

Sequential drinking water sampling as a tool for evaluating lead in flint, Michigan

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ABSTRACT

Eliminating the sources of human lead exposure is an ongoing public health goal. Identifying the make-up of household plumbing and service line material type is important for many reasons including understanding lead release sources and mechanisms, targeting locations for lead service line (LSL) removal, and assessing the effectiveness of lead remediation strategies. As part of the response to Flint, Michigan's drinking water lead public health crisis, a return to their original drinking water source (Lake Huron) and an increase in orthophosphate dose was implemented in late 2015. In 2016, EPA performed multiple rounds of sequential or "profiling" water sampling to evaluate corrosion control effectiveness and identify lead sources in homes and service lines, as well as to evaluate the effectiveness of corrosion control treatment with time on the different plumbing components. The results showed that lead levels, including high lead levels likely associated with particles, decreased with time in homes sampled during the 11-month evaluation period. Although sequential sampling indicated that brass fittings, brass fixtures, and galvanized pipes were lead sources, LSLs were the greatest source of lead when present. Following the removal of LSLs, the total mass of lead contributed to the drinking water decreased by 86% on average.

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1. Introduction

Eliminating the sources of lead exposure from the environment is an ongoing public health goal. Lead is a neurotoxicant that can cause permanent cognitive and behavioral impairments in children, and cardiovascular and kidney problems in adults (Fowler and Duval, 1991; ATSDR, 2007; Lanphear et al. 2018). Major regulatory and primary prevention strides have reduced lead concentrations in water, paint, dust, gasoline and soil, with corresponding reductions in observed blood lead levels (BLL) (Pirkle et al. 1994; Jain, 2016; Tsoi et al. 2016). These changes, however, have not occurred fast enough to keep up with the continually decreasing threshold for the level of lead exposure known to be harmful. In 2012, after concluding that no BLL could be considered "safe," the Centers for Disease Control and Prevention (CDC) reduced its former BLL of concern from 10 $\mu\text{g}/\text{dL}$ to a reference value of 5 $\mu\text{g}/\text{dL}$

to be used for the screening of children (CDC, 2012; CDC, 2016). Recent research has indicated intellectual, behavioral, and attention deficits linked to children's BLLs below 5 $\mu\text{g}/\text{dL}$ (NTP, 2012; EPA, 2013). In order to mitigate health effects, efforts to eliminate lead sources continue.

Although lead levels in water have decreased since the 1970s (Karalekas et al. 1975), drinking water can still be the dominant source of total daily lead exposure (Triantafyllidou et al. 2007). Lead in drinking water originates from the corrosion or dissolution of lead-containing plumbing materials. Lead service lines (LSLs), which connect the water main to the premise (i.e., indoor or household) plumbing, are considered the largest contributor to total lead in drinking water, responsible for up to 75% of the lead measured in drinking water (Sandvig et al. 2008). The use of LSLs was banned in the United States in 1986 (U.S. EPA, 1986). Estimates vary widely for the number of full or partial LSLs remaining, ranging from approximately 6.1 million (Cornwell et al. 2016) to 10.2 million (EPA, 1991a; 1991b, 1991c, 1992). Other important plumbing sources of lead include brass fixtures and fittings, lead solder (Subramanian et al. 1995), flux, water meters, lead

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goosenecks, and galvanized steel pipes (HDR Engineering, Inc., 2009).

Identifying the make-up and material type of drinking water service lines and premise plumbing is important for many reasons, including understanding lead release sources and release mechanisms, targeting locations for LSL removal, and assessing the effectiveness of lead corrosion control strategies. However, service lines and other plumbing materials are often buried beneath soil or inside finished walls, preventing direct observation. Uncertain and unique configurations of mixed premise plumbing materials, as well as nonexistent or unreliable utility LSL records (Karalekas et al. 1975), also make identifying plumbing materials a challenge. Furthermore, unpredictable and inconsistent drinking water lead levels across the distribution system of a community (Del Toral et al. 2013; Wang et al. 2014), in addition to other water quality fluctuations, are often observed. There is a critical need to establish a drinking water sampling protocol that can inform and address these challenges.

Many reasons to perform lead drinking water sampling exist, including lead exposure assessment, corrosion control efficacy benchmarking, lead source determination, LSL identification, and regulatory compliance assessment. Also, many factors can affect lead sample concentration and potential variability in lead concentrations. Therefore, the sampling protocol must be carefully selected and implemented to allow meaningful results and interpretation.

“Sequential” sampling or “profiling” can be a valuable approach to identify lead sources in plumbing and service lines, as well as to evaluate corrosion control effectiveness over time. Plumbing lengths and inside diameter (ID), and visible material are surveyed for interior premise plumbing and service lines, using the approximate route to the water main. After stagnation, a series of successive drinking water samples are collected. Sample volumes can vary depending on the precision needed to differentiate components such as bubblers, faucets, valves, tubing, and inside-wall plumbing. Sample results for metals including lead (Pb), zinc (Zn), copper (Cu), tin (Sn), and iron (Fe) can then be related to plumbing volumes and distance from a sampling faucet to identify the location of leaded materials, including a partial LSL.

Although there are multiple potential assessment benefits of sequential sampling, very little work has demonstrated the practical value of sequential sampling particularly in a full-scale field setting. An extensive sequential sampling effort was initiated and documented by EPA in Flint, Michigan. The objective of this work is to summarize the findings of the sequential sampling program in Flint. The findings will illustrate the usefulness of sequential sampling as a tool for identifying lead sources, assessing corrosion control treatment and other related benefits.

2. Background

Sequential samples arguably provide the clearest picture of the lead leaching from plumbing sources at a given sampling location. The protocol involves taking a predetermined number of samples, typically 10 to 20, in series from the same tap after a defined stagnation period. The first few samples are usually smaller volumes, such as 125 mL or 250 mL, in order to isolate the contributions from the different short sections of plumbing typical of brass faucets, elbows, lead-tin solder, and valves. The remaining samples can be larger, such as 1 L, as the plumbing moves away from the faucet and becomes more uniform. The specific sample volumes and sequence can be customized for each case, based on previous inspection of the lengths and diameter of premise plumbing and service line materials.

Together, the samples create a lead (and other metal)

concentration profile of the plumbing from the faucet all the way to the water main. Matching the water sample volumes to the plumbing volume can identify which part of the plumbing is the biggest source of lead (van den Hoven and Slaats, 2005; Sandvig et al. 2008; Clark et al. 2014). Taking the appropriate number of samples at the appropriate sample volume, combined with the accurate mapping of these volumes, has been shown to achieve acceptable resolution of the different plumbing parts (Schock and Lemieux, 2010). Samples as small as 50 mL can successfully detail materials down to the contribution of lead-tin solder (Hoekstra et al. 2004; Triantafyllidou et al. 2015). Lytle et al. (1996) applied sequential sampling to identify lead sources in a new building with elevated lead levels and evaluate the success of corrosion control strategies (orthophosphate and silicate addition) to reduce lead corrosion. A series of 30-mL and 60-mL samples were used to distinguish between brass and leaded solder lead sources and demonstrate the relative effectiveness of the corrosion inhibitors to reduce lead (Lytle et al. 1996).

Sequential sampling is particularly informative when combined with the identification of other metals within the sample. For example, the presence of lead along with an appreciable concentration of tin suggests the lead source is lead-tin solder, while the co-occurrence of zinc and lead may indicate that a brass fixture is the lead contributor. Diffusion effects will skew the metal contributions to a degree (Hayes et al. 2013; Leer et al. 2002), and this effect is seen as a gentle curve (approximately bell shaped) with the middle of the LSL at the peak, instead of sharp increases (Giani et al. 2004). However, not all peaks necessarily correspond to the LSL. For example, lead stagnation profile peaks after 6 h of stagnation in one report varied from 9.1 µg/L to 96.5 µg/L at LSL sites, and lead peaks did not always correspond to the LSL volume-estimated location (Hayes et al. 2016). Because discrete lead contributions can be diluted by larger sample volumes (Cartier et al. 2011), accurately isolating smaller fixtures requires appropriately small samples (Schock, 1990) and an accurate plumbing inspection (Hoekstra et al. 2009). At the lowest end of the sample size spectrum, the large number of samples to represent the plumbing volume would increase the analytical costs.

“Spikes” occasionally occur in the profiling samples, representing the presence of colloidal or particulate lead-containing materials suspended in the water. The exact source of the particles cannot be precisely determined, because it is physically unlikely that they were carried along with the background “parcel” of water with the dissolved lead. However, it can be inferred that the particulates originated somewhere between the tap where the sample is drawn, and the position in the pipe network represented by the location from which the background water “parcel” originated, because the particles cannot flow faster than the dissolved ions and complexes in the water. The presence of lead particulate-related spikes is sporadic and would not necessarily be captured during a single sampling event. By sampling the water at flow rates most similar to typical household use, over multiple sampling events, the frequency and amount of particulate release will give the best approximation of the degree to which consumers could be exposed to the particulates in normal use.

