disinfection

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A switch from free chlorine to chloramine disinfectant triggered problems with excessive lead in Washington, D.C., drinking water. High levels of lead originated in the service lines, but excessive lead was also derived from solder or brass plumbing materials. In many cases, the highest lead concentrations emerged from the tap after about one minute of flushing— a troublesome outcome, given that routine public notification recommended that consumers flush for about a minute to minimize lead exposure. Bench-scale testing found that chlorine reacts with soluble Pb^{+2} to rapidly precipitate a red–brown-colored lead solid that was insoluble even at pH 1.9 for 12 weeks; this solid did not form in the presence of chloramine. Further experiments indicated that chloramines sometimes dramatically worsened lead leaching from brass relative to free chlorine, whereas new lead pipe was not strongly affected.

role of
chlorine and chloramine
in corrosion
of lead-bearing plumbing materials

The leaching of lead into potable water from corrosion of lead-bearing plumbing materials has been managed nationwide by the US Environmental Protection Agency (USEPA) Lead and Copper Rule (LCR) (USEPA, 1991). Although recent studies have heightened concerns regarding low lead exposure on the cognitive development of children (Fewtrell et al, 2004; Troesken, 2003; Weizsaecker, 2003; Garavan et al, 2000; Bellinger et al, 1991), actual levels of lead in children's blood have dropped nearly 80% in the last quarter-century because of improved control of lead paint and dust, a national ban on leaded gas, and the success of the LCR (CDC, 2000). The average national contribution of drinking water to blood lead is currently believed to be on the order of 7–20% (Guidotti, 2004; Shannon & Graef, 1988). In light of these trends, serious problems with lead contamination of potable water were largely considered historical. Given that new plumbing materials are expected to have a much lower propensity to leach lead, further reductions in drinking water lead concentrations were anticipated based on momentum of past efforts.

SEVERAL FACTORS PREVENTED PROMPT RECOGNITION OF THE PROBLEM

The water for Washington, D.C., is produced by the Washington Aqueduct and transmitted to consumers by the DC Water and Sewer Authority (WASA). Washington is an example of a city that once had a lead problem in drinking water but later successfully met the lead action limit. LCR sampling through 1999 continually confirmed that there were no problems with 90th-percentile lead (Figure 1). How-
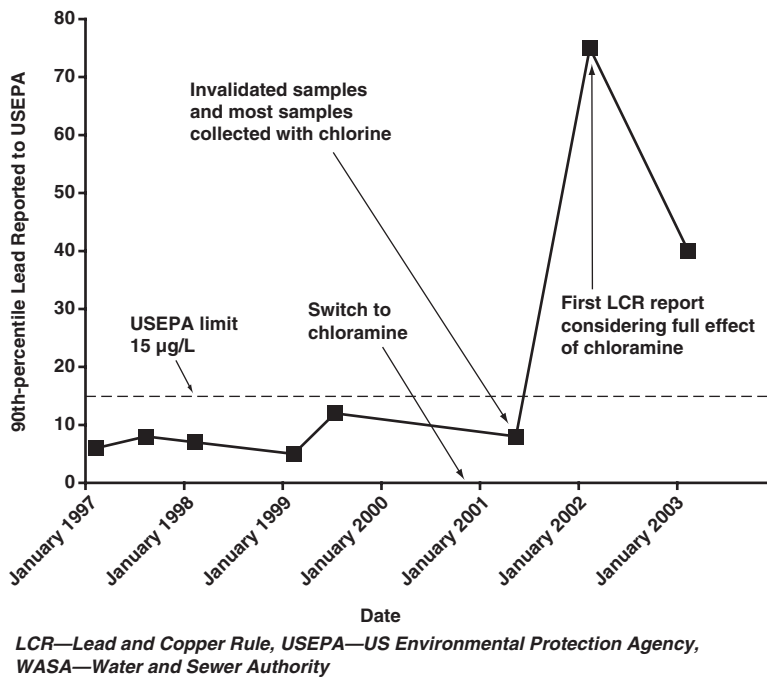
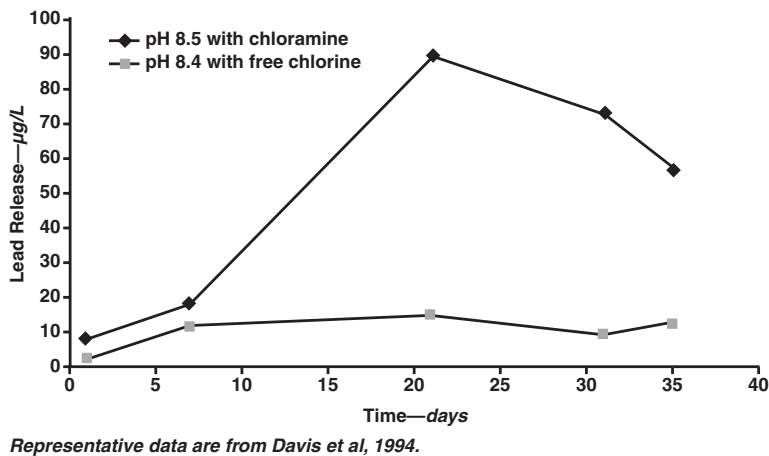## FIGURE 1 WASA 90th-percentile lead in LCR sampling

