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Effects of ortho- and polyphosphates on lead speciation in drinking water

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Lead is a potent neurotoxin and drinking water represents an important route of exposure, especially where legacy lead pipe is widespread. Polyphosphates are often added to drinking water to sequester iron and calcium, but they may form coordination complexes with lead, increasing its solubility. This risk is not well characterized in practice: the prevalence of lead-polyphosphate complexes in drinking water systems is not known. We used size-exclusion chromatography (SEC) with multi-element (ICP-MS) detection to compare the speciation of lead below 0.45 μm in two low-alkalinity water systems dosing phosphate-based corrosion inhibitors at different ortho : poly ratios and doses. In one system dosing polyphosphate at 0.05 mg P L^{-1} (3 : 1 ratio), it reverted almost completely to orthophosphate during distribution. In another system dosing polyphosphate at 0.20 mg P L^{-1} (1 : 1 ratio), it was detectable at points of use. Under the influence of polyphosphate, lead and iron were present as dissolved species strongly associated with phosphorus. Moreover, experiments with sodium hexametaphosphate confirmed our ability to detect lead as a coordination complex using SEC. In the absence of polyphosphate, lead and iron were present as colloidal particles. Orthophosphate on its own also appeared to reduce lead solubility, as estimated using paired sample profiles collected at seventeen single-unit residences. Increasing orthophosphate from 0.5 to 1.0 mg PO_4 L^{-1} accompanied decreases in total lead concentrations of 38% (95% CI: 15–51%) within eight months. Analysis of recovered lead pipe corrosion scale was consistent with the presence of an insoluble lead phosphate compound: hydroxypyromorphite ($Pb_5(PO_4)_3OH$).

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Water impact

Polyphosphates are widely used in drinking water systems for iron and calcium sequestration, but they may increase lead solubility *via* complexation. In practice, this potential health risk is not well understood. Separation of environmental samples *via* size-exclusion chromatography with multi-element (ICP-MS) detection represents a promising approach to understanding the prevalence of lead complexation by polyphosphates.

1 Introduction

Lead service lines (LSLs) were installed widely throughout the first half of the twentieth century; in the United States, millions remain in place.[1] Legacy lead pipe is a significant public health concern because lead in drinking water is a risk factor for elevated lead in blood.[2–4] High blood lead levels in childhood are strongly associated with lasting deficits in cognitive and academic skills.[5–8] The effect of childhood lead exposure is non-linear: at lower levels, increases in blood lead accompany steeper declines in cognitive performance.[5,6,8]

Orthophosphate is added to drinking water to limit corrosion and release of lead from distribution networks.[9] Orthophosphate inhibits lead release by forming insoluble lead phosphate compounds: possibilities include hydroxypyromorphite ($Pb_5(PO_4)_3OH$), chloropyromorphite ($Pb_5(PO_4)_3Cl$), and tertiary lead phosphate ($Pb_3(PO_4)_2$).[10,11] Orthophosphate may also inhibit dissolution of lead carbonates or other lead compounds by adsorbing to and passivating mineral surfaces,[12] as has been suggested in the case of calcite.[13] However, certain chemical species can interfere with these mechanisms. Successful formation of a phosphate-rich corrosion scale requires lead-phosphate supersaturation: species that form soluble complexes with lead—including carbonate and natural organic matter (NOM)[14,15]—can increase the equilibrium solubility of lead-phosphates (*e.g.*, hydroxypyromorphite solubility increases with increasing dissolved inorganic carbon).[12] Furthermore, precipitation of other metal-phosphates (*e.g.*, hydroxyapatite, $Ca_5(PO_4)_3OH$, in hard waters) may interfere with lead solubility control.[10]

Orthophosphate has been shown to inhibit lead release to drinking water in both laboratory and pilot studies.[16,17] Field

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data have provided additional confirmation—using random daytime,[18–20] 30 minute stagnant,[21] or 6 hour stagnant sampling[22,23]—that orthophosphate is effective in limiting lead release under at least some conditions (*e.g.*, alkalinity less than 30 mg L^{-1} as $CaCO_3$). In other circumstances (*e.g.*, at higher alkalinity), orthophosphate-based inhibitors have yielded ambiguous, insignificant, or adverse results with respect to lead corrosion control.[22,24] Nevertheless, orthophosphate treatment has been an important component of the response to severe instances of drinking water lead contamination, including those that occurred in Washington, DC (2001–2004)[3] and Flint, MI (2014–2016).[25] After orthophosphate dosing had been initiated, lead pipe corrosion scale recovered from the Washington, DC distribution system was dominated by hydroxypyromorphite.[26]