While expensive relative to other sampling protocols, due primarily to the analyses of the large number of water samples, sequential sampling creates the most comprehensive and informative view of the degree of the lead exposure sources at a residence. The large number of sequential water samples ensures that the local water concentration is obtained from every piece of plumbing that could leach lead (Clark et al. 2014). Creating a full profile is especially useful for identifying LSL peaks, which are typically past the fifth liter (Giani et al. 2004), although the number can vary depending on home plumbing configuration, location of

sampling tap relative to service line location, etc. Another practical benefit of this sampling procedure is that a more accurate estimate for flushing duration can be calculated if the resident wishes to implement a flushing regimen (Clark et al. 2014). Flushing the tap before using water for consumption after long stagnation periods has been standard advice from both the EPA and state agencies in the United States. Advice for flushing time varies, with some suggesting a mere 30 s; however, this is often insufficient for flushing the full length of premise plumbing (Cartier et al. 2011; Del Toral et al. 2013; Clark et al. 2014). Profile sampling in Washington, D.C., for example, indicated that a 10 min flush at 2 gallons per minute was required to reach the lowest lead levels at those residences (Giani et al. 2004). Thus, sampling programs that rely on timed samples (e.g., after 30 s or 45 s) are inherently inaccurate at reliably intercepting the elevated lead release from water stagnated in the service line. This is because the “distance”, in terms of water volume between the sampled tap and the water in contact with the LSL, will be a function of the effective ID and length of the interior piping network to the entry point to the house. These parameters are additionally affected by decreases in clear ID caused by corrosion tuberculation, changes in pipe ID throughout the house, and even hydraulic drag from the nature of deposits in the pipes. Because these factors and water flow rate are very site-specific, time-based sampling is prone to error. Profiling gives a much more accurate and reliable estimate of the “location” of a LSL relative to the amount of water used (or intentionally wasted) during sampling.

3. Materials and methods

Sequential drinking water sampling was conducted at single-family residences in four rounds using comparable protocols in Flint, MI, between January 28, 2016 and November 15, 2016 (Table 1). EPA selected the sampling locations based on records provided by the City of Flint, available analytical results showing high lead levels in first draw samples, and field observations. The locations included a variety of residential plumbing configurations (e.g., LSLs and copper interior plumbing, LSLs and galvanized iron interior plumbing, and LSLs and plastic interior plumbing). The number of sites sampled in each round varied with changes in participation and inclusion of new sites.

At each sampling site, a sample tap was identified where water was drawn for human consumption (e.g., drinking, cooking, formula preparation, etc.). Any existing filter was removed from the faucet (or put in bypass mode) prior to flushing or sampling. At least 6 h prior to sampling, any point-of-use filter was removed (or bypassed) and water was run at the sample tap for at least 5 min. Flushing the pipes prior to sequential sampling is necessary so the lead contribution from individual pipe segments can be more

clearly distinguished.

Following the above actions, residents were asked not to use any water from the home plumbing for at least 6 h prior to samples being collected (i.e., no showering, no flushing toilets, no washing laundry, no usage of other water taps, etc.). After at least 6 h of stagnation time, two 125-mL water samples followed by approximately 15 sequential 1-L water samples were collected for metals analysis, depending on the lengths and diameters of plumbing materials to the water main. Cold water (with the tap opened fully) was used to fill each sample bottle. Samples were collected without the water being shut off in between samples and with minimal water spillage.

Distribution system water quality characterization sampling, consisting of a fully flushed “distribution system” sample collected after running the water for 5 min following the completion of sequential sampling, was conducted at each location. Water samples for water quality parameters including total phosphorous, alkalinity, chloride, sulfate, and fluoride were placed in ice-packed coolers as soon as possible after collection. Water samples were also collected for field analysis of pH and chlorine, and, if chlorine residual was low, samples were also collected for laboratory analysis of coliform bacteria.

EPA field sampling coordinators collected samples, maintained field sampling records, and shipped properly preserved samples under chain-of-custody to an EPA regional laboratory. EPA field sampling coordinators worked with the residents to collect information, if possible, regarding plumbing, including any recent repairs and whether any water outlet in the home (regardless of whether they were used for human consumption or not) was leaking. EPA field sampling coordinators recorded the stagnation time prior to sequential sampling based on information from the resident; EPA considered resampling if the resident reported water had been used.

EPA regional laboratory personnel received samples under chain-of-custody and analyzed them for total metals and other water quality parameters based on EPA drinking water methods. Metals analysis was consistent with EPA 200.7/200.8 (EPA, 1990; 1994), using inductively coupled plasma mass spectroscopy (ICP-MS) and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Quality assurance and data verification reviews were performed by the EPA regional laboratories analyzing a given sample set before data reporting. Field sampling records and laboratory analytical results were stored in a project database and reviewed with respect to the sampling objectives. The analytical results have been shared with the residents of participating sample sites and have been posted on the EPA website. Specifically, EPA support efforts to Flint including sampling data and technical assistance documents can be found at: <https://www.epa.gov/flint>.

Each sampling round contained sampling location “exceptions”

Table 1
Summary of sampling effort by round.

	Round A	Round B	Round C	Round D
Dates	1-28 to 3-31-16	7-12 to 7-22-16	9-1 to 9-24-16	10-26 to 11-15-16
Number of Distinct Sites Sampled	105	48	53	46
Sites Included	77	42	48	41
Total Number of Samples	1672	758	833	747
Included Samples	1132	654	753	660
Private-Side Service Line Material (Included Sites) (Total Sites/Total Samples)				
Copper/Brass	41/603	19/272	18/276	14/213
Galvanized Iron	19/267	7/108	10/146	10/159
LSL Intact	4/56	12/196	16/268	12/208
LSL Replaced	4/79	4/78	4/62	5/80
Unknown	9/127	0/0	0/0	0/0

that, based on field observations and other information, had reasonable cause to be excluded from analysis. Reasons for exceptions included: an in-line filter was in place (or very likely in place) during sequential sampling, no pre-stagnation flushing was performed, it was a non-residential site, home was outside Flint limits (Genesee County water), home was unoccupied, uncertain or insufficient stagnation time was indicated (e.g., water use occurred during stagnation), and disturbances to the pipes were thought to have occurred between rounds.

4. Results

Four rounds of samples were collected with comparable protocols during 2016 and are the focus of this evaluation. A total of 252 sets of sequential samples, collected from 124 homes, comprised 4010 individual samples. After removing exceptions, a total of 208 sets of sequential samples, comprising 3199 individual samples and representing 107 different homes, were included in this evaluation (see Table 1). For each home, the two initial 125-mL samples were followed by anywhere from 8 to 28 1-L samples in each round, based on estimates of the plumbing structure at that location.

Samples were grouped according to the observed service line material entering the homes. Copper, galvanized iron, 'LSL intact', 'LSL replaced', and unknown were the identified categories (Table 1). Sites labeled as LSL intact had a confirmed LSL entering the home and those labeled as 'LSL replaced' had their LSL removed and replaced with copper pipe before the time of the sampling event. An important point of clarification is that these categorizations do not reflect what the pipe material may be on the city-owned side of the service line. In most cases, the material of the city-owned side of the service line was unknown. As a result, sites that might have a lead portion on the city side of the service line could be included in the copper, galvanized iron, and unknown categories. Lastly, the city only performed full LSL replacements and galvanized iron service line sections were also removed.

Home plumbing surveys were compiled by the EPA field team. Information regarding the diameter of plumbing materials and components, and the associated length from the sampling tap to the water main were directly measured by hired plumbers, estimated when not visible (e.g., behind walls, underground, etc.) and/or based on city records in the case of service lines. Plumbing schematics are superimposed on sequential water sample profiles in following discussions as equivalent plumbing volumes (based on diameter and length) for comparison. Given the uncertainty of measurement estimates (where necessary) and service line records, the schematics are approximations.

4.1 Water treatment effectiveness on LSLs

LSLs are the largest source of lead in water contamination when present (Sandvig et al. 2008). Beginning in late 2015, the intended strategy to reduce the release of lead from LSLs in Flint was to form relatively insoluble lead-phosphate minerals on the lead pipe wall and other leaded surfaces over time by adding orthophosphate at the Flint water treatment plant. Examination of sequential lead, copper, zinc, and iron profiles over time can be used to assess the effectiveness of the orthophosphate passivation strategy at reducing lead originating from LSLs. A full benefit analysis, however, was not possible because the sequential sampling program was not initiated until the return to Detroit water and enhanced orthophosphate treatment had started.

