The occurrence of particulate lead in drinking water deserves increased scrutiny. This is especially true because models of human exposure to lead, sampling protocols, analytical methods, and environmental assessments are often based on the presumed dominance of soluble lead in drinking water. Recent cases of childhood lead poisoning were tied to solder particles that detached from the plumbing and contaminated the potable water supply. In cases such as these, common sample-handling procedures can "miss" particulate lead present in water samples. In some instances, the actual amount of lead present in drinking water samples may be five times higher than that obtained using approved protocols. The presence of chloride, warmer temperature, and lower pH in the human stomach may render a significant fraction of this "missed" particulate lead as bioavailable when ingested.

Lead Particles in Potable Water

BY SIMONI TRIANTAFYLLIDOU, JEFFREY PARKS, AND MARC EDWARDS

Reddish-colored particles were observed on the bottom of plastic sampling bottles even after three months' exposure to 0.15% nitric acid.

Drinking water is not currently considered a major source of lead exposure in the United States; it is believed to account for 14–20% of lead exposures nationally (USEPA, 1991, 2005). Public health authorities have largely assumed that implementation of the US Environmental Protection Agency (USEPA) Lead and Copper Rule (LCR) has eliminated lead in public drinking water as a predominant source of lead poisoning. The confidence in this assumption is illustrated by the fact that when environmental assessments of lead-poisoned children are performed, potable water sampling is recommended only if no other potential sources of lead exposure are identified in the home (Edwards, 2004; CDC, 2000).

Recent events have highlighted disturbing instances in which childhood lead poisoning was belatedly tied to lead in drinking water. Specifically, instances of blood lead poisoning in Greenville, N.C., were tied to elevated particulate lead in water after a year passed, in which no other sources of lead could be identified (Allegood, 2005; Bachelor, 2005). In several instances in Washington, D.C., in 2003, it also took nearly a year of investigations until tap water was considered a possible source for children's elevated blood lead levels (Renner, 2006; Copeland, 2004). In all of these cases, blood lead levels continued to rise while authorities focused on lead paint, dust, and other possible sources such as toys. After North Carolina passed a policy requiring sampling of the drinking water in cases of childhood lead poisoning, another case of blood lead poisoning from water was detected in Durham, N.C. (Gronberg, 2006). Durham was in compliance with the USEPA LCR.

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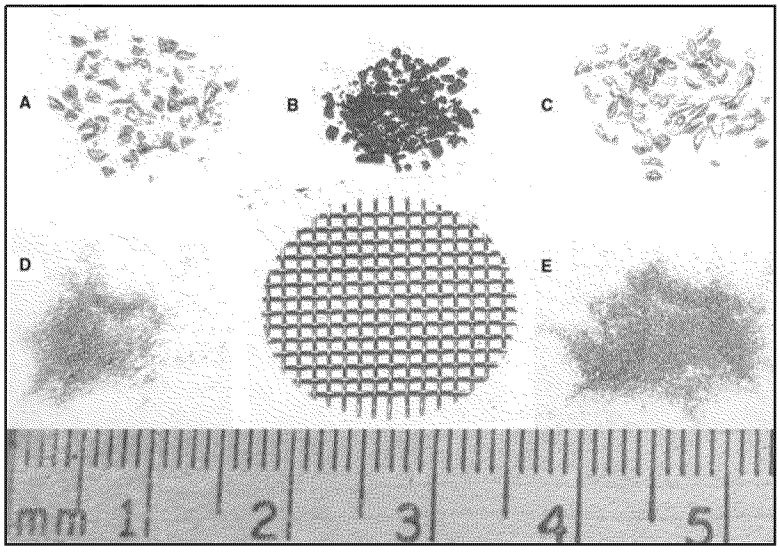


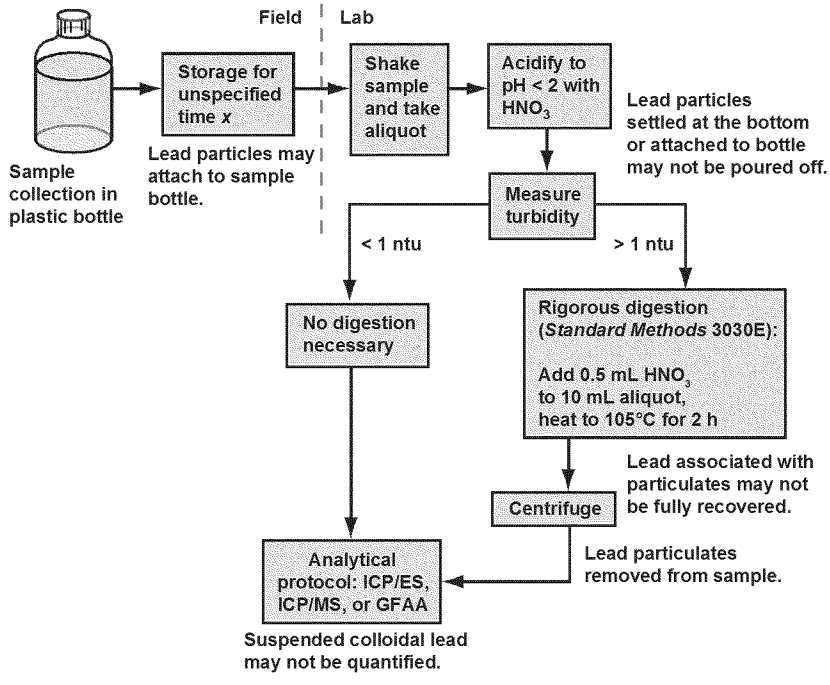
Particle types examined in the experiment include (A) pure lead, (B) lead (IV), (C) solder (50:50 lead:tin), (D) red brass, and (E) yellow brass. These particles were small enough to pass through the 1.0-mm × 1.0-mm openings of a faucet aerator screen (bottom center).