Orthophosphate is frequently dosed with polyphosphate as a blended formulation.[9] Polyphosphates form stable complexes with many metals and are useful as sequestering agents for the prevention of coloured water and scaling due to iron oxidation and calcium carbonate precipitation, respectively.[9,27,28] Polyphosphates may form soluble complexes with lead, increasing solubility over a wide alkalinity range by maintaining low activity of the metal cation and undersaturation of the solubility-controlling phase.[27] Polyphosphates have been shown to enhance metal release from lead pipes in laboratory studies.[16,29] These have been corroborated by observations of elevated lead in systems dosing polyphosphates.[22,30] Nevertheless, polyphosphates revert to orthophosphate over time, and blends could be effective in hard waters—where reversion is predicted to be relatively fast[28]—or when metals other than lead are preferentially complexed.[29] Inhibition of copper release by polyphosphates has been attributed in previous work to orthophosphate reversion.[31]

We evaluated the effect of ortho- and polyphosphates on lead speciation and the effect of orthophosphate on lead release/solubility. Data were collected in three separate water distribution systems *via* point-of-use sampling. These systems were characterized by low alkalinity along with several risk factors for elevated lead release: (1) distributed water pH in the circumneutral range (pH 7.2–7.3), (2) distribution by unlined cast iron mains,[32,33] and (3) in two systems, a chloride-to-sulfate mass ratio above the critical threshold of 0.5–0.77 identified in previous work as a driver of galvanic corrosion.[34,35]

2 Materials and methods

2.1 Study area

The study area comprised both single-unit residences and non-residential buildings that were known or suspected to be at risk for high lead levels in drinking water due to building age and the presence of lead service lines. Residential study sites were supplied by one of two water systems, denoted A and B. Non-residential sites were supplied by system C. Participating residences within system A had full (12 sites) or partial LSLs (6 sites, including one site with a public LSL and a private line of unknown composition). Among the sites with partial LSLs, none had recently undergone replacement. Within system B, service line configurations at participating residences were not known. However, based on a threshold of 1 μg Pb L^{-1} in flushed samples collected at near-peak water temperatures,[36] six sites were suspected to have service lines composed at least partially of lead. Non-residential outlets in system C included fountains and faucets but none of the service line configurations were known.

Sample sites in system A were supplied by cast iron distribution mains. In system B, two sites were supplied by cast iron, and the rest were supplied by either cement-lined mains or those of unknown composition. While unlined cast iron mains were common in system C, the composition of distribution mains supplying study sites was not known. Sample sites in systems A and B received distributed water from facilities described elsewhere.[37] These facilities employ enhanced coagulation by alum and free chlorine disinfection. System C was supplied by a facility employing enhanced coagulation with poly-aluminum chloride, membrane microfiltration, and free chlorine disinfection. Treated water quality is summarized in Table 1 for systems A–C.[38] Initially, all three systems applied blended ortho/polyphosphate corrosion inhibitors (systems A and B dosed a 3 : 1 and system C a 1 : 1 ortho : poly formulation). In September 2015 A and B switched to formulations that did not include polyphosphate, and in April 2016, A and B increased the orthophosphate dose from 0.5 to 1.0 mg PO_4 L^{-1}. Comparisons of lead release at 0.5 and 1.0 mg PO_4 L^{-1} reflect the influence of orthophosphate without polyphosphate. SEC separations, on the other hand, compare two polyphosphate doses: 0.05 (system A) and 0.20 mg P L^{-1} (system C).