Home "eq" had a verified LSL entering the home. Lead sequential profiles collected in three successive sampling rounds showed the gradual decrease in lead peaks over time (Fig. 1a). Lead levels

reached a maximum at about 2.25 L, then dropped off to a high and relatively constant level between approximately 2.25 L and 7.25 L, which is consistent with the location of the LSL based on the plumbing configuration. The first 2.25 L also contained a significant but generally smaller amount of lead (except for the first 125 mL sample in Round C of 36 $\mu\text{g/L}$), and may have reflected the contribution of lead accumulated in the galvanized iron scale in the internal premise plumbing and elevated zinc levels in the same volume (Fig. 1c). In addition, brass fittings that could also contribute lead to the water separated the galvanized and lead pipes. The location of the brass fittings was near the sample volume (2.25 L) containing the maximum lead, suggesting a mixed lead source contribution or galvanic corrosion activity (Nguyen et al. 2010; Wang et al. 2012; DeSantis et al., 2018). Peak lead levels dropped over time from 27 $\mu\text{g/L}$ (Round B in July 2016) to 9 $\mu\text{g/L}$ (Round D in November 2016) (Fig. 1a). Lead levels were similarly reduced across the entire sequential range (Fig. 1a), indicating that treatment was effective at reducing lead from all sources at this site. However, orthophosphate was not effective at reducing zinc levels (Fig. 1c).

A second site with a confirmed LSL, home "ex," with a less complicated plumbing configuration showed similar reductions in lead between July 2016 and November 2016 (Fig. 2). Interestingly, lead levels reached peaks at approximately 3.25 L and 6.25 L (Fig. 2a). The two peaks in lead were separated by a drop at 5.25 L that corresponded to the location of the shutoff. At the same location, copper increased, likely associated with a copper service shutoff (Fig. 2b). Zinc and iron were not detected in any of the samples, except for zinc detections at 0.125 L and 0.25 L associated with interior plumbing and one low iron detection at 5.25 L likely associated with the service shutoff (Fig. 2c and d) and originally from the main. Lead levels dropped similarly across the entire sequential range at this site with time; maximum lead levels decreased from 22 $\mu\text{g/L}$ (Round B in July 2016) to 15 $\mu\text{g/L}$ (Round D in November 2016) (Fig. 2a).

4.2 Lead source and plumbing material identification

Examination of the lead concentration of sequential samples can be valuable in identifying plumbing materials and revealing the relative location of lead source(s). When lead concentration profiles are compared to accompanying zinc, copper, and iron profiles, as well as plumbing surveys, the specific type and relative contribution of each lead source (e.g., brass, solder, galvanized pipe, LSL) can be assessed. The application of sequential sampling to identify whether LSLs are present is particularly useful and of great interest. Fig. 3 illustrates a series of sequential sampling profiles collected over multiple rounds/dates from home "dk," observed to have a copper service line visible entering the home. All of the lead profiles showed consistent lead curves between approximately 10 and 20 L of water, with peaks ranging from 17.2 $\mu\text{g/L}$ to 28.7 $\mu\text{g/L}$ originating from the approximate distance from the "unknown" service line portion of the plumbing (Fig. 3a) in each round. No corresponding peaks in copper (Fig. 3b), zinc (Fig. 3c), or iron (Fig. 3d) were observed in that same volume range and copper dropped to the lowest levels (Fig. 3b). These results suggest a LSL is most likely present on the city owned portion of the service line. In contrast, two large lead peaks as high as 87 $\mu\text{g/L}$ were present in the first 2.25 L of water in Round B (July 2016) only (Fig. 3). The initial (0.125 L) lead peak co-occurred with a zinc peak that was as high as 220 $\mu\text{g/L}$ in the same volume (Fig. 3c), and considering the relative sequence location, a brass fixture observed directly adjacent to the faucet during the plumbing survey was the most likely lead source. Similar co-occurrence of lead and zinc in other sampling rounds confirmed the brass fixture as the lead source in the first 0.125 L. The second lead peak (1.25 L–2.25 L) in July 2016 corresponded to a

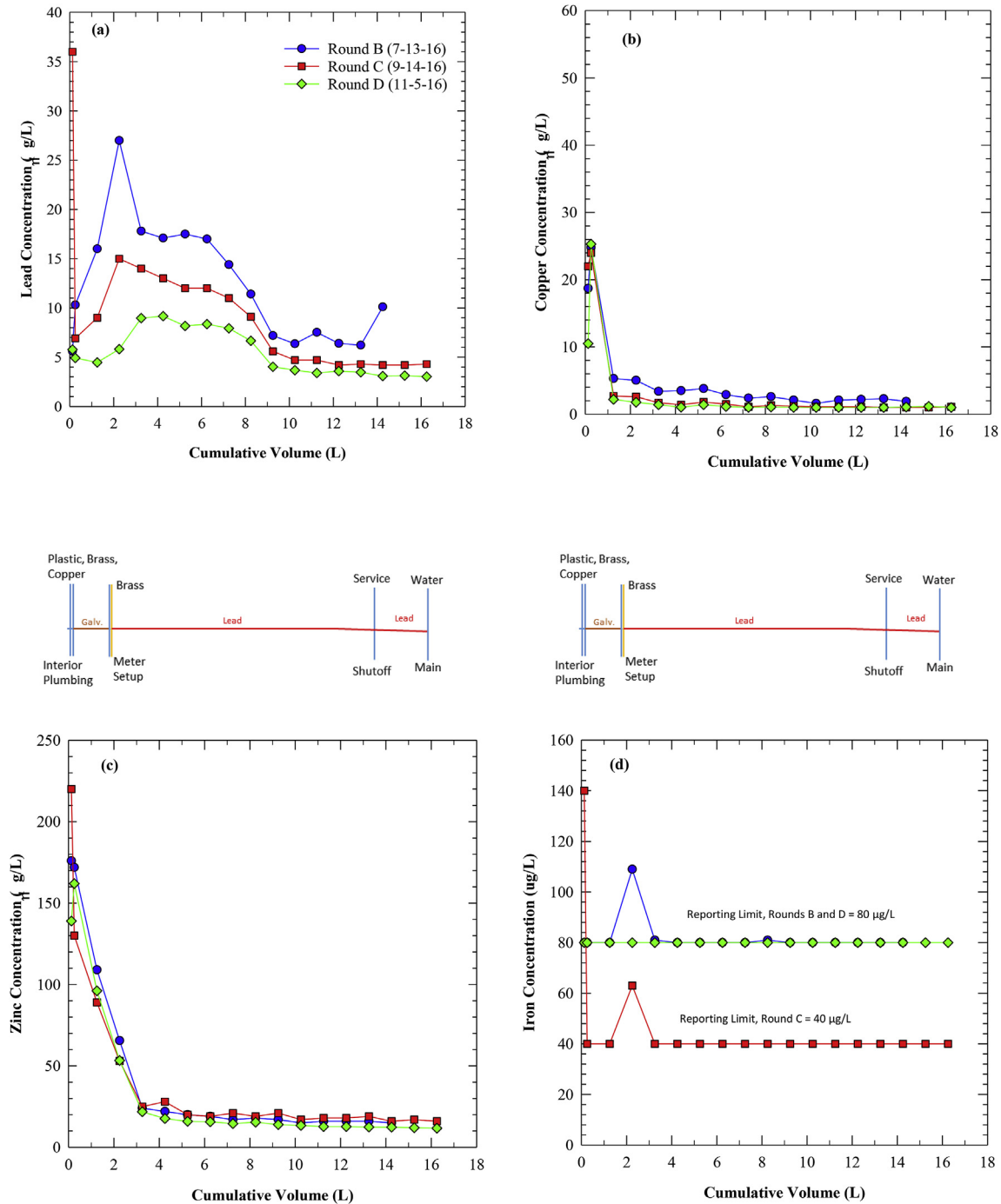


Fig. 1. Sequential drinking water sample metal profiles of verified lead service lines site eq: a) lead, b) copper, c) zinc, and d) iron (note the detection limit change because the regional laboratory running the samples changed).

relatively high spike of iron at 260 $\mu\text{g/L}$ (Fig. 3d) and a copper spike of 180 $\mu\text{g/L}$ (Fig. 3b). Although not separated in the field, based on the theoretical solubility of Fe(III), iron was assumed to be particulate in nature, and lead and copper were assumed to be associated. The plumbing survey did not identify an iron source such as galvanized pipe, and iron was not detected in the same volume during other sampling rounds. The most reasonable conclusion was that iron particles from the mains entered the service line and home, settled out in the premise plumbing, and accumulated lead (and copper), then were re-suspended during sampling as noted by others (Camara et al. 2013; Masters and Edwards, 2015).