Because routine sampling under the LCR involves homeowners, samples are typically collected in plastic bottles without acidification. After sitting for an unspecified time in the bottles unacidified, samples arrive at a laboratory for analysis. In the laboratory, an aliquot is taken from each water sample. The aliquot is then reduced to pH < 2.0 by addition of 0.15% nitric acid (HNO_3, v/v) (Figure 1). A minimum holding time of 16 h is required from the time of acidification, at which point the aliquot can be analyzed for lead. Older research (Miller et al, 1985) proved that this standard acidification process is adequate in quantifying lead when lead is soluble. However, problems with lead recovery may occur if lead particulates are present. This is especially true because, according to the current preservation method (USEPA, 1994; Lytle et al, 1993), only water samples with turbidity > 1 ntu must be subjected to an additional heated-acid digestion step to ensure that particulate lead (and copper) completely dissolves (see Figure 1).

Parks et al (2004) highlighted how this standard protocol could miss up to 100% of the particulate trivalent chromium [Cr (III)] present in potable waters. Several obvious problems were caused by particulates settling in the bottle and attaching to plasticware—these attached particles do not contribute to measured turbidity. Indeed, field samples that originally contained high turbidity often measured < 1 ntu when later measured in the laboratory after storage; typically these samples would not require full digestion. Moreover, even when full digestion was performed, undissolved particles that attach to the sample bottle are not poured out into the glassware in which full heated digestion occurs. The net result is that any Cr (III) not completely dissolved in 0.15% HNO_3 could be completely "missed" by the analysis. To recover the Cr (III) present in the samples, Parks et al (2004) recommended in-the-bottle digestion to prevent particles from attaching to the container.

Similar recovery problems are expected for any lead particles present in drinking water that do not dissolve in 0.15% HNO_3 (Figure 1). Although there are no reports of serious problems in the older research, Lytle et al (1993) assessed the adequacy of the stan-

FIGURE 1 USEPA sampling protocol for total lead and associated potential problems



GFAA—graphite furnace atomic absorption, HNO_3—nitric acid, ICP/ES—inductively coupled plasma/emission spectroscopy, ICP/MS—inductively coupled plasma/mass spectrometry

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dard USEPA sampling procedure for a case in which 60:40 tin:lead solder powder was introduced to deionized water. In that study, the authors concluded that the typical HNO_3 procedure recovered 100% of the lead in the solder powder used for laboratory simulation of the problem. However, the researchers qualified this conclusion by noting that "particle size and the time of acidification relative to the time of analysis also control the degree to which lead dissolves in the preservative. Lead or solder particles assumed to be present in the USEPA field study samples before acidification were given adequate time to dissolve and were not large enough to exceed the capacity of the acid to dissolve them." Moreover, the researchers noted that for some water samples collected in the field that prompted the investigation, lead concentrations increased with longer holding times. This observation suggests that the standard protocol of 16 h holding time is sometimes inadequate.

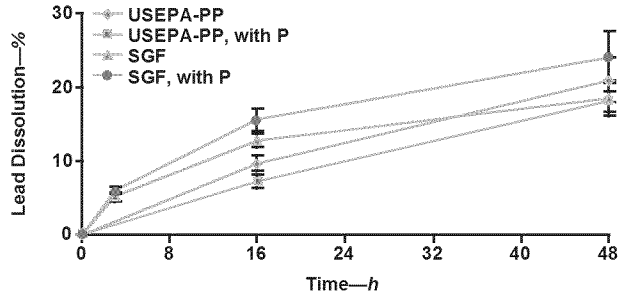
Edwards and Dudi (2004) reported on a much more disturbing problem with standard analytical procedures for drinking water samples collected in Washington, D.C. Reddish-colored particles were observed on the bottom of sampling bottles even after three months' exposure to 0.15% HNO_3 (see the photo on page 107). The red–brown particles were composed of lead oxides, and their color and recalcitrant nature were consistent with tetravalent lead [Pb (IV)] oxides found on lead pipe in Washington, D.C. (Schock et al, 2001; Renner, 2004; Lytle and Schock, 2005). Using a more aggressive procedure that included 5% HNO_3 and 100°C in-the-bottle digestion (i.e., digestion of the entire water sample inside the sampling bottle, not just an aliquot), the red–brown particles did dissolve after 24 h. After this more aggressive, in-the-bottle digestion, lead levels were 500% higher than those measured using standard USEPA protocol. The implication is that acid-resistant reddish-colored Pb (IV) oxides were detaching from the pipe and adhering to the sampling bottles. These Pb (IV) particles, which could have been consumed in the drinking water, would have been missed during routine sample collection, resulting in greater potential consumer exposure to lead and misclassification of some waters as "safe" when they were not. Similarly, a later study identified lead-solder particulates on aerator screens in Washington, D.C. (Edwards, 2004).

A number of researchers have noted the importance and even predominance of lead particles versus soluble lead. "Flaking lead" particles larger than 12 µm associated with scale detaching from a pipe were observed, along with colloidal lead fractions associated with iron oxides and humic acids (De Mora et al, 1987; Hulsmann, 1990). Particulate lead was clearly demonstrated to come from solder lead–tin joints in pipe rigs (Bisogni et al, 2000), and a small survey of lead in potable water from around the United States revealed numerous instances in which most of the lead was present as particulates (sometimes > 1,000 µg/L Pb) in first-draw tap samples (McNeill and Edwards, 2004).

The potential bioavailability of lead particles is another important consideration. If existing analytical procedures "miss" particulate lead in drinking water and these lead particles do not dissolve significantly in the stomach or elsewhere in the human body, the particles are likely to pose little or no danger to human health. In these instances, identified deficiencies in drinking water sampling might not be important or could even be deemed useful, because the samples are missing a fraction of the lead that does not endanger public health. However, elevated lead levels in blood have been reported to occur due to consumption of lead paint chips (Su et al, 2002; McElvaine et al, 1992), birds containing lead shot (Johansen et al, 2006; Dewailly et al, 2000), or lead fishing sinkers (Mowad et al, 1998), among other particles. These cases prove that some forms of particulate lead are bioavailable after they are consumed.