2.2 Sample collection

Following a random daytime protocol,[18] we collected 250 mL samples at non-residential buildings in system C. In order to compare orthophosphate doses, residents supplied by systems A and B collected profiles of six sequential 1 L samples (L1–L6) from kitchen cold-water taps without preflushing. These began with the first draw following a minimum 6 hour standing period and were followed by a 10 minute flush of each outlet. Immediately after flushing, a seventh 1 L sample (L7) was collected. Profiles were collected in April 2016 at an orthophosphate dose of 0.5 mg PO_4 L^{-1} (no polyphosphate), in June 2016 at an orthophosphate dose of 1.0 mg PO_4 L^{-1}, and at approximate two-month intervals through April 2017. Residents were instructed to record exact stagnation times, to sample at maximum flow, and not to remove faucet aerators. Data were excluded from analysis when these instructions were not followed; sample sizes differ by round for this reason and also due to incomplete resident participation. Polyethylene (HDPE) bottles and caps were immersed in 2 M reagent-grade HNO_3 for a minimum of 24 h and rinsed

Table 1 Typical values for treated water quality parameters, pre-distribution

Parameter	System A	System B	System C[a]
Alkalinity (as $CaCO_3$)	22.5 mg L^{-1}	19.0 mg L^{-1}	13 mg L^{-1}
Free chlorine	1.2 mg L^{-1}	1.3 mg L^{-1}	<0.5 mg L^{-1}
Hardness (as $CaCO_3$)	10.1 mg L^{-1}	32.0 mg L^{-1}	5.0 mg L^{-1}
Total organic carbon	1.6 mg L^{-1}	1.8 mg L^{-1}	1.9 mg L^{-1}
pH	7.3	7.2	7.4
Chloride	8.9 mg L^{-1}	7.5 mg L^{-1}	7 mg L^{-1}
Sulfate	7.9 mg L^{-1}	25.0 mg L^{-1}	3 mg L^{-1}
Turbidity	<0.10 NTU	<0.04 NTU	0.5 NTU
Iron	<0.05 mg L^{-1}	<0.05 mg L^{-1}	<0.05 mg L^{-1}
Lead	<0.5 μg L^{-1}	<0.5 μg L^{-1}	<0.5 μg L^{-1}
Total phosphorus	—[b]	—[b]	0.34 mg L^{-1}
Orthophosphate (as P)	—[b]	—[b]	0.19 mg L^{-1}

[a] Values represent flushed samples collected at a central location within the distribution system. [b] Concentrations are discussed within the text.

thoroughly with ultrapure water prior to use. As described elsewhere,[39] system A samples for SEC analysis were collected by residents as 4 × 1 L profiles.

2.3 Size-exclusion chromatography with UV and ICP-MS detection

The size-exclusion chromatography ICP-MS (SEC-ICP-MS) and SEC-UV methods applied for the separation of field and experimental samples have been detailed in previous work.[39] All paired SEC-UV and SEC-ICP-MS separations were performed on an agarose-dextran stationary phase (Superdex 200, 10 × 300 mm, 13 μm nominal bead size, GE Healthcare) with a 50 mM Tris-HCl mobile phase (pH 7.3) at a flow rate of 0.5 mL min^{-1}. Injection volumes for SEC-UV and SEC-ICP-MS were 180 and 212 μL, respectively. Thyroglobulin (monitored as ^{127}I) and ovalbumin (^{31}P) were purchased from GE Healthcare and the humic isolate (monitored as ^{208}Pb) from Alfa Aesar. Molecular weight determination for the humic isolate is described elsewhere.[32] All samples were filtered at 0.45 μm prior to size-separation; recovery of lead by cellulose nitrate membrane filters was 78.9%.[39] SEC analysis was performed within 36 h of sample collection.

2.4 Scale analysis

Crystalline phases in lead pipe scale recovered from system A were identified using an X-ray diffractometer (Siemens D500) equipped with CuKα radiation (λ = 1.54 Å) at 35 kV and 30 mA. Scans were performed with a step size of 0.05° (2θ) and a count time of 10.0 s per step. Scale was collected as a single layer from the interior of a recovered LSL section. Samples were held in a desiccator for 24 h and then finely ground with a mortar and pestle prior to X-ray diffraction (XRD). To determine elemental composition, scale samples were digested according to EPA method 3050B,[40] with modifications to accommodate the available sample mass and equipment. Digested samples were centrifuged at 3000 rpm for 10 m prior to dilution and analysis.

2.5 Other analytical methods

Total lead, iron, copper, aluminum, and phosphorus were measured by ICP-MS (Thermofisher X Series II, Standard Methods 3125 and 3030).[41] Reporting limits were 0.4, 6.0, 0.7, 4.0, and 4.9 μg L^{-1}, respectively. Orthophosphate was measured in a subset of samples, over the first two sampling rounds only, using a colorimeter (Standard Method 4500-P E).[41] Distributed water temperature data were obtained from the utility monitoring stations nearest the study sites.