LCR—Lead and Copper Rule, USEPA—US Environmental Protection Agency,
WASA—Water and Sewer Authority

FIGURE 2 Comparison of effects of lead leaching from brass in Potomac River water with free chlorine and chloramine

Representative data are from Davis et al, 1994.

limit, when actually the 90th-percentile lead did exceed the 15-µg/L action limit. Therefore, the late 2001 sampling round was the first time that the full effects of chloramine were apparent in reported 90th-percentile lead. Sampling rounds after 2003 used a dramatically different sampling pool; therefore results are not shown here, but they confirmed a widespread problem with lead throughout the system, until at least August 2004. Thus, Washington consumers have been exposed to relatively high levels of lead for more than three and a half years. Because chloramines decay to form ammonia that can then be converted to nitrites during nitrification, a literature review examining effects of these constituents on lead corrosion was undertaken to understand possible causes for the phenomenon.

Chloramines. There is a long history of water industry research documenting practical problems from chloramine attack on brass (Larson et al, 1956; Anonymous, 1951; Ingleson et al, 1949). Brass is an alloy of copper, zinc, lead, and other trace constituents. In tests by Larson using dechlorinated water, brass faucet seats were determined to fail three times faster in the presence of a chloramine residual. In these early studies of 1949–51, the breakdown of the brass faucet seats occurred in regions of the metal where lead had segregated. It is therefore reasonable to expect that chloramine would increase lead leaching from brass under some circumstances, even though such measurements were not made in these older investigations.

In a later study of chloraminated versus chlorinated water in Portland, Ore., (Portland Bureau of Water Works, 1983), 220 ft (67 m) copper coils were tested with 50/50 lead–tin solder joints at 20 ft (6 m) intervals. Over an 18-month study, the samples exposed to chlorine leached median lead values of ~10 µg/L, with only 1 of 19 samples exceeding 50 µg/L lead. In contrast, in the same water exposed to chloramine, median lead was about 100 µg/L, and 13 of 19 samples exceeded 50 µg/L lead. Thus, compared with the use of chlorine, the use of chloramine increased median lead leaching by about a factor of 10. The typical pH of this water was ~6.9, and measurements of pH tended to be lower in the chlorinated water relative to the

ever, after WASA switched to chloramines in November 2000, serious problems with lead leaching started to occur.

Certain factors prevented prompt recognition of a problem. In the LCR monitoring round that ended in spring 2001 (Figure 1), the majority of samples were collected before the disinfectant changeover took place. Moreover, five samples collected in that sampling round after the switch to chloramine contained 31–113 µg/L lead, and these samples were improperly invalidated (Holder, 2004; Leonnig, 2004). The sample invalidation caused the reported 90th-percentile lead to meet the action

At pH 5.5, solutions with 48,000 µg/L Pb^{+2} are clear because most of the lead is soluble (far left). At pH 8.5, a white solid precipitates (middle left). When chlorine is present at pH 5.5 or 8.5, a highly insoluble red–brown solid precipitates (middle right). The red–brown solids are hard to distinguish from "red water" samples caused by corroding iron (far right). The filter paper attached to each container indicates the color of the captured particles.

chloraminated water. If lead leaching is assumed to increase at lower pH, the relative adverse effect of chloramine versus chlorine is even more profound than these data indicate. It was speculated that the chloramine enhanced galvanic corrosion between the copper and solder in the pipe rig because the weight loss of pure lead was not increased by the presence of chloramine relative to free chlorine.