The Greenville, N.C., incident, along with previous observations of particulate lead not being detected by

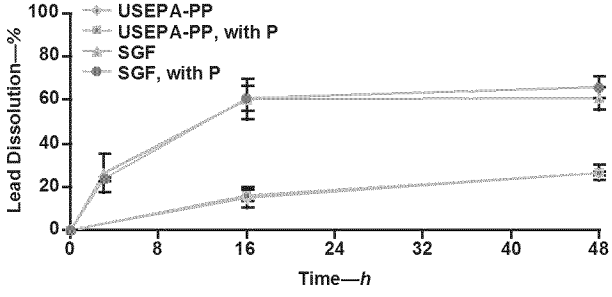
FIGURE 2 Lead dissolution versus digestion time of pure lead particles



P—phosphorus, SGF—simulated gastric fluid, USEPA-PP—US Environmental Protection Agency preservation protocol

The error bars denote 95% confidence intervals.

FIGURE 3 Lead dissolution versus digestion time of lead (IV) particles



P—phosphorus, SGF—simulated gastric fluid, USEPA-PP—US Environmental Protection Agency preservation protocol

The error bars denote 95% confidence intervals.

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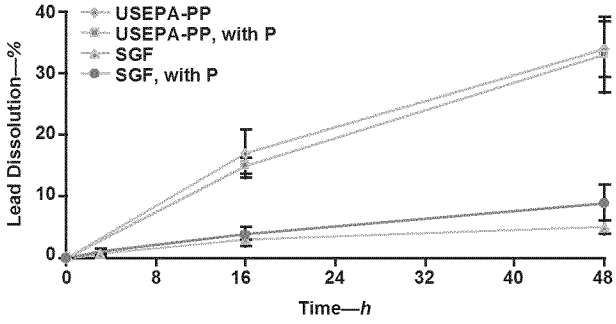
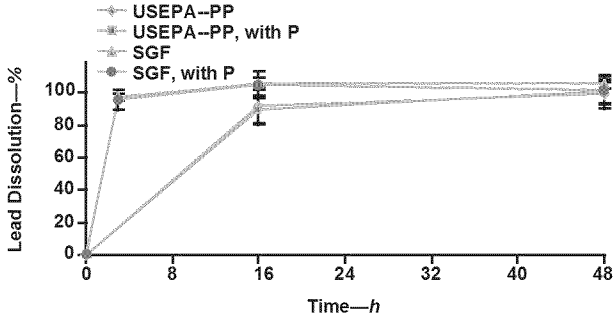
FIGURE 4 Lead dissolution versus digestion time of solder particles



P—phosphorus, SGF—simulated gastric fluid, USEPA-PP—US Environmental Protection Agency preservation protocol

The error bars denote 95% confidence intervals.

FIGURE 5 Lead dissolution versus digestion time of red brass filings



P—phosphorus, SGF—simulated gastric fluid, USEPA-PP—US Environmental Protection Agency preservation protocol

The error bars denote 95% confidence intervals.

routine analytical procedures in Washington, D.C., prompted careful reconsideration of all aspects of lead in drinking water as it relates to public health. This study emphasizes the extent to which the standard USEPA sample-handling protocol could miss human exposure to particulate lead and assesses potential bioavailability of various types of particulate lead.

MATERIALS AND METHODS

A well-defined laboratory study of particulate lead occurrence was undertaken, followed by analysis of various real-world water samples.

Laboratory simulation of particulate lead occurrence in drinking water. The authors' first objective was to simulate conditions known to occur in Greenville, N.C., and Washington, D.C., drinking water. That is, situations in which lead particles small enough to pass through a medium-sized faucet aerator screen are present in drinking water samples. The goal was to evaluate the effectiveness of USEPA method 200.8 (USEPA, 1994) in recovering lead from representative particles that might be present in drinking water. As part of that evaluation, the authors examined solubility of leaded particles in simulated gastric fluid (SGF). Assuming that lead solubility and lead bioavailability are directly related, the intent of the SGF tests was to assess potential bioavailability of those particles once they are ingested.

Representative leaded particles were added to water samples, and lead dissolution was investigated. The particles to which the water was exposed and the methods of preparing them were as follows (letters identifying these sections are keyed to the photo on page 108):

A—Pure lead. The practice of using pure lead pipe in home plumbing systems was eliminated in 1986 (Lytle and Schock, 1996). However, pure lead may still be present in older residences and in the publicly owned distribution system. Pure lead particles can also contaminate water systems when lead pipe is cut during partial service line replacements. Simulated pure lead particles used in this experiment were shaved off the external surface of pure lead pipe.

B—Lead in the (IV) oxidation state (tetravalent lead). Lead from plumbing can be oxidized from the (II) to the (IV) oxidation state in the presence of strong oxidants such as chlorine. Transition to the (IV) oxidation state has been shown to reduce lead solubility (Edwards and Dudi, 2004; Schock et al, 2001). Lead (IV) particles were obtained by completely oxidizing lead (II) in a lead chloride solution (1,000 mg/L as Pb) to lead (IV) solids. This was accomplished with the addition of hypochlorous acid (HOCl) in excess (i.e., more than the calculated stoichiometric amount), so as to oxidize all the lead. After stirring for 30 min, the red–brown solids that formed were collected on a 0.45-µm-pore-size filter.

C—Leaded solder (50:50 lead:tin). Lead-containing solder was used in the past to seal joints in copper pipes. Although leaded solder in water plumbing has been banned since 1986 along with lead pipe (Lytle and Schock, 1996), older households and distribution systems still have leaded solder present. Solder particles were obtained by shaving off 50:50 lead:tin solder wire.