2.6 Data analysis

System A and B profiles collected before and after the increase in orthophosphate were paired by civic address. Metals concentrations in each of the seven litres were summed, and total masses over each profile were compared using two-tailed signed rank tests by follow-up round.[42] Natural log transformations were applied to the paired data to promote symmetry in the distribution of differences. Multiplicative differences in lead levels were quantified using a Hodges–Lehmann estimator, c, where c = median(A_{ij}) and $A_{ij} = (D_i + D_j)/2$ for all $i = 1, \ldots, n$ and $j \geq i$. The variable $D = \ln(x_i) - \ln(y_i)$ denotes the set of pairwise (log-transformed) differences, where x and y represent lead levels at n sites before and after the increase in orthophosphate to 1.0 mg PO_4 L^{-1}. The quantity c estimates the ratio of lead levels, where $y = \exp(c)\, x$.[43]

3 Results and discussion

3.1 Lead sequestration by polyphosphate

The apparent size distributions of lead and iron were strongly influenced by the presence or absence of polyphosphate. This is illustrated in Fig. 1, *via* size-exclusion chromatograms representing typical separations of point-of-use samples collected in two water systems (A and C). These data provide little evidence of metal complexation within system A (Fig. 1a). Lead in particular was never observed at low apparent molecular weight—indicating complexation—in anything more than trace quantities. This is probably because

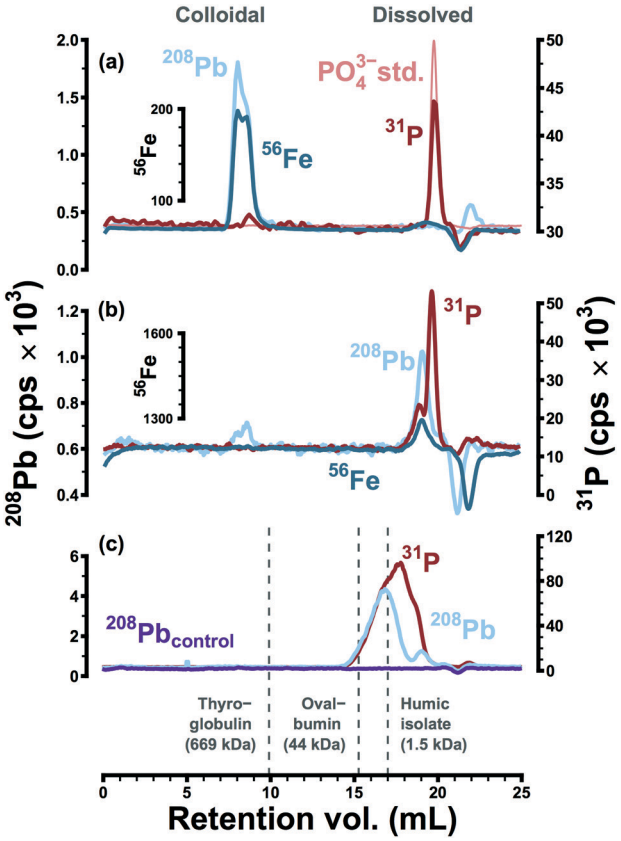

Fig. 1 (a) In system A size-separations (<0.05 mg P L^{-1} polyphosphate), ^{208}Pb eluted in a high molecular weight colloidal fraction —along with ^{56}Fe—while ^{31}P eluted in the same retention volume as the orthophosphate anion. (b) In system C size-separations (0.20 mg P L^{-1} polyphosphate), ^{208}Pb and ^{56}Fe eluted in a low molecular weight (dissolved) fraction along with ^{31}P and consistent with sequestration by polyphosphate. (c) ^{208}Pb and ^{31}P coeluted at low apparent molecular weight in deionized water with sodium hexametaphosphate, a strong complexing agent for lead. Peak retention volumes of thyroglobulin (hydrodynamic diameter: 17 nm), ovalbumin (diameter: 6 nm), and a Pb-tagged humic isolate are provided as qualitative points of reference.