A second example, home “cd,” represents a home where a galvanized iron was observed as the service line material entering the home and used throughout the home’s internal plumbing (Fig. 4). Two significant broad lead peaks were obvious in all sampling rounds with maximums at sequential volumes of 2.25 L and 8.25 L, respectively (Fig. 4a). The first broad lead peak located within the home’s internal plumbing ranged between 6.11 $\mu\text{g/L}$ and 61.8 $\mu\text{g/L}$, and corresponded to elevated zinc and, in two rounds, elevated iron concentrations (Fig. 4c and d, respectively). Zinc concentrations in these volumes (1.25 L–3.25 L) were excessive and as high as 1910 $\mu\text{g/L}$. These observations suggested that the brass

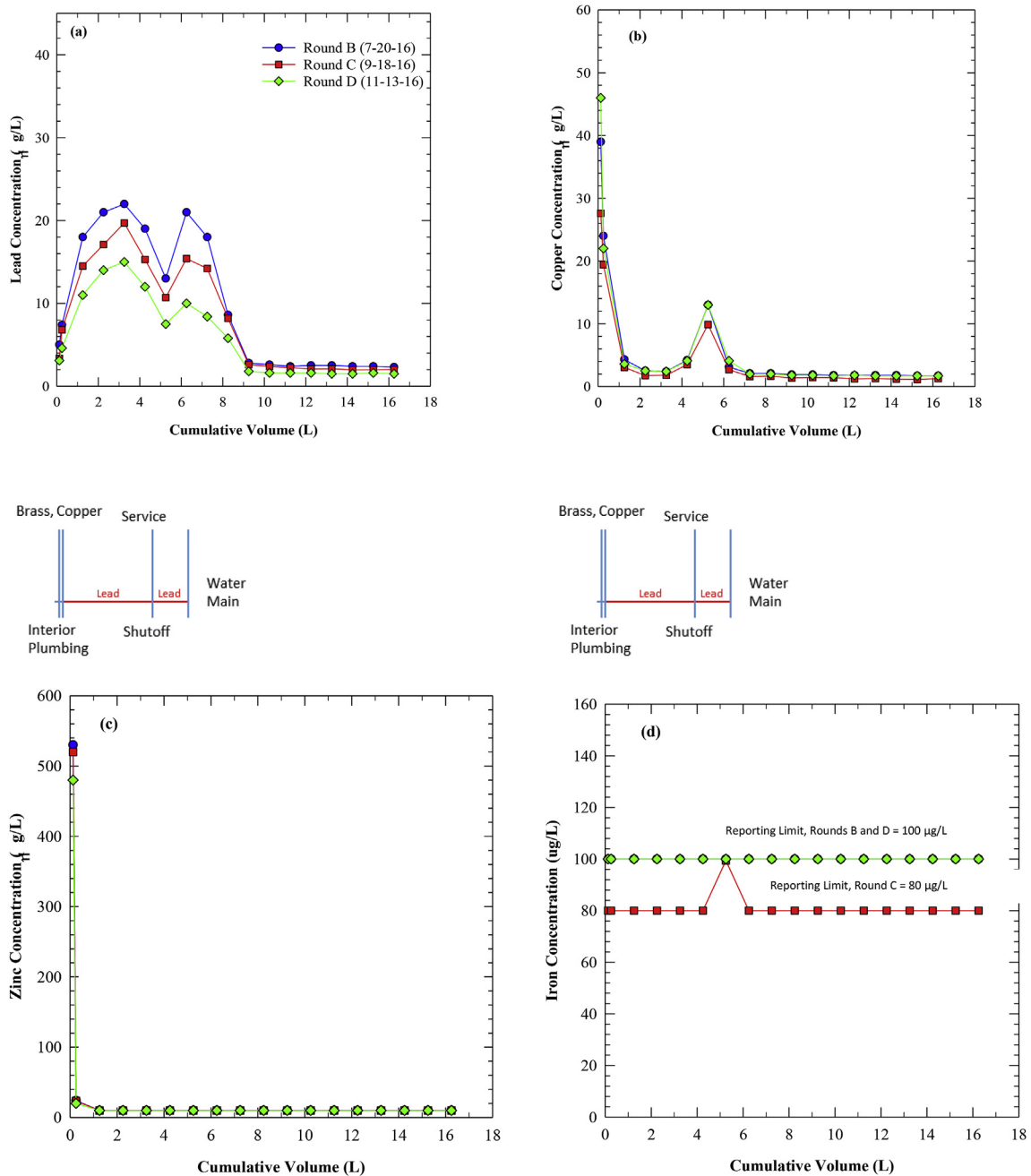


Fig. 2. Sequential drinking water sample metal profiles of verified lead service lines site ex: a) lead, b) copper, c) zinc, and d) iron (note the detection limit change because the regional laboratory running the samples changed).

faucet and fitting, and galvanized iron pipe, were the source of the first lead peak. The concentration of lead in the zinc coating on galvanized pipe installed from 1950 to 2008 was reported to range from non-detect to nearly 2% based on surface analysis (Clark et al. 2015). Additionally, iron corrosion by-products can accumulate lead from the coating or other sources of lead in the upstream plumbing and service line (Camara et al. 2013; Masters and Edwards, 2015), making the exact source of the lead leached or released as particulate into the water difficult to precisely apportion. The second lead peak between 7.25 L and 9.25 L was located in the “unknown” service line region of the sequential profile, and ranged between 3.39 $\mu\text{g/L}$ and 21.7 $\mu\text{g/L}$ (Fig. 4a). Corresponding elevated zinc and iron peaks (Fig. 2c and d, respectively) were not

apparent, suggesting that a city-side partial LSL was likely present in the “unknown” plumbing region. Lastly, copper levels were generally very low (Fig. 2b), consistent with galvanized iron premise plumbing, with the exception of two peaks at 3.25 L and 7.25–8.25 L. The two copper peaks corresponded with the location of a brass meter and shutoff valve well particularly considering the elongated profile expected with diffusion considerations (van der Leer et al., 2002).

4.3 Lead service line removal effectiveness assessment

The city of Flint is implementing a program referred to as the ‘FAST Start Initiative’ to remove all LSLs from their distribution

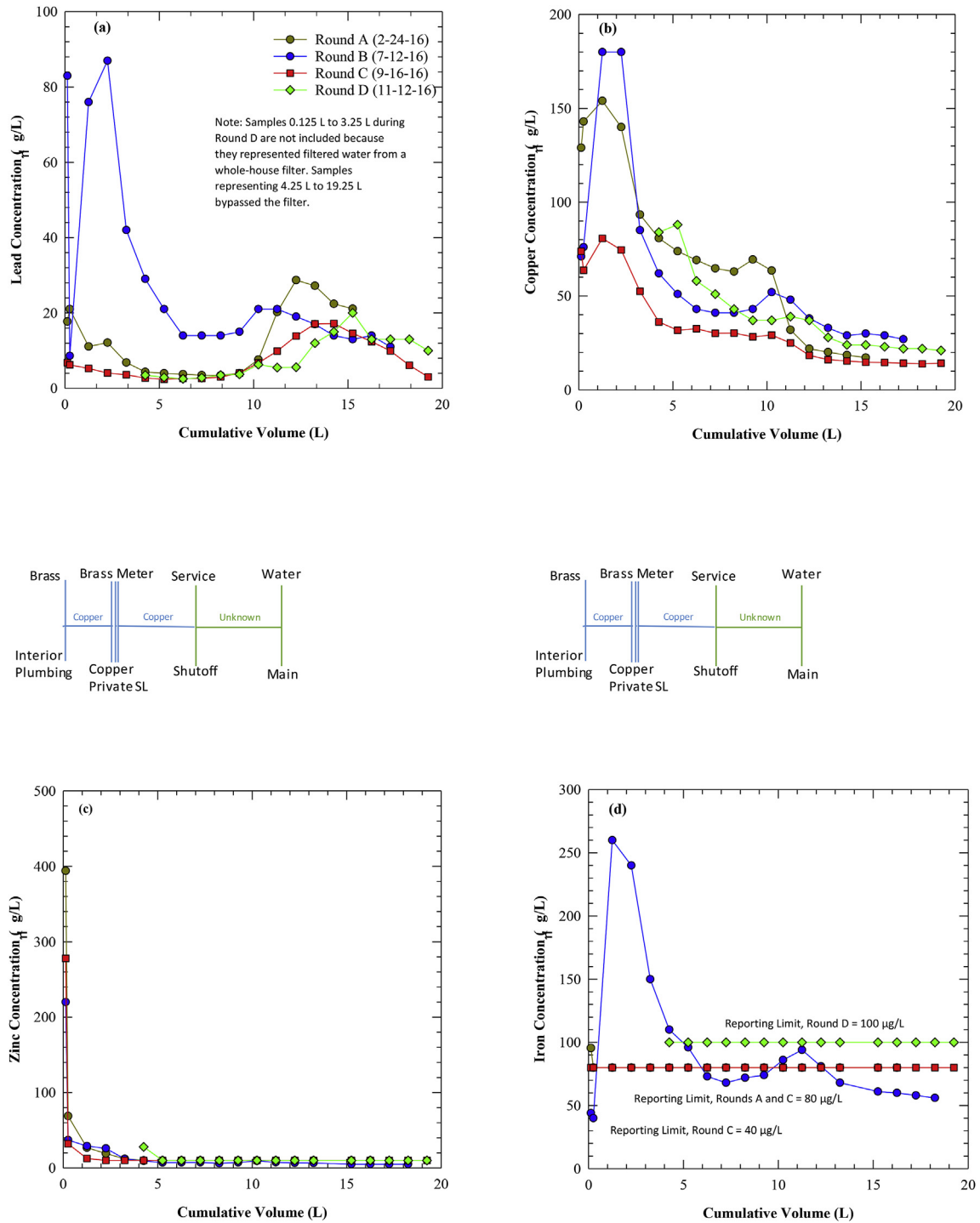


Fig. 3. Sequential drinking water sample metal profiles of site dk with private-side copper service line and apparent public-side LSL: a) lead, b) copper, c) zinc, and d) iron (note the detection limit change because the regional laboratory running the samples changed).

system and set a goal of doing so in three years (City of Flint, 2018). There is interest in quantifying the benefit of removing LSLs given the cost associated with excavation and replacement. The value of removing LSLs has been noted by others (Smargiassi et al. 2006; Sandvig et al. 2008; Mylwyk et al. 2009) and can be illustrated in this work by examining sequential sampling profiles collected before and after LSLs removal. EPA sequential sampling included eleven homes where pre- and post-LSL removal profiles were collected. In five of the homes, the LSLs were removed following

sequential sampling at the sites during Round A, and monitoring was continued in multiple sampling rounds, with the first post-removal sampling also during Round A (“Round A LSLR”). The other six homes were only monitored one round after LSL removal and were left out of detailed analysis in this section.

