Forensic Estimates of Lead Release from Lead Service Lines during the Water Crisis in Flint, Michigan
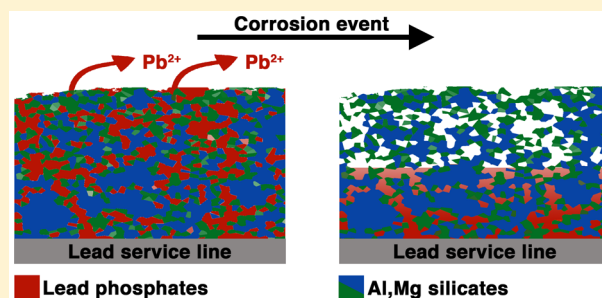
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Ⓢ *Supporting Information*

ABSTRACT: Corrosion pipe scale samples were collected from 10 lead service lines (LSLs) in Flint, Michigan, after corrosive conditions associated with the Flint water crisis of 2014−2015 caused citywide release of lead into its drinking water. Elemental analysis of metals in the LSL scale revealed that the scale was relatively depleted of lead compared to a literature survey of LSL scale from 26 U.S. utilities. Flint LSL scale was also significantly enriched with aluminum and magnesium compared to reported literature LSL scale compositions. Using correlative associations of lead with aluminum and magnesium in Flint scale samples, and average LSL abundances of aluminum and magnesium from the literature, we estimated that at least 2.7 ± 1.5 g of lead per meter of Flint's LSLs was released from the pipe scale during the corrosion episode. The findings provide evidence that selective dissolution of lead phosphate minerals occurred because of the absence of orthophosphate during the crisis.

■ INTRODUCTION

Drinking water quality in the City of Flint, Michigan, became severely degraded when, in April 2014, the City began drawing and treating water from a new source, the Flint River, without adequate corrosion control (orthophosphate). Prior to the switch, the City purchased treated water containing orthophosphate as a corrosion inhibitor from the Detroit Water and Sewerage Department (DWSD). Free chlorine was used as a disinfectant before and after the water switch. Supply of the improperly treated water continued over a 17.5 month period, until elevated lead levels in resident blood and tap water were discovered and Flint returned to DWSD as a water source in October 2015.[1] Lead concentrations in Flint tap water during and following the corrosion episode were often in excess of the U.S. Environmental Protection Agency Lead and Copper Rule action level, 15 μg/L, and in some cases, lead concentrations exceeded hazardous waste levels (>5000 μg/L).[2,3] Lead service lines (LSLs) were thought to be an important lead source. Flint has undertaken a program to replace its LSLs and has prioritized replacement of approximately 18000 service lines over the next three years. While there is still uncertainty about the total number of service lines that need to be replaced, recent estimates by the City indicate 29100 replacements are needed.[4] Given that many communities in the United States and around the world have legacy LSLs, quantifying the contribution of these distribution system components to Flint's lead water crisis could help utilities and the public understand the risk that LSLs pose.[5−7]

Sudden changes in water quality, such as the shift in disinfectant from chlorine to monochloramine in Washington, DC, in 2004[8] and improper pH adjustment in Sebring, Ohio, in 2016,[9] have caused incidents of drinking water lead contamination. Flint's lead problem has been attributed to the City's decision not to continue adding orthophosphate as a corrosion inhibitor,[2] although this assessment is not universally accepted.[10] The findings we present here provide evidence that a lack of orthophosphate corrosion control was indeed an important reason for the release of lead from Flint's service lines.