polyphosphate in system A (dosed at 0.05 mg P L^{-1}) reverted to orthophosphate during distribution; phosphorus in system A samples eluted in the same retention volume as the orthophosphate anion. Data from a pilot-scale model of system A[46] were also consistent with the apparent reversion of polyphosphate in field samples: as a linear predictor, phosphorus in LSL effluent explained 99% of the variation in orthophosphate (β_1 = 2.8 ± 0.3, 95% CI). Under the assumption of complete reversion, the expected slope (β_1 = 3.1) was within the confidence bound of the linear model. Furthermore, SEC data provided assurance that polyphosphate complexation was not significant within the model system: lead eluted in an entirely separate fraction from phosphorus in typical separations.[46]

In the absence of detectable polyphosphate (system A), lead and iron consistently coeluted as colloidal particles at high apparent molecular weight (Fig. 1a). These particles may have originated from an iron-rich lead corrosion scale or they may represent adsorption of lead to suspended colloidal iron (oxyhydr)oxides.[39,44–46] Consistent with the occurrence of colloidal particles rich in these elements, filtration of system A field samples at 0.1 or 0.05 μm altered high molecular weight lead and iron peaks significantly and in near-identical fashion.[39] Furthermore, high molecular weight lead and iron eluted consistently on stationary phases with opposite surface charges, while dissolved metal standards were retained completely at environmentally relevant concentrations.[39] In previous work, lead and iron elution profiles and peak areas were highly correlated ($R_{average}^2$ = 0.96 and R^2 = 0.82, respectively).[39]

Polyphosphate was persistent within system C: at points of use, only 55% of total phosphorus was present as orthophosphate (Table 1). Under the influence of polyphosphate (dosed at 0.20 mg P L^{-1}), lead and iron were consistently observed at low molecular weight, strongly associated with the phosphorus signal (Fig. 1b). The apparent size distribution of phosphorus in system C was bimodal, and lead coeluted with the higher apparent molecular weight peak. This was interpreted as a consequence of sequestration/complexation: polyphosphates form stable coordination complexes with many metals, including lead,[27] and polyphosphates can increase lead solubility due to complexation.[16,27] Random daytime samples collected within system C had a 90th percentile total lead concentration of 33 μg L^{-1} (n = 14), and lead and iron concentrations in 0.45 μm filtrate ranged from 0.9–17.6 and >6.0 to 211.3 μg L^{-1}, respectively.

The ability of SEC to detect lead-polyphosphate complexes was confirmed by separating deionized water with sodium bicarbonate (60 mg L^{-1}), lead nitrate (65 μg Pb L^{-1}), and sodium hexametaphosphate (2 mg P L^{-1}), a strong complexing agent for lead. After 16 hours at pH 7.9, lead and phosphorus coeluted at low apparent molecular weight (Fig. 1c). Without sodium hexametaphosphate, lead was retained on the stationary phase as expected. While lead did elute in the presence of polyphosphate, lead and phosphorus peaks did not correspond entirely. This may have been due to the complex speciation of sodium hexametaphosphate.[28] That is, the ^{31}P signal may represent multiple poorly resolved peaks, only one of which was associated with ^{208}Pb. Secondary interactions (*e.g.*, charge exclusion) may also have been an important factor in observed molecular weight distributions. While high apparent molecular weight peaks representing colloidal metals were relatively consistent on stationary phases with opposite surface charges,[39] soluble species may be more susceptible to electrostatic interactions with the stationary phase, as reported elsewhere in the case of iodide,[47] vanadate ($H_2VO_4^-$),[48] and for a range of low molecular weight organic compounds.[49]

Given that increased lead solubility due to polyphosphate complexation is predicted over a wide alkalinity range,[27] our speciation approach would be expected to apply to high alkalinity distributed waters. However, field data reported here represent low alkalinity conditions exclusively and further

investigation would be required to validate the approach for high alkalinity water systems.

3.2 Complexation of lead by natural organic matter

Complexation of lead by humic or fulvic acids can also increase lead solubility by maintaining undersaturation of the solubility-controlling phase (*e.g.*, hydrocerussite or hyroxypyromorphite).[14] SEC with UV and multi-element detection has been used previously to characterize complexation of lead with NOM, and a strong correspondence between lead and UV absorption is typical in the presence of lead–NOM complexes.[32,50,51] Previous size-separation of a humic isolate that contacted metallic lead over 48 h was consistent with formation of an organic lead complex.[32] System A field data, in contrast, suggest that the strongest complexing fractions of NOM were removed during coagulation and filtration.[52] In separations of system A samples, lead never eluted in the same fraction as the principal UV_{254} signal at appreciable signal-to-noise ratios.[39] Complexation of lead by NOM within system C was considered unlikely as well: as in system A, removal of complexing NOM fractions *via* enhanced coagulation/filtration was expected. NOM may, however, have influenced lead mobility by promoting colloidal dispersion of lead-rich particles.[53] This possibility is consistent with system A size-separations: colloidal lead and NOM (as UV_{254}) consistently eluted together at high apparent molecular weight.[39]