The LSL in home “eh” was removed in mid-March 2016 (Fig. 5). Prior to LSL removal (Round A), a very high lead spike of 149 µg/L was observed at 1.25 L, and lead then remained elevated for several samples before dropping to 8 µg/L by 12.25 L (Fig. 5a). The same

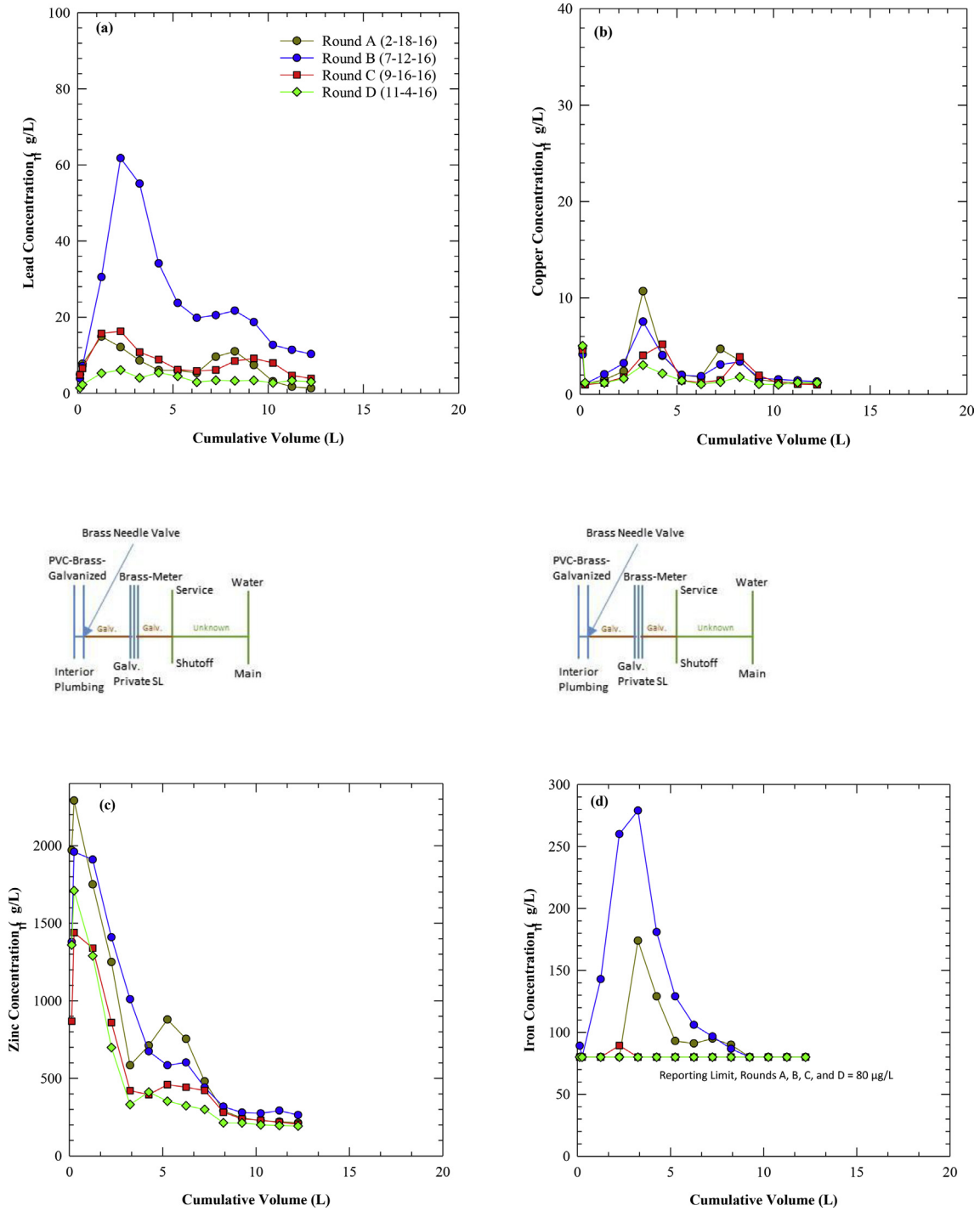


Fig. 4. Sequential drinking water sample metal profiles of site cd with private-side galvanized service line and apparent public-side LSL: a) lead, b) copper, c) zinc, and d) iron.

peak shape at approximately 1.25 L was observed for copper and iron (Fig. 5b and d, respectively) and, to a lesser extent, zinc (Fig. 5c). These results, in combination with a complex mix of plumbing materials including galvanized iron pipe and brass, suggest a complicated mix of lead sources. Following LSL removal, the large spike of lead disappeared (Fig. 5a). However, a lead peak, as high as 19.5 µg/L, remained between 1.25 L and 2.25 L, within the interior plumbing volume of approximately 2.6 L. Zinc and iron peaks were present in the same area (Fig. 5c and d, respectively). The lead reflects the contribution of lead from the galvanized iron

and possibly brass. After the LSL removal, copper peaks were evident between 3.25 L and 10.25 L, consistent with the region where the LSL was replaced with new copper pipe (Fig. 5b).

Home “ed” also had a LSL removed in Round A (mid-March 2016), but had a relatively simple plumbing configuration (Fig. 6). Prior to the LSL removal, a broad elevated lead peak as high as 21 µg/L was observed between 4.25 L and 10.25 L (Fig. 6a), consistent with the service line observed to begin at approximately 4.1 L. No other metal peaks corresponded to the same peak (Fig. 6b to d), indicating that the LSL was the primary lead source. Elevated zinc