Our team originally focused on characterizing the changes in water quality and service line corrosion scale before and after LSL replacement at homes in Flint. During this process, it became apparent that our scale characterizations could forensically be used to estimate the lead source contribution of LSLs during the crisis. A forensic prediction was adopted because no LSL samples that were not exposed to corrosive water during the water crisis were available for a direct pre- and postcorrosion comparison. In this report, we present scale characterization data, a discussion of how these results differ from scale characterizations of LSLs in cities without substantial corrosion, and an analysis of the potential mass of lead that was lost from the service lines in Flint during the corrosion event.
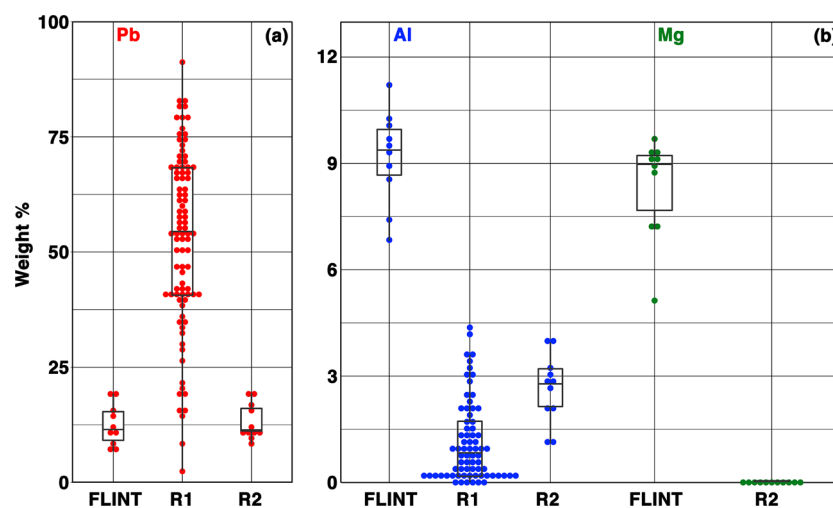
Figure 1. Frequency plot abundances of (a) depleted and (b) enriched elements in LSL corrosion scale as measured in this study (FLINT; $n = 10$) relative to two published studies: R1, Schock et al.[12] ($n_{Pb} = 91$, and $n_{Al} = 73$); R2, Kim and Herrera[13] ($n = 11$). Mg was not quantified in the R1 data set.

■ MATERIALS AND METHODS

Sample Collection. Lead pipe segments were collected during the first (March−May 2016) and second (September− December 2016) phases of Flint's "FAST Start" LSL replacement program. The two sample collection periods started approximately 23 and 47 weeks after Flint reconnected to the DWSD water supply. The pipes were collected from different regions of Flint in a manner that was determined by the City's "FAST Start" LSL replacement program schedule.

Elemental Characterization. Approximately 10 cm long coupons were cut radially using a tube cutter from each of the service line samples for bulk elemental analysis of the scale via inductively coupled plasma mass spectrometry (ICP-MS). The pipe coupons were cut in half longitudinally with a stainless steel saw. Lead pipe shards from the cutting were carefully removed from the scale surface with compressed nitrogen gas. Scale samples were collected from the longitudinal coupons with a stainless steel spatula and dried in a 100 °C oven for approximately 90 min. Dry masses of scale samples were measured and ground to a homogeneous fine powder using an agate mortar and pestle. Acid digestion of the scale was conducted according to a modified EPA Method 3050B,[11] in which 10 mL of 1/1 concentrated nitric acid and 18.2 MΩ × cm Milli-Q water was added to approximately 0.20 g of dried scale in an acid-washed glass beaker. The slurry was covered with a watch glass and placed on a magnetic stir/hot plate at 95 ± 5 °C without boiling for 15 min. The sample was allowed to cool before 5 mL of a concentrated nitric acid solution was added, and the solution was stirred and heated again for 20 min. After cooling, the digested sample was filtered through cotton α-cellulose filter paper with a particle retention of 5−10 μm and diluted to 100 mL. Samples were transferred to two 50 mL PPE centrifuge tubes for storage at 4 °C.

Standards for metals analysis with an Agilent 7900 ICP-MS instrument were prepared through serial dilution of a custom stock standard solution prepared by Ricca Chemical Co (Arlington, TX). Digested scale samples were diluted by a factor of 1000 and analyzed via the high-energy helium acquisition mode for Pb, Al, Mg, Fe, Mn, Cu, Cd, Zn, Ni, Cr, As, V, P, and Co. The metal abundance was normalized by the mass of dry scale digested for each sample.

Characterization by Microscopy. To examine LSL scale sample morphology in terms of porosity, 5 cm long LSL coupons were cut radially and the scale was analyzed with a JEOL 7800F low-vacuum scanning electron microscope (SEM). Details of the sample preparation and analysis are provided in Figure S2.