3.3 Controlling lead solubility with orthophosphate

While polyphosphate in system C appeared to sequester/complex lead in solution, orthophosphate may have had the opposite effect in systems A and B by reducing lead solubility. Seven months after switching to an inhibitor formulation that did not include polyphosphate, the orthophosphate dose in these water systems was increased from 0.5 to 1.0 mg PO_4 L^{-1}. This change accompanied significant decreases in lead release (Fig. 2).

Available data suggest that observed lead levels were a strong linear function of temperature within system A at 0.5 mg PO_4 L^{-1} ($r_{average}$ = 0.88).[54] Group comparisons were structured to account for this source of variation: a significant reduction in lead was observed over the shortest interval for which temperature was approximately constant. December 2016 lead levels, at 1.0 mg PO_4 L^{-1}, were 62% of paired observations at 0.5 mg PO_4 L^{-1} the previous April (Table 2, 95% CI: 49–85%). Lead levels in March and April 2017 were lower than paired observations in April 2016 by similar magnitudes: 68 and 71%, respectively. Averaging by site over the last three sampling rounds, lead levels at 1.0 mg PO_4 L^{-1} were 67% of those observed at 0.5 mg L^{-1} (Fig. 2 and Table 2, final row, 95% CI: 54–82%). Despite the probable influence of seasonally varying water quality, variation in lead release over the 6 sampling rounds at 1.0 mg PO_4 L^{-1} was generally low: standard deviations by site ranged from median 0.5 (L7) to 3.3 μg L^{-1} (L3) (systems A and B).

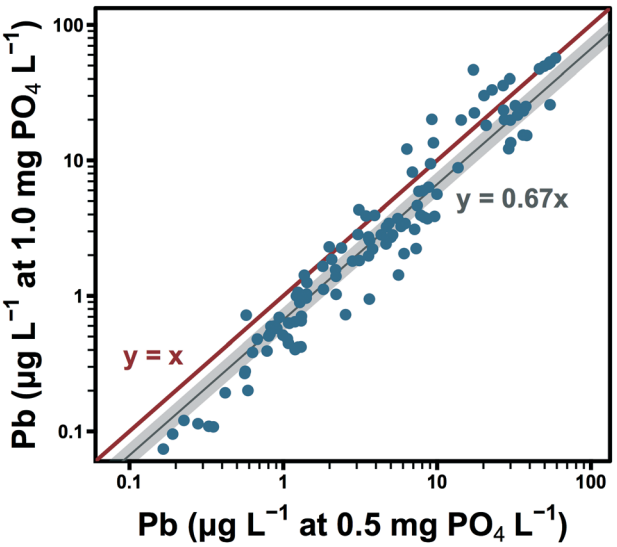

Fig. 2 System A and B lead concentrations at 1.0 mg PO_4 L^{-1} were an estimated 67% of concentrations at 0.5 mg PO_4 L^{-1} (paired measurements at 17 residences comparing Apr. 2016 with an average of Dec., Mar., and Apr. 2017). The gray shaded region represents the 95% CI around the group difference estimate of 0.67.

In agreement with the expected co-precipitation of lead and phosphate or the adsorption of phosphate to corrosion scale, phosphorus declined during stagnation. Precipitation of phosphate with copper is also possible: compared with the 0.5 mg PO_4 L^{-1} dose, lower copper levels were observed at 1.0 mg PO_4 L^{-1} (Table 2). Orthophosphate reduces copper release by promoting formation of relatively insoluble copper–phosphates, such as $Cu_3(PO_4)_2$, over the more soluble cupric hydroxide ($Cu(OH)_2$).[55–57] Iron levels did not exhibit a negative trend (α = 0.05): orthophosphate has reduced iron release from corroded iron pipes,[58,59] but in other cases it has increased or had little effect on iron levels in water.[60] Orthophosphate demand at each study site was estimated as the largest difference between phosphorus in the flushed sample (L7) and each of the standing samples (L1–L6). By this estimate, median phosphorus demand at 0.5 mg PO_4 L^{-1} was 13.3 μg L^{-1}. Increasing orthophosphate accompanied higher phosphorus demand, from 59 μg L^{-1} in June to 35 μg L^{-1} the following April.