D and E—Red brass and yellow brass. Leaded brass is a major source of lead leaching from newer faucets and fixtures (Lytle and Schock, 1996). In some cases of corrosion, small grains of brass with lead have been seen to detach into water (Sundberg et al, 2003). For this experiment, leaded brass particles were filed off the external surface of red and yellow brass faucets.

The particles created, as described earlier, were sieved through a medium-sized faucet aerator screen with mesh openings of 1.0 mm × 1.0 mm (see the photo on page 113). Then, 15 ± 0.5 mg of each particle type were added to 250-mL water samples using plastic bottles. This is a sig-

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nificant amount, but in Washington, D.C., water samples contained as much as 48 mg of pure lead per litre of water (Edwards and Dudi, 2004). The brass particles (both red and yellow) differed from the rest of the particles examined in that they were in the form of filings and of smaller size (see the photo on page 113). Four experimental conditions were examined for each particle type (Table 1). Samples were prepared in triplicate bottles, including blanks (water without the leaded particles), for quality assurance/quality control (QA/QC) reasons. The known concentration of lead (average concentration ± standard deviation) in each triplicate bottle set was (a) 61,770 ± 296 µg/L for pure lead, (b) 61,170 ± 320 µg/L for lead (IV), (c) 30,780 ± 345 µg/L for lead solder, (d) 1,233 ± 5 µg/L for red brass, and (e) 1,237 ± 12 µg/L for yellow brass.

Synthesized Potomac River water, with a pH of 7.6, was used to simulate Washington, D.C., water (Rushing and Edwards, 2004). Synthesized Potomac water without (case I) and with (case II) phosphorus was tested following standard USEPA LCR sample-handling procedures, with the exception that acidification of each sample was performed inside the original 250-mL bottle, not in just an aliquot. Therefore, the water samples were acidified with 0.15% HNO_3 (to pH < 2.0) at room temperature, in the bottle. After a minimum holding time of 16 h, the unfiltered samples were analyzed for total lead using inductively coupled plasma/mass spectrometry (ICP/MS), a method with a very low lead detection limit (0.4 µg/L).

SGF without (case III) and with (case IV) phosphorus was tested. The SGF (Table 1) consisted of sodium chloride, pepsin, and HCl (HCl; US Pharmacopoeial Convention, 2005; Yu et al, 2006).

The SGF samples were adjusted to a pH of about 1.2 via addition of HCl and then heated at 37°C (body temperature) with gentle mixing. This is in contrast to the USEPA method, which uses mild HNO_3 at room temperature without mixing (Table 2). Test results simulate dissolution of lead from particles in the stomach if they are ingested. To compare SGF results with those at the minimum USEPA holding time of 16 h, a typical stomach retention time of 3 h was used (Table 2). This holding time inside the stomach is within the typical range of a few hours determined for solid meals (Hellmig et al, 2006; Singh et al, 2006). Lead recovery in the SGF samples was also quantified using ICP/MS analysis.

Real-world water analysis. Recovery of lead using the USEPA preservation protocol of 0.15% HNO_3 was compared with a stronger 2% HNO_3 in-the-bottle digestion in two water systems. The dissolution behavior of lead particles in two cases of lead poisoning was also carefully examined using USEPA preservation with 0.15% HNO_3 and SGF.

RESULTS

After establishing the dissolution behavior of particulate lead in well-controlled experiments, a range of practical real-world experiences are described.

Behavior of simulated particles in USEPA sampling protocol and simulated gastric fluid. For all particle types, lead dissolution (%) was calculated at specified time intervals, using the following formula:

$$\% \text{ Lead dissolution} = \frac{\text{Measured lead concentration in water sample}}{\text{Known lead concentration in water sample}} \times 100 \quad (1)$$

The measured lead in the water sample refers to that quantified using ICP/MS. The known lead concentration in the water sample refers to that which would occur based on the measured mass and percentage of lead in each metal. This was reported earlier for each particle type. For purposes of this article, we did not distinguish between soluble and colloidal matter. Therefore, dissolution is defined as the

TABLE 1 Experimental conditions examined for each particle type

	Case I Water in USEPA Digestion	Case II Water With Phosphorus in USEPA Digestion	Case III SGF	Case IV SGF With Phosphorus
Simulated Potomac water constituents	82 mg/L $CaCl_2 \cdot 2H_2O$	82 mg/L $CaCl_2 \cdot 2H_2O$	82 mg/L $CaCl_2 \cdot 2H_2O$	82 mg/L $CaCl_2.2H_2O$
	89.6 mg/L $CaSO_4 \cdot 2H_2O$	89.6 mg/L $CaSO_4 \cdot 2H_2O$	89.6 mg/L $CaSO_4 \cdot 2H_2O$	89.6 mg/L $CaSO_4 \cdot 2H_2O$
	84.1 mg/L $NaHCO_3 \cdot 3H_2O$	84.1 mg/L $NaHCO_3 \cdot 3H_2O$	84.1 mg/L $NaHCO_3 \cdot 3H_2O$	84.1 mg/L $NaHCO_3 \cdot 3H_2O$
Simulated gastric fluid constituents	N/A	N/A	0.2% NaCl	0.2% NaCl
			0.32% Pepsin	0.32% Pepsin
			0.7% HCl	0.7% HCl
NOM (Lake Pleasant fulvic acid)	0.3 mg/L as C	0.3 mg/L as C	0.3 mg/L as C	0.3 mg/L as C
Na_2HPO_4	N/A	1.0 mg/L as P	N/A	1.0 mg/L as P

C—carbon, $CaCl_2$—calcium chloride, $CaSO_4$—calcium sulfate, HCl—hydrochloric acid, N/A—not applicable, NaCl—sodium chloride, $NaHCO_3$—sodium bicarbonate, Na_2HPO_4—sodium phosphate, NOM—natural organic matter, P—phosphorus, SGF—simulated gastric fluid

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TABLE 2 Standard USEPA preservation protocol versus simulated gastric fluid

Characteristic	USEPA Preservation	Simulated Gastric Fluid
Constituents	HNO_3 at 0.15% (v/v)	HCl at 0.7% (v/v) NaCl Pepsin
Typical pH	1.9	1.2
Temperature—°C	20–22 (room temperature)	37 (body temperature)
Mixing pattern	Stagnant	Gentle motion
Holding time	16 h (minimum)	3 h (per typical stomach holding times for solid food)

HCl—hydrochloric acid, HNO_3—nitric acid, NaCl—sodium chloride, USEPA—US Environmental Protection Agency

fraction of lead recovered from the particles and suspended in the water, which could be soluble or colloidal.