■ RESULTS AND DISCUSSION

The elemental abundance of selected metals in Flint LSL corrosion scale ($n = 10$) is summarized in Table S1. The mean lead content of the scale (±one standard deviation) was 12.4 ± 4.6% by weight. Metals with the greatest abundance were Pb, Al, Mg, Fe, and Mn, in order of decreasing abundance. Similar characterizations of scale composition from LSLs are available in the literature, including a study of 91 pipe coupons from 26 U.S. drinking water utilities by Schock et al.[12] and another investigation of 11 pipe specimens from the City of London, Ontario, by Kim and Herrera.[13] At the time of the London study, both London and Flint's supplier, DWSD, drew water from the Great Lakes and provided conventional treatment with alum and chlorine disinfection. The London utility did not use orthophosphate to control corrosion but instead relied on a pH (7.9) somewhat higher than the pH in DWSD water (7.4)[14] to encourage lead carbonate mineral scale formation and control corrosion. Examination of the Flint and London pipe scale elemental compositions indicates that comparable lead abundance was observed in both studies, but relative to London pipe scale, Flint pipe scale is considerably enriched with magnesium and aluminum, as shown in Figure 1 (R2 represents results for London). When the Flint scale composition is compared to the much larger database in the study of Schock et al.,[12] also shown in Figure 1 (R1), Flint's pipe scale appears to be significantly depleted of lead (unpaired Wilcoxon test, p value of 1.1×10^{-6}) and again significantly enriched with aluminum (unpaired Wilcoxon test, p value of 3.5×10^{-7}). Magnesium was not measured in their study.

In a separate study of 10 water utilities, lead pipe scale layers were characterized in terms of their relative atomic metal content using energy dispersive spectroscopy.[15] Detroit, Michigan, was one of the cities in this study. Lead and aluminum were analyzed in two layers of scale from two Detroit
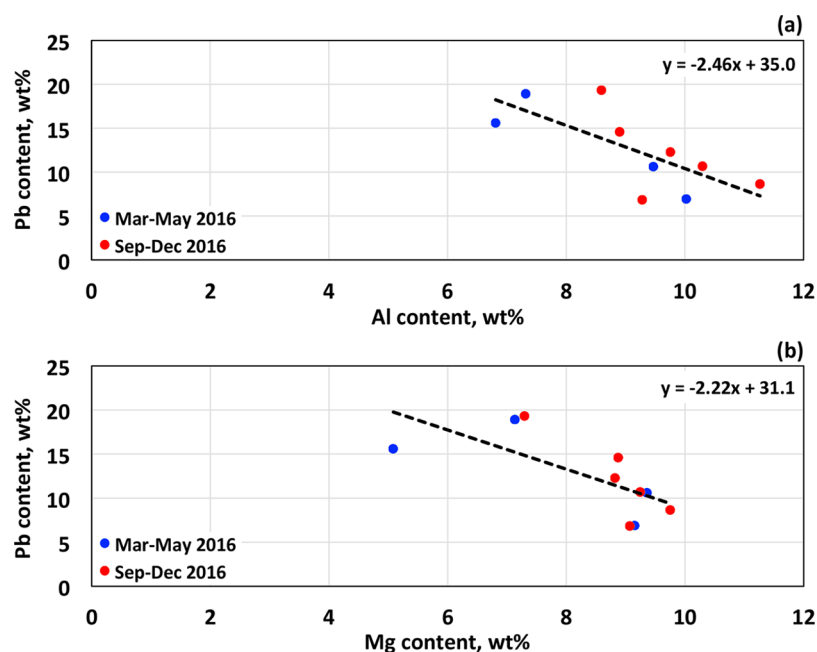
Figure 2. Correlational relationships between Pb and (a) Al ($\rho_{Al,Pb} = -0.72$; $R^2 = 0.53$) and (b) Mg ($\rho_{Mg,Pb} = -0.70$; $R^2 = 0.50$) abundance in Flint LSL corrosion scale collected during the two sampling periods.

lead pipes. Magnesium was not measured. While it is not possible to compute lead and aluminum mass fractions from their Detroit pipe scale data, the individual layers had Pb/Al mass ratios ranging from 2.7 to 17.6, as listed in Table S4. In Flint, the average bulk scale Pb/Al mass ratio determined from the data in Table S1 was 1.4 ± 0.7. Thus, Flint LSL scale is depleted of lead relative to its aluminum content when compared to any of these Detroit pipe scale samples. The Detroit scale layers also had uniformly higher P/Al mass ratios relative to that of Flint LSL scale, suggesting Flint scale may also be depleted of phosphorus.