While increasing orthophosphate to 1.0 mg PO_4 L^{-1} accompanied a decrease in lead release over the study sites as a group, peak lead levels remained high. The highest concentration at 0.5 mg PO_4 L^{-1} was 58.8 μg L^{-1} and the highest at 1.0 mg PO_4 L^{-1} was 60.3 μg L^{-1}. At comparable pH and alkalinity levels to those characterizing systems A and B, equilibrium lead solubility has been predicted at approximately 30 and 20 μg L^{-1} at 0.5 and 1.0 mg PO_4 L^{-1}, respectively.[10] Excess lead may be attributed to the presence of particles: particulate and colloidal lead in system A were predominant.[39,54] Both equilibrium solubility predictions and observed lead levels suggest that orthophosphate might offer additional benefits at doses higher than 1.0 mg PO_4 L^{-1}. Due to the positive effect of carbonate complexation on lead

Table 2 Fraction of initial (2016-04) lead and copper levels remaining after increasing orthophosphate (without polyphosphate) from 0.5 to 1.0 mg PO_4 L^{-1}

Date (*yyyy-mm*)	% of initial Pb remaining		Distributed water temp. (°C)	% of initial Cu remaining		Paired sample size
	Estimate[a]	95% CI		Estimate	95% CI	
2016-04	—	—	9.6	—	—	—
2016-06	91	67–120	15.1	79[y]	71–87	19
2016-08	89	64–130	21.8	73[z]	58–85	19
2016-10	79	43–110	16.7	73[z]	62–83	14
2016-12	62[y]	49–85	9.4	68[z]	57–80	16
2017-03	68[y]	55–87	6.4	67[y]	55–88	14
2017-04	71[y]	52–84	8.1	79[y]	65–93	15
Average[b]	67[z]	54–82	8.0	71[z]	62–84	17

[a] Statistical significance: *y*: $p < 0.01$, *z*: $p < 0.001$. [b] Average of last three sampling rounds (if a study site was only sampled once over this period, this profile replaced the average in the calculation).

solubility, systems distributing high alkalinity water are predicted to require higher orthophosphate doses than those reported here to achieve comparable effects.[10]

3.4 Identification of elements and crystalline phases in lead corrosion scale

Lead pipe corrosion scale collected from system A was characterized by a primary and a secondary crystalline phase: hydrocerussite and hydroxypyromorphite, respectively ($Pb_3(CO_3)_2(OH)_2$ and $Pb_5(PO_4)_3OH$) (Fig. 3). The former phase is thermodynamically favoured under the expected pH and alkalinity conditions and the latter is expected under orthophosphate control of lead solubility. Elemental analysis was consistent with the presence of hydroxypyromorphite as a secondary phase: phosphorus represented 2.6% of scale mass while the theoretical phosphorus content of hydroxypyromorphite is 6.9%. Despite the presence of hydroxypyromorphite in scale, other phases may have also played a role in controlling lead solubility.

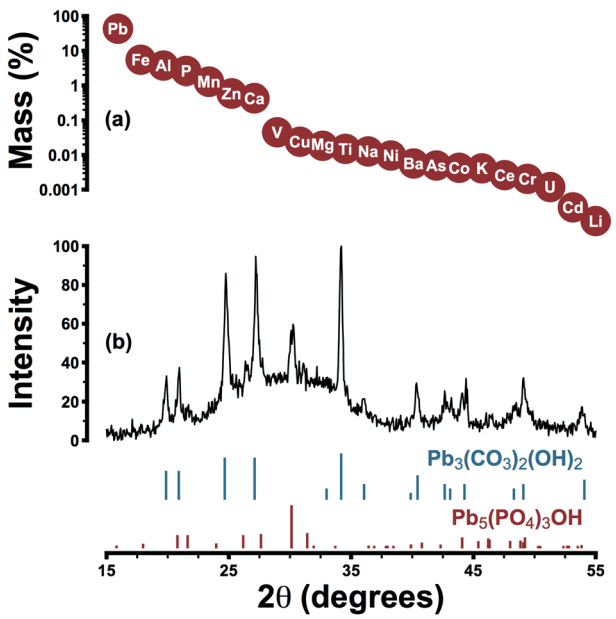

Fig. 3 (a) Median mass fraction by element for triplicate scale samples representing an LSL recovered from system A. (b) XRD analysis was consistent with the presence of hydrocerussite, $Pb_3(CO_3)_2(OH)_2$, and hydroxypyromorphite, $Pb_5(PO_4)_3OH$.