Less than 20% of the pure lead particles dissolved after a 16-h holding time, and slightly more than 20% dissolved after 48 h for all four conditions examined (Figure 2). In other words, if samples containing these lead particles had been collected at the tap, the measured lead concentration would have been about 20% of the actual. This is because the particulate lead would typically not be poured into a sample tube for quantification; even if it were poured into the sample, it is likely that it would not reach the instrument (for example, the ICP/MS) and/or be accurately quantified. The measured turbidity of the water in this sample was also much less than 1 ntu, because the heavy particles quickly settled to the bottom of the turbidity meter or container. After 3 h in SGF, 6% of the lead was dissolved. When compared at a common time of 16 h, the SGF dissolved 5% more of the lead than the USEPA preservation. The SGF dissolved 4% less of the total lead after 3 h versus 16 h in the USEPA preservation solution, even though this difference was not significant at a 95% confidence level (Figure 2).

Only about 20% of Pb (IV) dissolved in the samples that were preserved with 0.15% HNO_3 (standard USEPA preservation) after 16 h. Three times more Pb (IV) dissolved in the simulated gastric acid after 16 h (Figure 3). Even after just 3 h in SGF, 10% more lead dissolved than in the 0.15% HNO_3 after 16 h. This suggests that standard USEPA methods would miss most of the lead present in water with these particulates, but much of the Pb (IV) would likely be bioavailable after just a few hours in the stomach. The 20% recovery of Pb (IV) particulates in these samples is consistent with earlier reports by Edwards and Dudi (2004) for the reddish lead discovered in samples of Washington, D.C., drinking water.

The solder particles dissolved more readily in the 0.15% HNO_3 than in the SGF. Even so, after 16 h of sample holding time, less than 20% of the lead was recovered using the USEPA method (Figure 4).

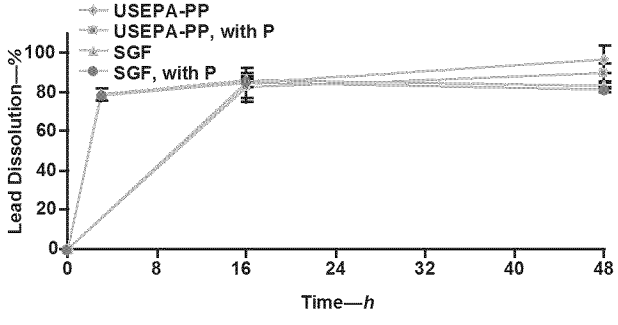
The lead in red brass filings dissolved slightly more readily in the SGF than in USEPA preservation after 16 h; this difference was not statistically significant. Virtually all of the lead dissolved after 3 h in SGF versus 90% after 16 h in the 0.15% HNO_3 (Figure 5). The much smaller size of brass particles relative to pure lead is also a factor to consider when comparing the results in Figure 5 to those in Figure 2. It is possible that use of larger leaded brass particles would have given much lower recoveries. However, the relative aggressiveness of the 0.15% HNO_3 versus SGF is compared using the same size of particles in each case.

After considering that no sample was collected after 3-h exposure to the solution with 0.15% HNO_3, there was no significant difference between dissolution of lead from yellow brass in the two solutions. After 16 h, about 80% of the lead was recovered in all cases using the small yellow brass filings (Figure 6).

The presence of phosphorus in the water did not affect lead dissolution in any of the cases (Figures 2–6). Phosphorus was included in the current study because many US utilities use phosphorus-based corrosion inhibitors, and previous research had suggested that phosphate in soils could make lead less bioavailable (Hettiarachchi et al, 2001; Lambert et al, 1997). However, under the authors' test the conditions, phosphate had no effect at a level of 1.0 mg/L as P.

Real-world sampling results. ***Montgomery County, Va.*** Sampling results from 10 representative schools in Montgomery County did not suggest any problem with stan-

FIGURE 6 Lead dissolution versus digestion time of yellow brass filings



P—phosphorus, SGF—simulated gastric fluid, USEPA-PP—US Environmental Protection Agency preservation protocol

The error bars denote 95% confidence intervals.