In a more recent study (Reiber, 1993), chloramine, compared with free chlorine, did not have noteworthy adverse effects on the corrosion of copper, brass, bronze, and soldered joints. However, that research focused primarily on elastomers, and the limited work conducted with metallic plumbing did not measure lead leaching to the water. Furthermore, water was flowing continuously during these tests, which is an obvious and important difference from LCR sampling for lead after mandatory stagnation periods.

Effects of chloramine on lead corrosion have been studied in Potomac River water (Lin et al, 1997). The Potomac River serves as the source water for Washington. In contrast to free chlorine, chloramine actually reduced lead leaching in tests using pure lead materials in a one-month experiment at pH 7.2–8.5. Likewise, a parallel experiment demonstrated that chloramine caused less lead leaching than free chlorine did when pure lead was galvanically coupled to copper. However, in the tests with brass (3% lead) comparing chloramine and free chlorine, the presence of chloramine worsened lead leaching by a typical factor of ~2. The greatest difference occurred at pH 8.5, at which chlo-

ramine caused leaching of approximately five times more lead than did the same water with free chlorine (Figure 2). This occurred despite the fact that overall corrosion rates on brass were lower in the presence of chloramine; thus, chloramine selectively increased lead leaching from the brass (as could be inferred from careful reading of earlier research by Larson and others). Drinking water with high lead levels collected at Washington homes had pH values up to 8.67, so the Lin et al (1997) result was considered highly relevant. This study also showed that phosphate inhibitors might reduce the adverse effects of chloramines on lead leaching from brass.

One confounding factor in the study by Lin and co-workers is that the original report (Davis et al, 1994) indicated that the tests were all performed at different times. Tests with free chlorine at different pH values were conducted from September until October, whereas the corresponding tests with chloramine were conducted from February until March.

Nitrate–ammonia. It is well understood that in alkaline solutions, high concentrations of nitrate break down pure lead passivity and cause pitting (Rehim & Mohamed, 1998). However, all testing in that study was performed at pH 13 or greater and at >0.01 M nitrate. Thus, the study's relevance to the current problem is uncertain, even though the data suggested that the problem would become even worse at lower pHs. The direct attack of metallic lead by nitrate was reported by Uchida and Okuwaki (1998): $NO_3^- + Pb \rightarrow NO_2^- + PbO$. The nitrite

FIGURE 3 Drinking water collected at a Washington, D.C., sampling site after 1-h stagnation time and 1-min flush time
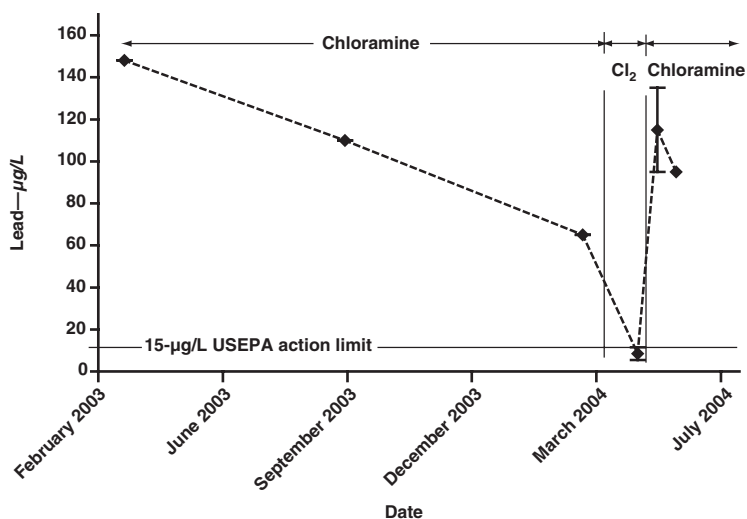
Cl$_2$—free chlorine, USEPA—US Environmental Protection Agency
Error bars during and after switch to free chlorine are 90% confidence intervals on triplicate sampling events during the same day.

FIGURE 4 Lead profile from a tap as a function of flushing time (with >10-h stagnation)
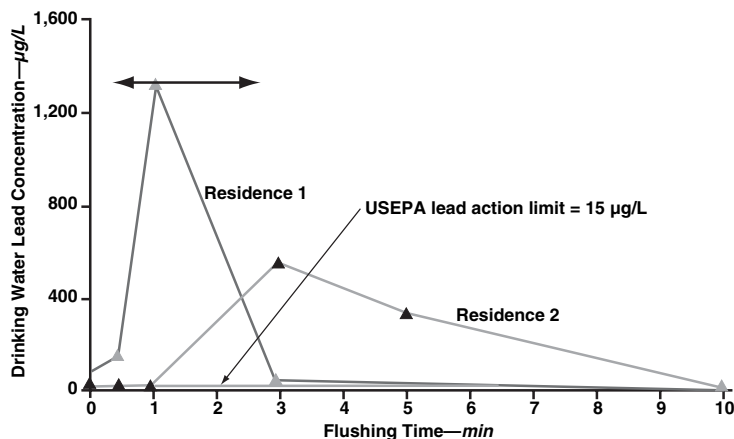
USEPA—US Environmental Protection Agency
Heavy bar with arrows indicates samples that would have been collected according to written recommendations to protect public health, i.e., after a flushing time of 30 seconds to a few minutes.

