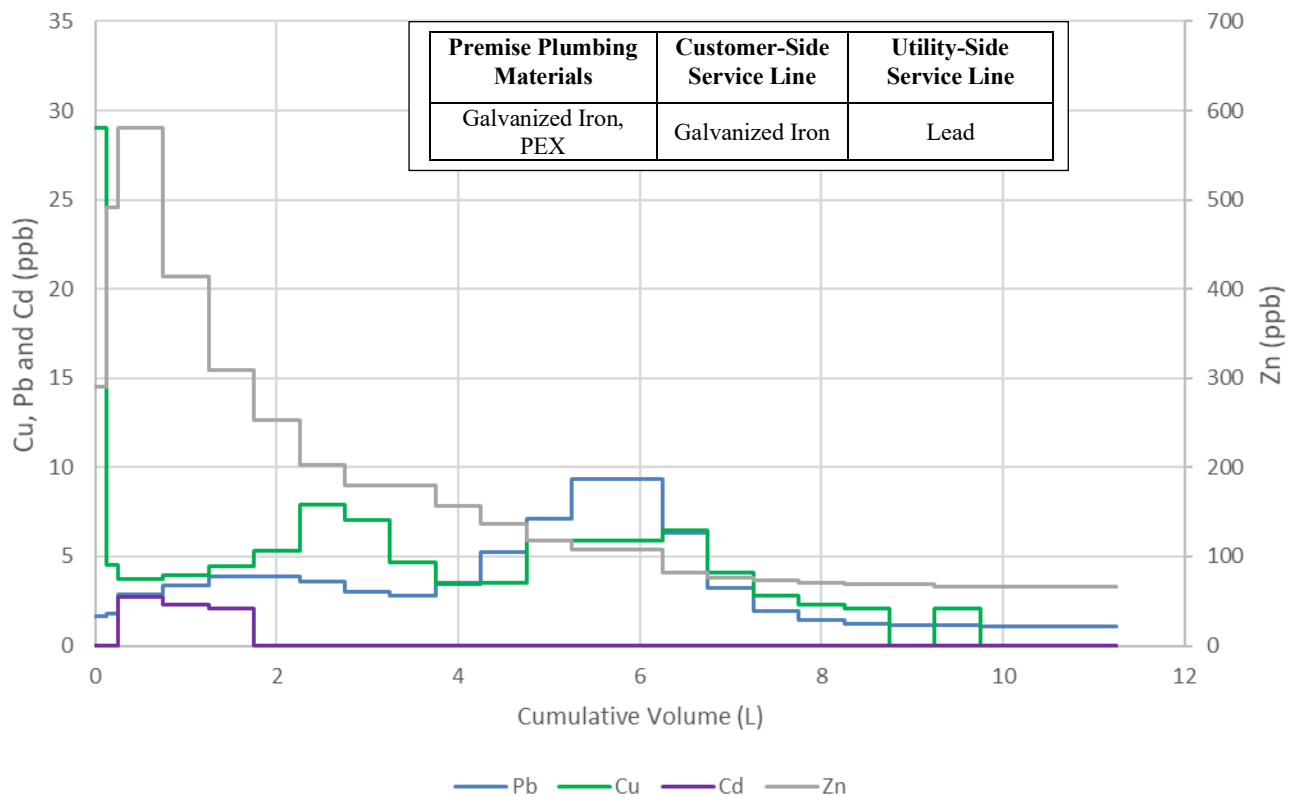
4730 Multiple Metals Profile



4827 Profile



4827 Multiple Metals Profile



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