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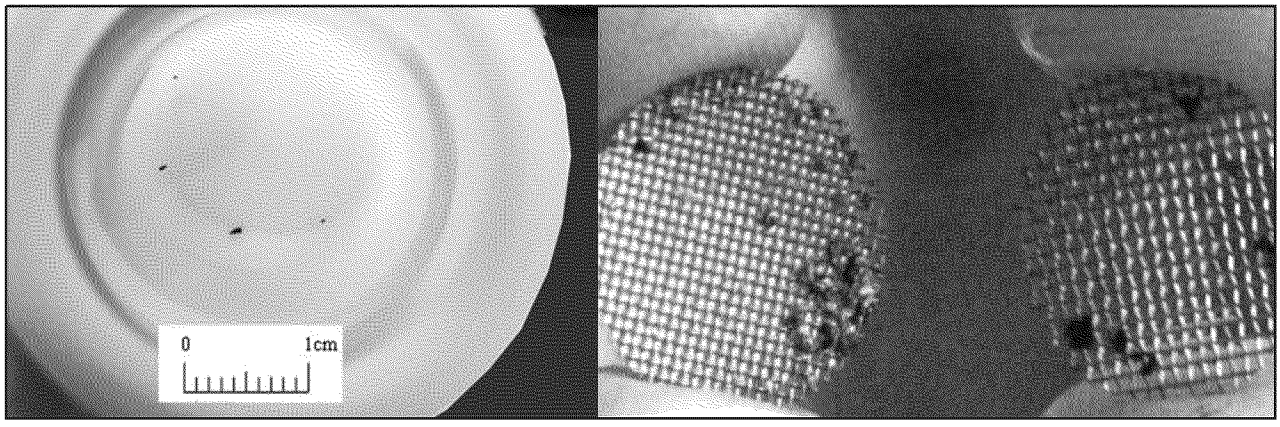


Undissolved lead-containing particles can be seen at the bottom of a plastic sampling container (left) after preservation of the water sample with 0.15% nitric acid, in accordance with the standard US Environmental Protection Agency protocol. These solder particles trapped on faucet aerator screens (right) were found in the apartment building of a lead-poisoned child.

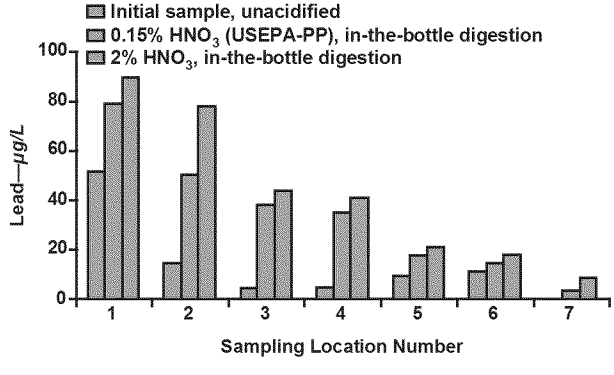
dard USEPA sampling procedures. That is, the USEPA preservation of 0.15% HNO_3 recovered the same amount of lead as did a more aggressive digestion of 2% HNO_3 in 10 out of 10 water samples (Nicholson and Edwards, 2005). In all samples, lead levels were below the 15-µg/L action level. The Montgomery County water supply is extremely noncorrosive, and the utility, which successfully implements zinc orthophosphate corrosion control, has historically met the LCR action level for lead with ease. This likely reflects the fact that in most instances where particulate lead occurrence in drinking water is not an issue, typical procedures are adequate.

Tellico Village, Tenn. The USEPA preservation method was only partly effective in other systems where lead is more prevalent in drinking water. Sampling at homes in Tellico Village showed a systematic inability of the USEPA method to recover all lead present in multiple drinking water samples. Specifically, lead release was higher when more aggressive digestion was implemented (2% HNO_3, in the bottle), typically by 20–50% but up to 250% in one case, compared with the USEPA preservation method (Figure 7). In some cases, visual observations verified that particles were still present (had not fully dissolved in the bottom of sampling bottles) after USEPA preservation (see the photo at left above). Along with higher lead recoveries, the more aggressive digestion allowed for much higher recoveries of other elements, including copper, zinc, and tin. This is expected based on prior work by Parks et al (2004) and the earlier data with synthetic particles presented here.

Behavior of lead particles in Greenville, N.C., and Durham, N.C. Extensive sampling in Greenville, N.C., demonstrated that particulate lead in drinking water can directly cause lead poisoning. Lead particles were found trapped in the aerator screen of the affected child's kitchen faucet and elsewhere in the apartment building (see the photo at right above). Six similar particles weighing 5.0 ± 0.3 mg were collected from the screen and used in experiments. Each particle was exposed to 1 L of simulated Potomac water without phosphorus in plastic containers. Three of the particles were exposed to standard USEPA protocol; the remaining three were exposed to SGF (Table 1). Percent lead dissolution was enumerated at specific time intervals using Eq 1, and total lead was determined after a full heated digestion at 85–90°C at the end of the experiment. Full digestion showed that total lead (denominator of Eq 1) in each triplicate sample set (USEPA versus SGF) was 1,777 ± 363 µg/L.

After the minimum USEPA holding time of 16 h, the particles exposed to simulated gastric fluid dissolved at a level of 47% versus 27% in the USEPA preservation solution for the Greenville samples. The difference was significant at a confidence level > 90% (error bars on triplicate experiments plotted; Figure 8). Lead release in SGF after 3 h was slightly lower than release in the

FIGURE 7 Lead release in water samples collected at homes of Tellico Village, Tenn., following different preservation protocols



HNO_3—nitric acid, USEPA-PP—US Environmental Protection Agency preservation protocol

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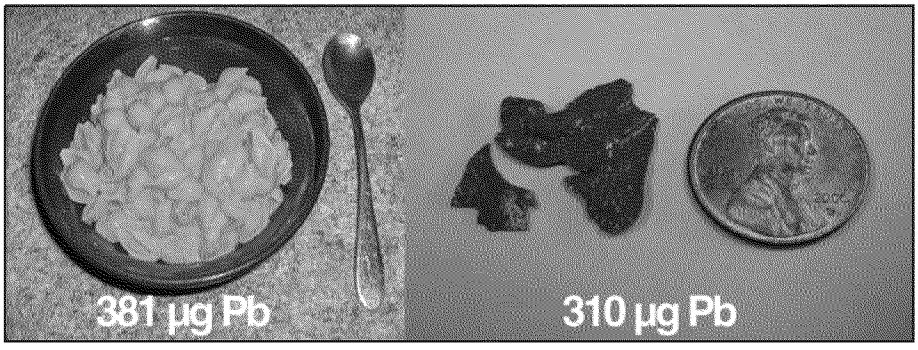

Food cooked with tap water containing lead particles collected from the home of a lead-poisoned child contained more lead than a lead paint chip approximately the size of a penny.