that is produced can react further with lead to form ammonia or N$_2$ gas: NO$_2^-$ + 3Pb + 2H$_2$O → NH$_3$ + 3PbO + OH$^-$ or 2NO$_2^-$ + 3Pb + H$_2$O → N$_2$ + 3PbO + 2OH$^-$.

Thus, nitrate alone can be considered aggressive to lead. If nitrifying bacteria were growing on the lead surface, the abiotic reactions described could remove NO$_2^-$ produced by the bacteria, regenerating ammonia and alkalinity required for their further growth. Under some circumstances, this could be an especially dangerous synergistic reaction in water systems. Specifically, nitrifying bacteria could derive substantial benefit by accelerating the corrosion of lead surfaces.

Even low levels of ammonia can rapidly attack copper alloys. If a brass metal sample has residual internal tensile stresses, the ammonia can cause a phenomenon known as "stress corrosion" in which brass is physically cracked (Guo et al, 2002). This problem becomes more likely above pH 7.0 and in one study was worst at pH 11.4. Implications of stress corrosion cracking have not been studied at the levels of ammonia typical of drinking water, but it certainly can be involved in degradation of brass by chloramines.

There is also a suggestion that the combination of ammonia and higher nitrate would synergistically drive lead corrosion. Specifically, lead weight loss in the 1998 Uchida & Okuwaki study increased with higher concentrations of ammonia and nitrate in the water. A followup study (Uchida & Okuwaki, 1999) found that the lead corrosion rate in the presence of nitrate was higher only if ammonia was also present. Scanning electron microscopy suggested that ammonia was interfering with formation of a passive scale layer on the pure lead samples. The pH values were not reported, the temperatures studied were high (typically above 40°C), and the levels of the ammonia and nitrate constituents were also at least 10 times higher than levels typically found in drinking water.

Focus of this study. The literature review and LCR monitoring by WASA supported the idea that chloramine dosing sometimes might increase lead leaching to drinking water. Field experiments were undertaken to characterize the problem in greater detail. Rigorously controlled bench-scale experiments directly examined the effects of chlorine and chloramine on lead solubility, lead pipe, and brass corrosion. The important effects of chloramine on lead leaching from plumbing materials that are galvanically connected to copper pipe are discussed in a companion study (Dudi, 2004).

MATERIALS AND METHODS

Laboratory experiments were conducted to understand the effects of oxidants on lead solubility and lead leaching from brasses or pure lead pipe. In all experiments discussed here (with the exception of the field tests) the synthesized water contained 82 mg/L CaCl$_2$ × 2H$_2$O, 89.6 mg/L CaSO$_4$

× 2H$_2$O, and 84.1 mg/L NaHCO$_3$. This recipe was used successfully in previous research to simulate the corrosivity of Potomac River water and is based on typical levels of hardness, alkalinity, sulfate, and chloride (Rushing & Edwards, 2004). This solution is termed synthesized Potomac water in subsequent discussion.

Lead solubility experiments. For lead solubility experiments, three types of synthesized Potomac water were used, including water without disinfectant, synthesized Potomac water with chlorine (10 mg/L as Cl$_2$), and synthesized Potomac water with chloramine (10 mg/L as Cl$_2$ and ammonia at a 1:1 ratio of Cl$_2$ to N). Each water was further tested at pH 7.5, 8.25, or 9 (adjusted using 1N hydrochloric acid or 1N sodium hydroxide base) to arrive at a total of nine tests.