Aluminosilicate deposits are well-known to form in drinking water distribution systems.[15,16] Precipitation of these phases is thought to occur slowly in systems in which alum coagulation results in elevated dissolved aluminum levels, in the presence of ambient silica concentrations. Magnesium is also known to further depress the solubility of aluminum. In jar tests conducted by Kvech and Edwards,[17] for example, the formation of complex $Al_xMg_y(OH)_z$ and $Al_yMg_x[Si(OH)_4]_y(OH)_z$ solids was observed at pH 9, although specific crystalline identification with X-ray diffraction (XRD) was not achieved. In this study, the Al/Mg stoichiometric ratio was approximately 1/2 in the controlling solids.[17]

We hypothesized that the aluminum and magnesium "enrichment" in Flint pipe scale relative to the data from the published studies[12,13,15] was a result of selective dissolution of lead phosphate minerals during the corrosion event. As a corollary to this hypothesis, a negative correlation between lead and aluminum as well as lead and magnesium would be expected in the Flint pipe scale samples. In our study, negative pairwise Pearson correlation coefficients (ρ_{xy}) of -0.72 and -0.70 for $\rho_{Al,Pb}$ and $\rho_{Mg,Pb}$ (p values of 0.018 and 0.023, respectively), respectively, were determined. Plots illustrating the association of lead with aluminum and magnesium are shown in Figure 2. The correlations did not appear to be influenced by sampling period.

A strong positive correlation (Figure S1) between magnesium and aluminum ($\rho_{Mg,Al} = 0.90$; $p < 0.001$) was also found with an implied stoichiometric Al/Mg ratio of approximately 3/4. In the London study, lead abundances were weakly, but positively, correlated with aluminum and magnesium ($\rho_{Al,Pb} = 0.55$, and $\rho_{Mg,Pb} = 0.52$; p values of 0.07 and 0.09, respectively), and as in Flint, aluminum and magnesium correlated strongly with each other ($\rho_{Mg,Al} = 0.74$; $p = 0.009$).[13] Using Fourier transform infrared spectroscopy, Kim and Herrera[13] observed a hydrated aluminosilicate with a relatively low Si/Al ratio in the London scale that was not identified by XRD. The solid phase was thought to be amorphous. Interestingly, plotting the average values of aluminum and magnesium abundance in London LSL scale on the Al−Mg correlation in Figure S1 yields a point that lies very close to the extrapolated Flint correlation line.

The similarity of the lead abundance in London and Flint LSL scale raises an interesting question: Does the use of orthophosphate for corrosion control generally lead to a greater relative lead abundance in LSL corrosion scale? Because orthophosphate corrosion control was not practiced in London, lead would not have been stored in the scale as lead phosphate minerals. The lead minerals identified in the London pipes were in fact predominantly Pb(II) carbonates, hydrocerussite and cerussite, with some Pb(IV) oxide near the pipe itself.[13] On the basis of the postcorrosion event composition of Flint LSL scale, its relative lead abundance appears to have been rendered similar to that of a community with no lead phosphate mineral scale. The current literature databases, however, do not contain sufficient information to evaluate whether there are differences in the absolute abundance of lead in LSL scale between cities that add or do not add orthophosphate. Such an evaluation would require an inventory of the masses of LSL scale collected per area of pipe surface, which were not reported. Surveys of LSL scale composition that examine relationships between absolute lead abundance in the scale and water chemistry variables, such as corrosion inhibitor and disinfectant type,

would improve our understanding of how these treatment chemicals change "leachable" lead storage masses in the system.

The database of Schock et al.[12] contains samples from many utilities that did apply corrosion control. However, while Flint's corrosion scale appears to be depleted of lead compared to the median value of 54.5 wt % lead reported by Schock et al.,[12] it is unclear from the wide range of lead abundance in their database what the precorrosion lead content might have been in Flint. Abundances of other elements, such as aluminum and magnesium, however, appear to be more narrowly distributed in the literature data of Figure 1. We hypothesized that a better estimate of the precorrosion lead content of Flint LSL scale could be obtained by relating the lead lost to the enriched elements. In this calculation, enriched elements such as aluminum and magnesium were thought to have been relatively conserved during the corrosion episode, and lead mass was thought to be lost as phosphate minerals dissolved. A detailed derivation and basis for the relationships between precorrosion abundances of lead and those of aluminum and magnesium is provided in section S.1.1 of the Supporting Information. The derivation reveals that the correlational relationships of panels a and b of Figure 2 should yield a common y-intercept equal to the weight percentage of lead in dissolving phosphate minerals. Least-square regression estimates of the y-intercept values (±standard error) were 35 ± 7.6 and 31 ± 6.7% for the Pb−Al and Pb−Mg correlations, respectively, with the estimates having overlapping standard errors.