USEPA solution after 16 h (21% versus 27%). After 48 h, the lead dissolution was 66% in SGF solutions and 40% in USEPA solutions (Figure 8). The results clearly demonstrate the likely bioavailability of lead particles present in the faucet aerator and the lack of complete dissolution in the USEPA protocol.

In addition to lead, the dissolving particles released significant amounts of tin but did not release copper or zinc, suggesting that they originated from lead–tin solder. It is noted that these lead–tin solder particles from the aerator behaved differently than those from new simulated lead:tin solder. Even though they exhibited similar behavior in the USEPA preservation, the real particles captured on the aerator dissolved much more readily in the SGF (Figure 8 and Figure 4).

A similar experiment was conducted with actual particles collected from water in the Durham apartment complex where a child was poisoned by lead. Six leaded particles, weighing 5.0 ± 0.5 mg, were exposed to USEPA and SGF, as in the case for Greenville. After the minimum USEPA holding time of 16 h, particles in SGF released about the same amount of lead as did particles in the USEPA preservation solution. After 48 h, lead dissolution was 24% in SGF and 21% in USEPA preservative (Figure 8), but the difference was not significant at > 90% confidence. As with the particles collected in Greenville, a final full-heated digestion verified that the Durham solids originated from leaded solder based on the presence of tin and lead. This is consistent with identification of lead solder joints in plumbing during the site investigation and with use of scanning electron microscopy (SEM) analysis. The full digestion showed that total lead (denominator of Eq 1) in each triplicate sample set (USEPA versus SGF) was 2,132 ± 353 µg/L.

The Durham particles did not dissolve at a level higher than 24% after 48 h (Figure 8). Dissolution had reached almost 70% in SGF after 48 h in the case of Greenville real particles (Figure 8). Even though the lead solder particles collected from these two systems did not behave similarly, a substantial fraction of the particulate lead was likely to be bioavailable in both cases.

DISCUSSION

It is worthwhile to discuss potential implications of these research data in relation to public health. Many faucets do not have aerators; as a result, it is quite possible that particles larger than those studied are occasionally present in water collected from taps. The authors collected lead-containing particles as large as 4 mm in diameter from faucets without aerators during sampling of schools. In such cases, the potential limitations of the 0.15% HNO_3 in recovering lead had been noted to be even greater.

In this study, particles were not allowed to sit before acidification. If they had been allowed to sit and if they had adhered to the surface of the sample bottle, they might be more resistant to dissolution in the USEPA method, because a smaller surface area would be exposed to the water.

All metallic particles tested in the laboratory investigation of simulated particles were new. It is possible that actual particles derived from distribution systems are somewhat less readily dissolved in the USEPA preservative, because they may have "aged" and developed a passivating layer as a result of exposure to drinking water. It is uncertain how this factor would alter the experimental results from the first part of the authors' research for each type of representative lead-bearing metal. However, the experiments with real solder particles from Greenville and Durham proved this factor could be important. That is, when new solder particles were used in laboratory simulation, lead release in SGF was lower than it was in the USEPA preservative. This finding indicates less of a public health concern because the recovery of lead using the USEPA method was still higher than potentially bioavailable lead. However, when the actual solder particles were used, lead release in SGF was either the same (Durham solids) or higher (Greenville solids) compared with lead release using the USEPA method, indicating that lead "missed" using the USEPA method would probably be largely bioavailable. The authors speculate that the relative difference between new and actual solder particles could arise from factors that include (1) greater surface area of the real particles, as was obvious based on SEM analysis; (2) enrichment of tin in a surface layer on the real particles; (3) oxide surface coatings on the old particles; and/or (4) more rapid dissolution of tin in the HCl of SGF than in the HNO_3 of the USEPA protocol. Future research should examine these factors in greater detail.

In relation to human exposure, it is quite possible that the results reported here for 3-h exposure to SGF may

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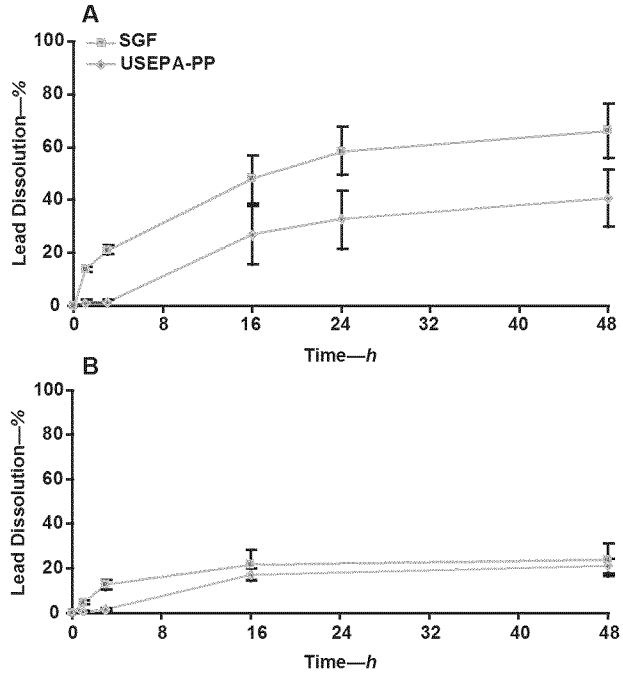
underestimate reality. Specifically, lead particles can be retained within the human digestive system, as in the case of consuming duck meat containing small lead shot, in which the lead was believed to lodge in the folds of the intestine (Dewailly et al, 2000). In such cases, the shot could serve as a source of lead for much longer than 3 h. Nonetheless, potential bioavailability of the metallic lead particles tested in this study was already quite high in simulated gastric acid. Overall, the evidence in this work indicates that a large fraction of the particulate lead in drinking water could be bioavailable.