To start the tests, all waters were dosed with 5 mg/L lead (using PbCl$_2$) and continuously stirred at 200 rpm for 48 h. Samples were collected for soluble and total lead concentration after 1, 8, 24, and 48 h. Soluble samples were passed first through a 0.45-µm pore-size filter before analysis. Free chlorine and total chlorine (±0.1 mg/L Cl$_2$) and pH (±0.2 units) were also monitored and maintained at the target value. After the 48-h sampling, the test waters were further dosed with 3 mg/L as phosphate (from NaH$_2$PO$_4$) and stirred for an additional 24 h; samples for lead were collected 1 and 24 h later. For comparison, the entire experiment was repeated with 3 mg/L as phosphate dosed before the Pb^{+2} was added.

Experiments with pure lead pipe. Another phase of experiments was conducted using 16-mm (0.6-in.) diameter pure lead pipes. Each lead pipe was cut into identical 65-mm (2.5-in.) pieces to hold 13 mL of water each. These lead pipes were thoroughly cleaned twice with deionized water, pickled in 1N hydrochloric acid for 6 h, and then thoroughly rinsed with distilled and deionized water. Rubber stoppers were used to plug both ends of the pipes. Quality assurance–quality control (QA–QC) measures determined the stoppers did not leach significant concentrations of inorganic or organic contaminants.

The lead pipes were exposed to five synthesized waters: (1) Potomac water, (2) Potomac water plus ammonia, (3) Potomac water plus chlorine, (4) Potomac water plus chloramines, and (5) Potomac water plus chloramines and orthophosphate. In these tests, ammonia was dosed at a level of 1.37 mg/L NH$_3$-N, and chlorine was dosed at a level of 5.13 mg/L as Cl$_2$ from a solution of sodium hypochlorite. Chloramines were formed by dosing the ammonia to the water before free chlorine at pH above 8. Measurements using the DPD method (*Standard Meth-*

FIGURE 5   Lead levels in drinking water collected from a residential tap after the indicated stagnation time and a fixed 1-min flushing
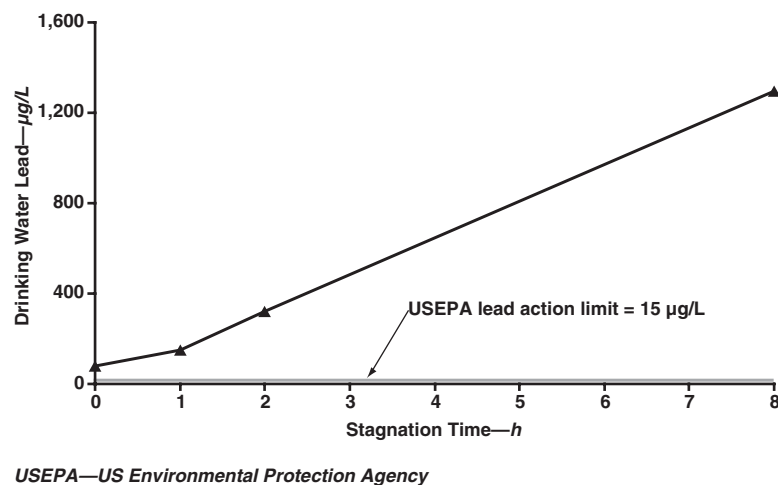
USEPA—US Environmental Protection Agency

ods, 1998) confirmed that free chlorine was near detection and that the vast majority of chloramines were present as monochloramine (as would be expected given the 1:3.7 mass ratio of N to Cl$_2$). Phosphate was dosed at a level of 1 mg/L as P using NaH$_2$PO$_4$. Each condition was tested in triplicate using three lead pipes, except for the condition with phosphate, which was tested in duplicate. Water was changed in the pipes using a dump-and-fill protocol every morning, Monday through Friday, with an extra change on Friday evening. Sample waters were collected after a 16-h stagnation time from each lead pipe at 2, 9, 25, and 28 days of exposure.

Experiments with brass. The final phase of laboratory experiments used brass devices. Because lead leaching from brass is known to be highly dependent on the alloy (Lytle & Schock, 1996), brass hose bibs were selected for testing because of the wide array of brass types that could be obtained and the easy adaptation of the device to experiments (Dudi, 2004). Eight distinct types of brass hose bibs were exposed to waters 1 through 4 (as described previously), with one hose bib per water (8 types of brass × 4 waters = 32 experiments). The same schedule of dump-and-fill water changes was used for brass as for pure lead pipes. After 60 days, the experiment was continued but with a spike of nitrate (10 mg/L as N from NaNO$_3$) to the water.