The irregular baseline of the XRD pattern may be attributed to the amorphous content of the sample: iron, aluminum, manganese, zinc, and calcium were detected in amounts ranging from 0.4–5.5% (by mass) but were not present as distinct crystalline phases. Rather, these elements—especially iron and manganese—probably occurred as poorly crystalline (oxyhydr)oxides.[61] While scale layers were aggregated for analysis, in place they were visually consistent with descriptions offered elsewhere: a layer composed predominantly of hydrocerussite beneath a surface layer of amorphous iron or manganese (oxyhydr)oxides.[61] This stratification may explain the near-universal occurrence of colloidal particles rich in lead and iron in system A samples. Traces of vanadium, copper, nickel, barium, chromium, arsenic, and cadmium in scale samples are consistent with previous reports,[61] and the zinc content (0.6%) was attributable to the phosphate formulation (zinc was present in distributed water at a median concentration of 65 μg L^{-1}).

3.5 Potential influence of aluminum on lead release

Aluminum is a potential determinant of lead levels[62,63] and may represent a source of seasonal variation. While median aluminum in system B was low and relatively constant at 8.3 μg L^{-1} with an interquartile range (IQR, lower to upper quartile) of 7.1–9.3 μg L^{-1}, aluminum in system A varied seasonally, with higher levels occurring in winter (IQR: 37.8–125.3 μg L^{-1}). At 0.5 mg PO_4 L^{-1}, median lead in system A first-draw samples was greater by 1.3 μg L^{-1} at the higher winter aluminum levels (signed rank test, paired data, n = 32 sites, 95% CI: 0.6–2.7 μg L^{-1}).[64] At these sites, first-draw sample temperatures were lower in winter by 0.7–4.3 °C (IQR).

While the effect of aluminum on lead release is not well characterized, colloidal aluminum and lead in system A field samples—as determined by SEC-ICP-MS—were often present

in a common size fraction.[39] This may be explained by adsorption of lead to suspended colloidal iron and aluminum or to simultaneous release of these metals from corrosion scale. Lead adsorption to suspended particles could promote lead release by reducing the activity of lead in solution, prolonging undersaturation of the dissolving phase. Alternatively, aluminosilicate particles at pipe surfaces may buffer against increases in pH that would otherwise reduce lead solubility.[63] In previous work,[65] manganese appeared to inhibit formation of protective lead pipe scale (PbO_2) in favour of an amorphous layer, and aluminum could also function in a similar manner. Conversely, some evidence suggests that aluminum deposits may act as a diffusion barrier to lead release.[66]

Despite the apparent effect of aluminum on lead release from premises plumbing, aluminum did not exert a primary influence on lead release over the full sample profile in system A. After controlling for changes in phosphorus, temperature, and iron *via* linear regression, aluminum was only weakly correlated with lead (r = 0.15). Nonetheless, relevant comparisons of lead release over time in system A were structured to minimize aluminum variation: the mass of aluminum over system A profiles in April 2017 (1.0 mg PO_4 L^{-1}) was 87% of the same mass measured in April 2016 (0.5 mg PO_4 L^{-1}, 95% CI: 78–96%).

4 Conclusion

This study demonstrated the use of size-exclusion chromatography with multi-element detection to better comprehend factors influencing lead mobility in drinking water systems. Orthophosphate was associated with colloidal particulate lead and iron in point-of-use samples and an overall reduction in lead release, while polyphosphate appeared to sequester lead as an aqueous complex. Previous studies have highlighted the risks of polyphosphate in systems with legacy lead plumbing, but these have largely relied on lab-scale experimental work or solubility modelling. Elemental speciation of environmental samples by SEC-UV-ICP-MS may allow for a more direct understanding of the potential for lead sequestration—by polyphosphate or NOM—in drinking water distribution systems.

Conflicts of interest

The author's have no conflicts to declare.

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