To estimate the precorrosion lead abundance in Flint scale from the correlations of panels a and b of Figure 2, values of the enriched element abundances in precorrosion scale are required. We assumed the aluminum and magnesium abundances in scale prior to corrosion resembled the mean abundances reported in the studies of Schock et al.[12] or Kim and Herrera.[13] Results of these calculations are listed in Table 1 and explained in section S.1.2 of the Supporting Information.

Table 1. Predicted Lead Content of Flint Precorrosion LSL Scale Based on Enriched Element Abundance

basis element	average scale abundance from the literature [wt % (standard deviation)]	predicted Pb abundance in Flint precorrosion scale (wt %)
Al	1.1 (1.1)[12]	32[a]
Al	2.6 (1.05)[13]	29[a]
Mg	0.04 (0.02)[13]	31[b]

[a]Calculated from correlation in Figure 2a. [b]Calculated from correlation in Figure 2b.

Predicted lead contents in precorrosion LSLs in Flint are in the range of 29−32% by weight, depending on the basis element and study. Given that the median values of lead content in the survey of Schock et al.[12] were still higher than our predicted lead content for Flint, this implies our precorrosion lead abundance estimate is relatively conservative.

Independent evidence that significant but selective mineral dissolution occurred during the corrosion episode is observed in SEM images of the scale (Figure S2). Figure S2 shows two typical back-scattered electron images of scale from the collected LSL samples. There is an evident increase in scale porosity toward the edge of the scale in contact with water, supporting the case in which non-uniform erosion of the scale occurred during the corrosion event.

Research has consistently demonstrated that most of the lead in water reaching the household tap is in a particulate form, because of the adsorption of lead onto suspended particulates and the release of lead-containing scale particles.[2,18,19] Lead released by dissolution from LSL scale followed by adsorption to suspended particles passing through the LSL or to downstream pipe surfaces could explain why dissolved lead is not the predominant form in tap water. Given the enrichment pattern of aluminum and magnesium in Flint LSL scale, as well as the SEM images, the dissolution−sorption pathway is likely to be an important lead transport process. Assuming aluminum and magnesium enrichment is due to selective phosphate mineral dissolution, an estimate of the amount of dissolved lead released from Flint LSL scale can be obtained by considering the predicted change in relative lead abundance. The resulting estimate is likely to underestimate the total mass of lead released from an LSL, because it ignores the possible parallel sloughing of lead particles from the scale.

Precorrosion estimates of the lead content in Flint LSL scale were used to estimate the average lead mass loss per length of service line that occurred as a result of the corrosion incident. The mean total mass of scale collected per length of LSL in our study was 0.147 ± 0.070 g/cm, and masses for individual samples are listed in Table S3. In most of the coupons, the inner pipe diameter is 1.9 cm (3/4 in.). Ignoring changes in overall scale mass that might have occurred as a result of the corrosive conditions, and assuming the lead content dropped from the estimated "pre-water crisis" level of 30.7% to the measured mean level of 12.4% after corrosion, we found the mass of lead released per length of LSL due to dissolution would be approximately 2.7 g of Pb/m with a standard error estimate of ±1.5 g/m after error propagation. Details of the calculation are provided in section S.1.2 of the Supporting Information. This mass estimate may underestimate the total lead loss, because changes in the overall scale mass would produce higher lead loss estimates and it does not consider sloughing of lead particulates.

Service lines typically consist of a shorter city-owned "public" segment between the main and the curb stop valve and a longer resident-owned "private" segment between the valve and the home. Most commonly, the pipe materials of these segments are dissimilar. Observations from Flint's current LSL replacement project indicate that the most common config-uration in which LSLs are found is a public lead pipe connected to either a galvanized iron or copper private service line. On the basis of unpublished data from Flint's LSL replacement project, the average length of the public segment is 6.5 ± 3.6 m (n = 246).[20] An estimate of the lead lost from the scale in the average public LSL suggests that approximately 18 g of lead would have been released to the connected home during the 17.5 month corrosion event. Of course, a larger lead burden would be expected at homes with both public and private lead pipe segments, although only 2−3% of Flint homes with a LSL have an entirely lead service line.[20] Given that our estimate of average lead mass release considers only lead mineral dissolution as a lead source and that the fate of dissolved lead as it traverses downstream plumbing is complex and unknown, our estimates do not represent a measure of household lead exposure.