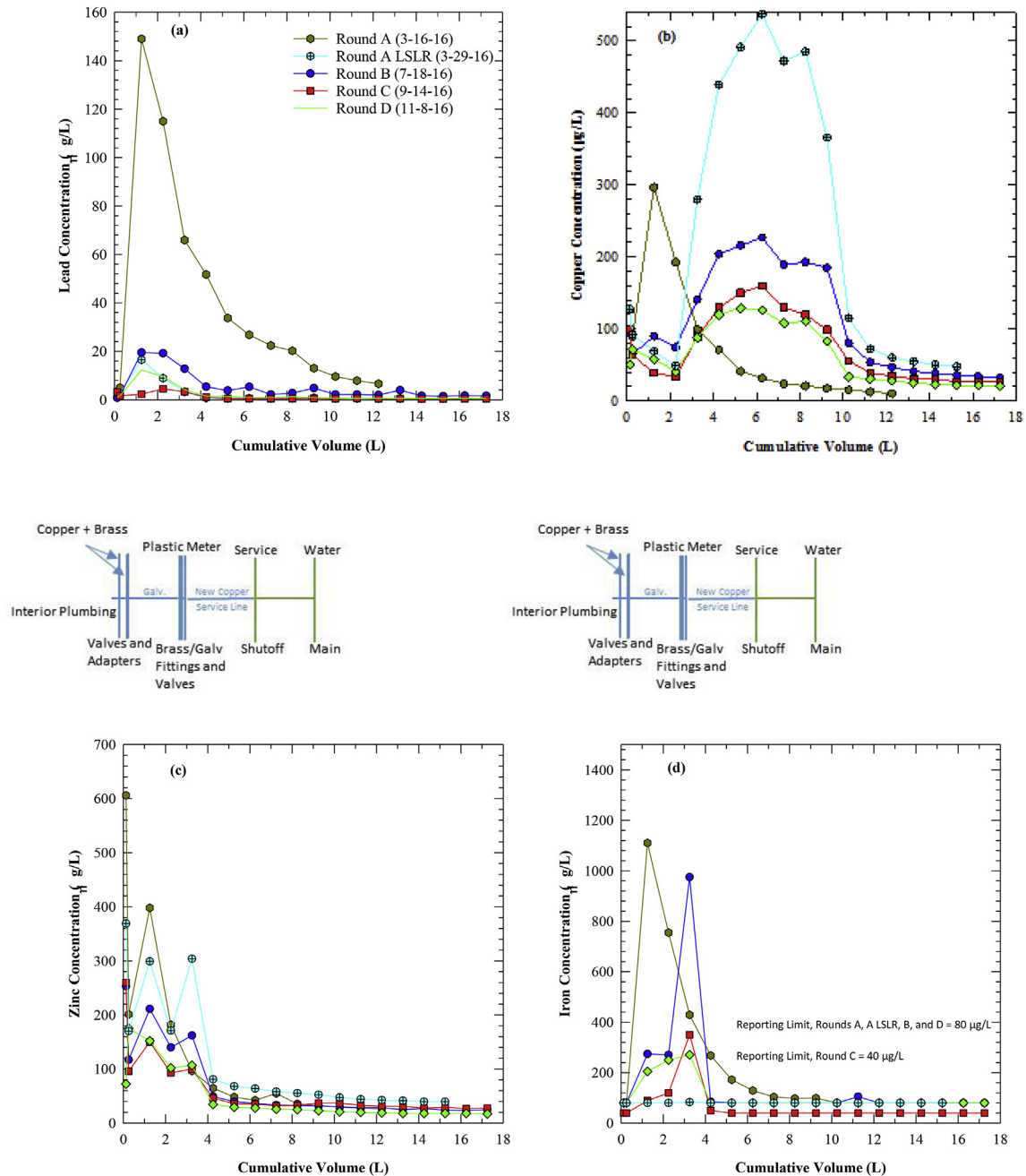


Fig. 5. Sequential drinking water sample metal profiles before and after the removal of a lead service line, site eh: a) lead, b) copper, c) zinc, and d) iron.

levels were observed in the first several sequential samples, consistent with brass plumbing components with minimal contribution of lead. Following LSL removal, a small lead peak as high as $11 \mu\text{g/L}$ was noted between 2.25 L and 5.25 L during Round B (July 2016) (Fig. 6a), and lead up to $5.7 \mu\text{g/L}$ in the first 0.25 L is likely attributed to brass fixture and fittings. Otherwise, lead levels following LSL removal were below approximately $5 \mu\text{g/L}$, with most at or near the reporting limit. The source of lead in the Round B (July 2016) samples may have been scale dislodged from the LSL during excavation that was trapped in the home plumbing and subsequently released, as suggested by the lack of corresponding zinc and iron peaks (Fig. 6c and d, respectively). Copper spikes were again evident after the LSL removal between 3.25 L and 11.25 L, consistent with the region where the LSL was replaced with a new

copper pipe (Fig. 6b). Peak copper levels generally decreased over time following LSL removal, demonstrating the effectiveness of orthophosphate for rapidly reducing copper associated with new copper plumbing.

4.4 Occurrence of elevated lead spikes

Elevated lead concentration "spikes" were reported by all investigators (State of Michigan, university researcher, other federal government sampling events) collecting drinking water samples in Flint in 2016 while the distribution system was recovering (Dolan, 2016a, 2016b, Wisely, 2016; Pieper et al. 2018; EPA, 2016). Considering the theoretical solubility of hypothetical Pb(II) -orthophosphate solid phases in Flint water, the co-presence of

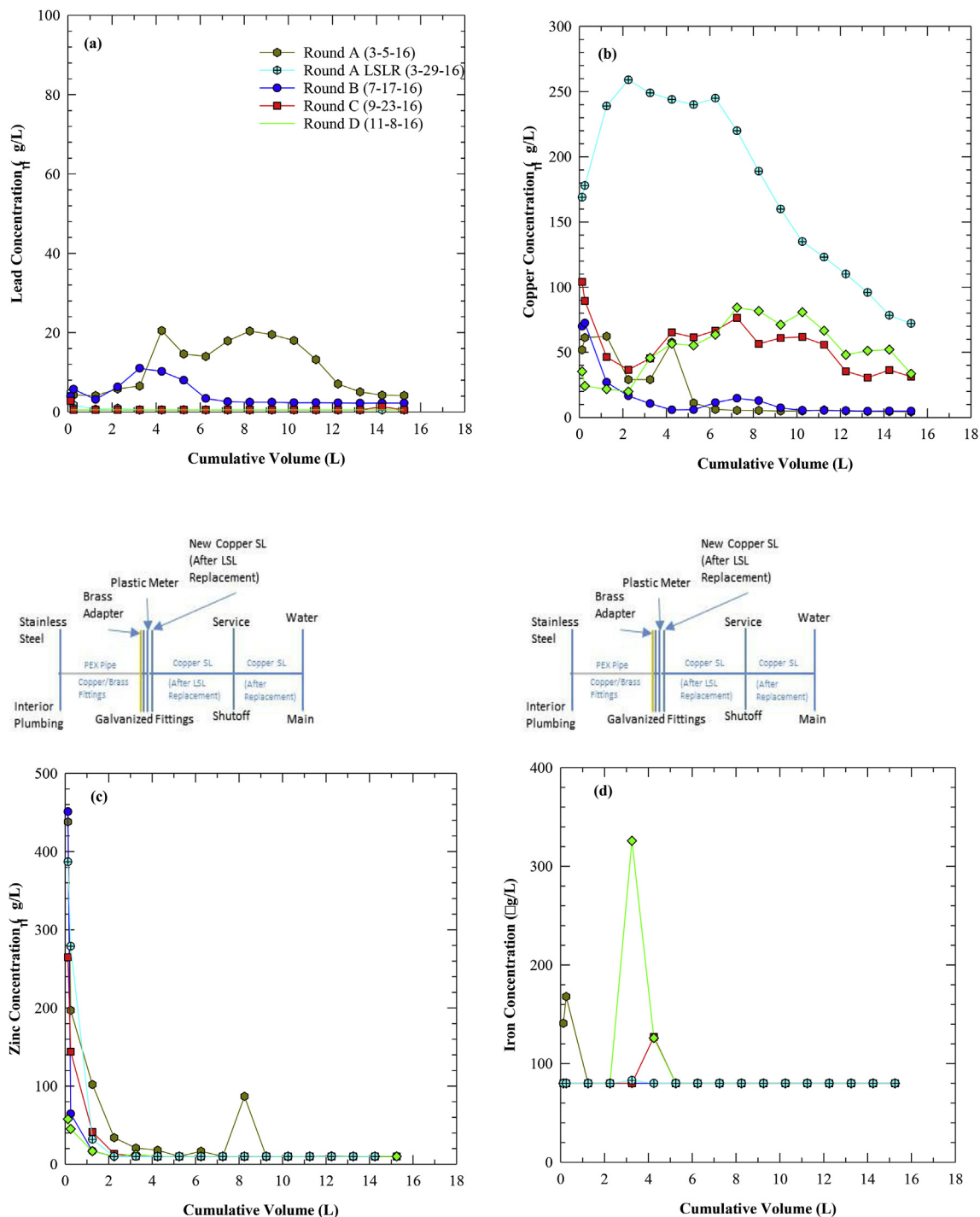


Fig. 6. Sequential drinking water sample metal profiles before and after the removal of a lead service line site ed: a) lead, b) copper, c) zinc, and d) iron (9-23-16 sampling was flagged because the stagnation time was short at 4.5 h).

elevated metals other than lead, and other unpublished EPA Flint water sampling events (<https://www.epa.gov/flint>), lead concentration spikes generally were assumed to be associated with particles, although no filtered water analyses were performed by EPA in this study to confirm the assumption. Sequential sampling provides some indication as to the nature of the lead (i.e., particulate versus dissolved) by examining whether lead peaks are observed in repeat sampling events at the same locations, and the amount of deviation of individual samples from the background shape of the

profile. Performing filtrations on all or a subset of sequential water samples would conclusively distinguish between lead forms. The release of particulate lead was attributed in part to low water usage patterns in Flint homes. With input from the state and EPA, the city initiated a “Flush for Flint” flushing program in May 2016 (EPA, 2016) to encourage residents to use their water to flush any lead particles from household plumbing.

Sequential sample analysis can be valuable in identifying the extent to which elevated lead spikes and particulate lead release

are important, and how corrosion control treatment, time and water use trends reduce their frequency. Unfortunately particle filtrations were not performed in this work, so the fraction of individual sequential samples with lead levels above an elevated 20 µg/L lead cutoff were examined to reflect trends in lead spikes and possibly lead particulate release. The 20 µg/L concentration serves solely as a benchmark for trend comparisons. In Round A (January to March 2016), 127 of the 1132 sequential samples collected (11% of the samples in the round) were greater than 20 µg/L (Fig. 7). In Round B (July 2016), 94 of the 654 sequential samples collected (14% of the samples in the round) were above 20 µg/L, which was very similar to Round 1 (January to March 2016). In Round C (September 2016) and Round D (November 2016), respectively, only 12 (1.6%) and 31 (4.7%) sequential samples were greater than 20 µg/L. The reduction in the fraction of sequential samples with lead levels greater than 20 µg/L, possibly associated with particulate lead, greatly decreased over time. This reduction in elevated lead spikes is attributed to increased effectiveness of orthophosphate treatment over time and efforts to increase water usage in Flint.