For all particles examined in this study, lead was finally recovered at a level of 90–100%, using a 2% HNO_3 (v/v) in-the-bottle digestion at 85–90°C after about one week. This method, in contrast to the much less aggressive 0.15% standard method, is easy to use and is therefore recommended for water utilities that want to accurately quantify particulate lead in their drinking water. On the other hand, in no instance did real or simulated samples with high particulate lead measure < 15 µg/L after use of the standard USEPA method. The 15-µg/L USEPA action level still has use when indicating potentially hazardous conditions at a given faucet, although circumstances may exist in which it might not always detect a hazard when it is present.

Because interviews suggested that some affected children had not directly consumed water, the authors determined how the lead poisonings from tap water could have occurred. A similar paradoxical case of lead poisoning from water that was not consumed was reported in Washington, D.C., where it was suggested that the exposure occurred by eating pasta, rice, and potatoes boiled in tap water (Copeland, 2004). Early research suggested that lead exposure via leaching of soluble lead during cooking could be significant in some instances (Little et al, 1981). In that study, adsorption of lead from water onto the surface of vegetables during cooking reached 80% in some cases. A more recent study asserted that lead accumulation in boiled potatoes occurred when tap water containing lead was used for cooking (Baxter et al, 1992).

The authors tested the food route of exposure of the lead-poisoned child in Greenville, where lead in the water was mostly particulate. Tap water was collected at a high flow rate from a faucet in the child's apartment. The high flow rate, typical of that used when preparing food (but atypical for sampling under the LCR), tended to abrade more particles on the aerator screen and introduced high concentrations of lead into the water supply. In this instance, the 1.5 L of water collected contained 535 µg/L lead. Although these particles were not easily visible, on close examination, some could be observed sinking to the bottom of the pot. The lead remained insoluble during cooking, because < 5% of particulate lead was poured off after cooking. In addition, 95% of the lead from the water remained in the pasta, because testing indicated it did not adhere to the pan.

FIGURE 8 Lead dissolution versus digestion time of real leaded particles collected from home faucets in (A) Greenville, N.C., and (B) Durham, N.C.



SGF—simulated gastric fluid, USEPA-PP—US Environmental Protection Agency preservation protocol

The error bars denote 90% confidence intervals.

The net result is that pasta prepared using this water had more lead per serving of pasta (eating half of the cooked amount) than would be consumed by eating a dime-sized paint chip (see the photo on page 114). This simple test demonstrates the very real public health threat that can arise from lead particles in drinking water and the underappreciated hazard of lead contamination from specific taps.

It is also noteworthy that the 381 µg Pb ingested per serving of pasta far exceeds the threshold of 175 µg Pb identified as a threshold for acute lead exposure health concerns by the Consumer Product Safety Commission (CPSC, 2007). If children's jewelry were to leach more than 175 µg Pb to an acid solution, the CPSC would conduct a further evaluation to determine whether a product recall or other corrective action is warranted. Even in cities meeting the USEPA action limit, it is not difficult to find situations where more than 175 µg Pb is found in at least some taps.

As a final point, utilities that meet the 90th percentile lead action level of 15 µg/L cannot guarantee that lead levels are safe at all taps. The Centers for Disease Control and Prevention and those assessing lead-poisoned children should always consider the potential for lead exposure from drinking water, which would require changing existing published guidance (Edwards, 2004). Based on the experiences reported here, North Carolina has a new pol-

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icy requiring that drinking water be tested in cases of elevated blood lead levels. The authors recommend similar rules be implemented elsewhere. Relative to paint, exposure to lead from water in a home can be inexpensively and effectively mitigated using filters certified by NSF International for lead removal.

CONCLUSIONS

Based on well-controlled laboratory experiments, as well as real-world sampling results, the following conclusions can be drawn:

In cases where new particles of pure lead or Pb (IV) pass through an aerator screen, standard USEPA methods can dramatically underestimate the actual amount of lead present in water samples. This is because water acidified with 0.15% HNO_3 for 16 h does not completely dissolve the lead.

In the case of Pb (IV), lead particles dissolve more readily in simulated gastric fluid than in the USEPA preservative, which means this lead is quite likely to be bioavailable. This is problematic in terms of protecting public health. Because of the likelihood that lead particles might be retained in the digestive tract for a long period of time, the potential seriousness of this deficiency in sample handling should not be underestimated.

In the case of new solder particles, the USEPA method did not completely dissolve the lead nor did the simulated gastric fluid. To the extent that small particles of lead may lodge in the intestine, the particles could serve as a long-term source of lead.

For new brass particulates, standard USEPA procedures adequately dissolved the lead. However, the brass particulates differed from all other lead particles tested in that they were filings (i.e., smaller in size).

In most water systems, routine USEPA sampling procedures will dissolve the lead present in water samples.

In unusual cases in which particulate lead is present in samples, such as those described here that were associated with childhood lead poisoning from solder particles, the USEPA sampling method can miss a fraction of the lead present.

Despite the noted limitations of the USEPA sampling method, no potable water samples tested using this protocol and which were later proven to have very high par-

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ticulate lead have tested below the 15-µg/L USEPA action limit. The action limit therefore has usefulness in identifying taps where high levels of lead may be found, but it cannot be construed to quantify the extent of the hazard.

Waterborne particulate lead in food can pose a human health hazard that is underappreciated. Lead poisoning can occur even when the contaminated water is not directly consumed but rather is used to prepare food.

In exceptional cases, such as those encountered in Greenville, N.C., Durham, N.C., and Washington, D.C., waterborne lead can be a key source of elevated lead in children's blood. These cases are extremely difficult to monitor, because the occurrence of particulate lead in drinking water is variable and sporadic. For these exceptional cases, it is important to sample in a way that truly captures the "worst case" in terms of human exposure.

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