The rate of lead release is certainly important from a human health perspective. At the slowest rate, assuming lead was released uniformly over the duration of the corrosion event (∼1.5 years) and assuming an average daily household water

usage of 333000 L/year (88000 gal/year),[21] the average lead concentration leaving a 6.5 m public LSL segment with a predicted release of 18 g of lead would be 36 μg/L. To examine the feasibility of this result, equilibrium estimates of total dissolved lead were determined using MINTEQ[22] by assuming saturation with hydroxylpyromorphite (HPM), $Pb_5(PO_4)_3OH_{(s)}$, and an average pH of 7.4 for Flint water.[23] Approximately 51 μg of total dissolved lead/L is predicted at saturation, suggesting our predicted lead release of 36 μg/L from the LSL is feasible. Additionally, this equilibrium calculation ignores the possible adsorption of lead by particulates that pass through the service line. If instead the average lead concentration of 36 μg/L included both dissolved and particulate lead forms, the 18 g estimate of lead released by the LSL becomes even more plausible.

In the presence of 1 mg/L orthophosphate as P, a dose commonly used in water treatment, MINTEQ calculations show the solubility of lead in HPM-equilibrated water is only ~2 μg/L at pH 7.4. Minerals such as HPM, therefore, are often thought to be relatively insoluble. These equilibrium calculations demonstrate, however, that at least in terms of the 15 μg/L EPA action level for lead, the protective effect these minerals afford is true only as long as orthophosphate is continually supplied. A consistent supply of orthophosphate was similarly shown by other researchers to play a role in controlling the release of lead from a simulated premise plumbing system.[24]

Modeling and experimental studies have shown that dissolved lead levels from LSLs are sensitive to the length of the water stagnation period, but that greater rates of mass transfer of lead from the scale to the bulk water occur under flowing water conditions.[25,26] While these studies did not consider the scenario in which lead phosphate mineral scales are suddenly exposed to low-phosphate water, the important impacts of stagnation and flow likely apply to this situation, as well. Intermittent but frequent water use patterns during the Flint corrosion episode, therefore, might have resulted in more intense and overall larger releases of the dissolution-induced lead burden into a household than the average lead concentration prediction of 36 μg/L.

Sampling in Flint and other communities has demonstrated that lead in tap water is predominantly associated with particles.[2,27,28] The random release patterns of particulate lead in the Flint system unfortunately confound lead exposure estimates because of the corrosion episode and account for reports of extreme lead concentrations that vastly exceed lead's solubility.[2] Sorption mechanisms could account for the conversion of soluble lead leached from the LSL to particulate forms. Likely sources of lead-adsorbing surfaces include suspended corrosion particles liberated from the distribution system. In addition, lead released by the LSL could adsorb to the scale in downstream galvanized iron service lines or premise plumbing.[27] Recent analyses of Flint scale in such a downstream private galvanized service line and galvanized section of indoor plumbing were reported to contain 1.7 and 0.2−0.3% lead, respectively.[2] More research is needed to comprehensively estimate the quantity of lead that might still be "stored" in premise plumbing after the service lines are replaced.

Forensic estimates of the lead released by LSLs in Flint would best be validated by comparing characterizations of pipe samples that have not been exposed to the corrosive water, either in Flint or in communities serviced by the same water

supply. Our team continues to search for such validation samples. In the meantime, our forensic evidence suggests that the absence of corrosion inhibitors during the Flint water crisis was an important factor causing the release of lead from LSLs. This evidence contradicts a recent claim by a regulator that treating Flint River water with orthophosphates would not have prevented the lead water crisis.[10] Our findings further suggest that LSLs generally should be considered a source of readily solubilized lead if they are exposed to interruptions in orthophosphate supply. Given that an average of at least 18 g of lead is predicted to have been released to individual Flint homes with a public LSL, lead pipes undoubtedly were a major source of Flint's lead-contaminated tap water.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.estlett.7b00226.

> Additional tables of elemental analyses, LSL scale masses, SEM images, and derivations and assumptions made in calculating the loss of lead from Flint LSLs (PDF)

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Notes

The authors declare no competing financial interest.

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