With the exception of Round A (January to March 2016), where the number of samples identified as having a copper service line entering the home far outweighed the number of samples in other categories (Table 1), homes identified as having intact LSLs had the greatest occurrence of lead spikes. The trend in reduction of lead spikes associated with intact LSLs followed that of all samples. The fraction of LSL homes with lead spikes greater than 20 µg/L decreased from 14% to 27% in Rounds A and B, respectively (January to March 2016 and July 2016) to 3% and 9%, respectively, in Rounds C and D (September 2016 and November 2016) (Fig. 7). No lead levels above 20 µg/L were measured in sequential samples collected from homes that had had the LSL removed.

Another broader indicator of change in the occurrence of high lead spikes was by comparing the maximum levels at each

sequential sampling location. The arithmetic means of the maximum lead concentration of all sequential profiles in Rounds A, B, C, and D (January–March 2016, July 2016, September 2016, and November 2016) were 85 µg/L, 49 µg/L, 14 µg/L, and 40 µg/L, respectively. Alternatively, the geometric means of the maximum concentration of all sequential profiles in Rounds A, B, C, and D (January–March 2016, July 2016, September 2016, and November 2016) were 14 µg/L, 13 µg/L, 8 µg/L, and 9 µg/L, respectively. Analysis using the Kruskal-Wallis One-Way ANOVA on Ranks test (data failed normality test, $P < 0.001$) indicated that the median values among the sampling datasets were not statistically different. The statistical results were not surprising given the relatively large range in maximum sequential lead values and resulting standard deviations in each round.

4.5 Weighted average sequential lead concentration (WASLC) and lead exposure estimate

Given the complicated nature of lead release, multiple lead sources, differences in lengths and positions of LSL segments, random water use patterns, water quality variability, and other factors, lead levels can range widely across a set of sequential samples from different houses. The profile is a snapshot of the highest and lowest lead levels a homeowner could consume based on a period of stagnation and current water quality not considering the random presence of elevated particulate lead release. The total mass released across the sequential profile or the WASLC can be used to assess system recovery over time and the effectiveness of corrosion control treatment. And while not a measurement of exposure, the WASLC gives an indication of the lead concentration across a household's plumbing.

The WASLC (µg/L) is defined as the total lead mass in all sequential samples divided by the total volume of all samples collected in the sequence and calculated according to:

$$WASLC = \frac{\sum_{i=1}^n (C_i)(V_i)}{\sum_{i=1}^n V_i}$$

where n is the number of sequential samples, C is the lead concentration (µg/L), and V is the sample volume (L).

In theory, the WASLC can be used to evaluate both the effectiveness of corrosion control over time and the benefit in lead reduction after LSL removal. The WASLC is presented as a percentile plot in Fig. 8, broken down by sampling round and plumbing material. The 90th percentile WASLC dropped from a high of 37 µg/L in Round A (January–March 2016), to 27 µg/L and 9 µg/L in Rounds B and C, respectively (July 2016 and September 2016). A slight uptick to 19 µg/L was observed in Round D (November 2016). Trends were broken down further by type and round in Fig. 9. It should be noted that analysis using the Kruskal-Wallis One-Way ANOVA on Ranks test (data failed normality test, $P < 0.001$) indicated that the median values among the sampling datasets were not statistically different.

Five homes (sites ec, ed, eh, az, and f) had a LSL removed in March 2016 and were sequentially sampled both before LSL removal (Round A, January–March 2016) and after replacement (Rounds B, C, and D in July, August, and November 2016). The average total lead mass (or WASLC) reduction in the four sampling rounds after LSL removal ranged between 80% and 94%. The average lead reduction of all five locations was 86%, illustrating the benefit of LSL removal. Because only one sequential profile set was collected prior to LSL removal, statistical comparisons between pre- and post-LSL data removal could not be performed. The results are considerably greater than the findings of Sandvig et al. (2008) that reported LSLs were responsible for 50%–75% of the total mass of lead measured at the tap. Many site-specific factors including water

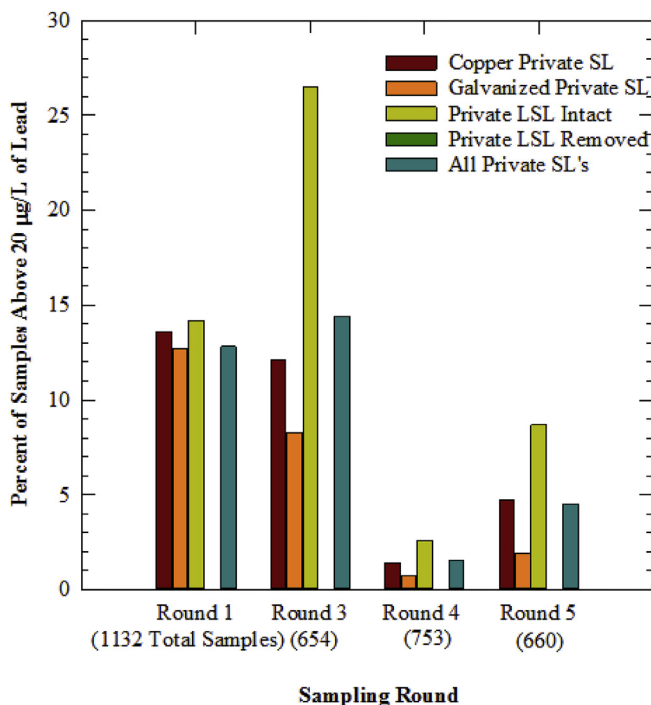


Fig. 7. Sequential sampling results by round showing percent (%) of all samples collected greater than 20 µg/L (Round A, 1–28 to 3–31–16; Round B, 7–12 to 7–22–16; Round C, 9–1 to 9–24–16; Round D, 10–26 to 11–15–16).

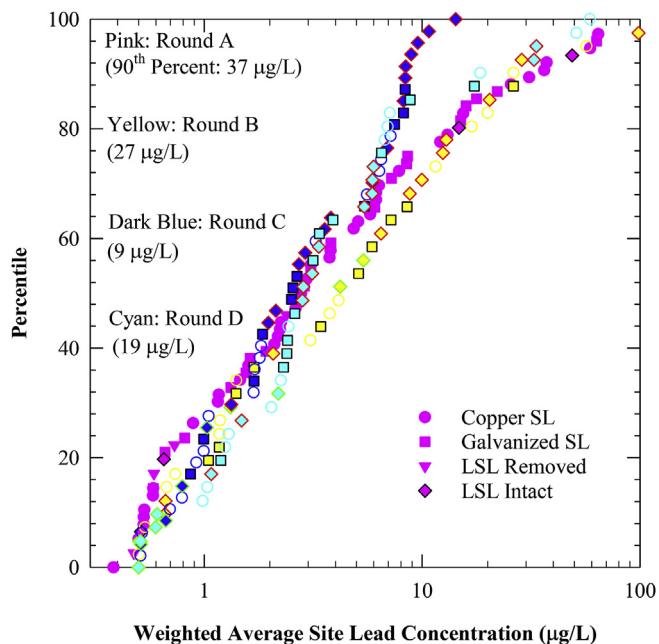


Fig. 8. Weighted Average Site Concentration Data for all rounds of testing with 90% LCR values (Round A, 1–28 to 3–31–16; Round B, 7–12 to 7–22–16; Round C, 9–1 to 9–24–16; Round D.

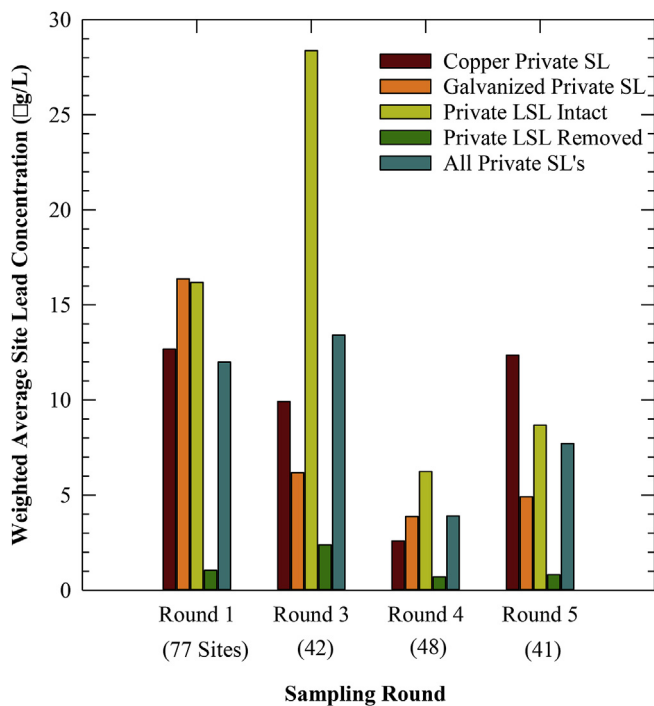


Fig. 9. Summarized sequential sampling results represented as weighted average lead concentrations by Round (Round A, 1–28 to 3–31–16; Round B, 7–12 to 7–22–16; Round C, 9–1 to 9–24–16; Round D, 10–26 to 11–15–16).

quality, degree of corrosion control and the presence of other lead sources could explain the difference. Also, although close examination of the sequential profiles showed that the LSLs were by far the main lead source, it can't be ruled out that a small fraction of lead reduction associated with other lead sources within the household plumbing or indirectly associated with the LSL (e.g.,

particles that released from the LSL and moved in to the plumbing) with time and treatment could have existed. The authors anticipate more significant reductions would be expected by implementing additional precautions (ANSI/AWWA, 2017) and if no galvanized plumbing is present in the home.

In principle, the benefits of corrosion control treatment (orthophosphate addition) over time could also be evaluated based on change in WASLC over time. However, several critical limitations of the dataset for this purpose were immediately apparent. A clear limitation that was expected was that sequential sampling did not begin until 2016, after treatment started in late 2015 (returning to Detroit drinking water with subsequently boosted orthophosphate dose). Additionally, the number of sites that had repeated sampling in multiple rounds was minimal, and there was inadequate representation of the different plumbing material types and only one site was sampled through all rounds. It is also possible that some of the remnant lead following LSL replacement can be attributed to dislodged scale and sediment from the LSL entering the home due to water usage during the excavation activities leading up to the LSL replacement. Therefore, conclusions are necessarily very limited and may be unreliable with respect to this evaluation. On average, a 37% decrease in WASLC was observed from Round B to D (July 2016 to November 2016), but there was a great amount of variability in the data.

4.6 Relative contribution of lead sources

Sequential sampling provides an opportunity to examine the relative contribution of lead sources from each sample bottle collected. The total mass present in each sequential sampling set was calculated as the sum product of each sample volume and sample lead level. The percentage of total lead mass in each sequential bottle during each round was examined (Fig. 10). Although outliers do exist where a significant portion of total lead mass occurs in the first two 125-mL bottles (specifically in Round A, Fig. 10a), in general a larger contribution of lead mass is found in subsequent bottles. Due to these subsequent bottles having a larger volume (1 L versus 125 mL), it is expected that they would contain a greater percentage of total lead mass. However, by comparing the average total volume represented by these bottles to the total mass they contained, a more accurate comparison can be made. While the first two 125-mL samples contain an average of 1.7%–1.9% of the sample volume from a site, they contain an average of anywhere from 2.2% to 6.1% of the total mass. Even this difference might not be entirely attributable to the relative sources of lead, however, as the flow rate of water from the tap changed between the collection of 125 mL samples (Samples 1 and 2) and the 1 L samples (Samples 3 and higher) in most cases. This was due to practical testing limitations, as any consistent flow rate between the two would have been either too large to avoid spilling from the much smaller 125-mL bottles or too small to fill the much larger 1-L bottles in a practical amount of time. While the exact effects of such a difference in flow rate are unknown, it is believed that flow rate does have some impact on exposure to particulate lead by creating the hydraulic and physical conditions to mobilize particles, and thus would have a relevant effect on relative contributions between samples within a site.

5. Conclusions

Sequential or profile water sampling was used by the EPA to assess lead in Flint, Michigan's drinking water between January 28, 2016 and November 15, 2016, as the distribution system recovered from a major upset triggered in large part by temporary source water and treatment changes and the absence of corrosion control.

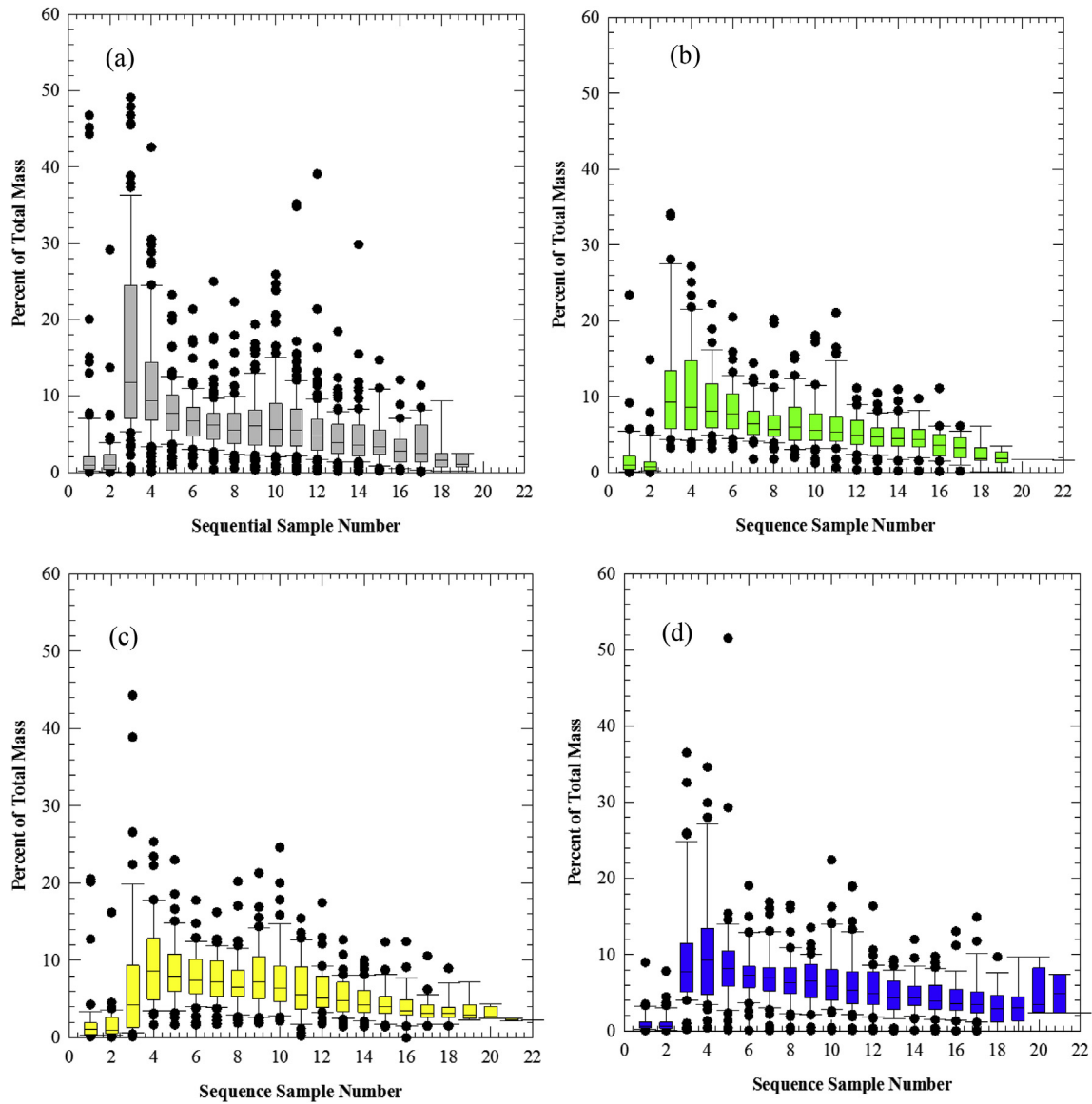


Fig. 10. Box plots showing percent of total mass collected in each sample bottle: a) Round A (1–28 to 3-31-16), b) Round B (7–12 to 7-22-16), c) Round C (9-1 to 9-24-16), and d) Round D (10–26 to 11-15-16) (samples 1 and 2 are 125 mL bottles, and others are 1000 mL bottles).

A total of 208 sets of sequential samples, collected in four sampling rounds from 107 different locations during the reporting period, were included in this evaluation. In addition to lead sequential sampling profiles, corresponding copper, zinc, and iron profiles were also examined. The following conclusions were drawn:

- Sequential sampling profiles (lead as well as copper, iron, and zinc) were valuable in identifying drinking water lead sources in homes that included brass fixtures and other brass components, galvanized iron pipes, and LSLs. Profiles were particularly valuable at identifying public-side LSLs not visible entering the home.
- Sequential sampling data can help evaluate corrosion control over time. The results showed that lead levels, including high lead levels likely associated with particles, decreased with time in homes sampled during the 11-month evaluation period.
- The first two 125-mL sequential samples represented approximately 4–7 feet of plumbing that included the faucet (presumably composed of lead-containing brass) and only

contributed between 2.2% and 6.1% of the total mass of lead in the homes. LSLs and possibly other lead sources (galvanized pipe, brass components, leaded solders, etc..) beyond the first 5.5 feet of plumbing contributed to the majority of lead to drinking water in homes.

- The removal of LSLs reduced the total mass of lead contributed to the drinking water on average by 86% in homes, which demonstrates LSLs were by far the greatest source of lead in homes when present as also illustrated in profiles. More significant reductions would be expected by implementing additional precautions (ANSI/AWWA, 2017), considering other lead sources, and if no galvanized plumbing is present in the home.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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