Soluble lead was determined after filtering the sample through a 0.45-µm pore-size filter. Samples collected for soluble and total lead were preserved with 5% nitric acid and held for at least 28 h before analysis by inductive coupled plasma–emission spectroscopy[1] according to method 3120 B (*Standard Methods,* 1998) with a 3-µg/L detection limit for lead. QA–QC confirmed that this method recovered 100% of all types of lead solids formed

FIGURE 6   Lead solubility in three beaker experiments: A—without phosphate , B—1 h after phosphate was dosed to the experiment running for 48 h without phosphate, and C—companion experiment started with phosphorus
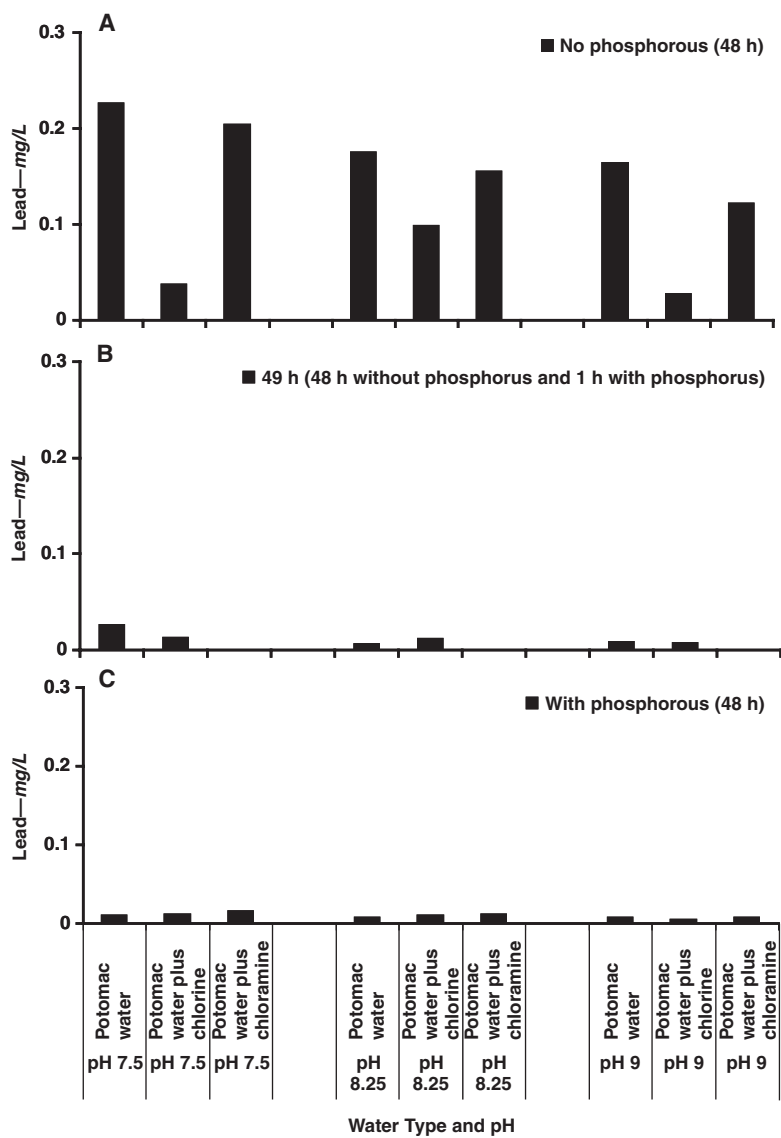
in this study; comparison of subsamples with lead detected using mass spectroscopy or graphite furnace was favorable.

Because of the obvious temporal link between the onset of lead problems in the WASA system and the switch from free chlorine to chloramines, field sampling was conducted in which "profiles" of lead concentration were collected as water ran from a WASA consumer's tap. To collect a typical profile, water was rinsed through the lines 10 min the night before, at which time a water sample was collected just before the faucet was closed. After the water was allowed to sit stagnant in the consumer's plumbing for 10 h, the faucet was opened at time zero,

and 1-L samples were collected after specified "flush" times. The faucet was opened to a maximum rate in order to approach a plug-flow regime as closely as possible. Similar profiles were collected by Britton and Richards (1981) and on a much smaller time scale by Lytle and colleagues (1995) to show sources of lead to potable water. Samples were also collected from sites after various stagnation times and flushing times as described here. In field work, lead was quantified using a field test kit. A comparison of field test results with those obtained using standard methods for lead quantification was favorable as long as a strong nitric acid digestion was used.

RESULTS AND DISCUSSION

Field testing was first conducted to define the nature of the lead problem as it occurred in Washington. This was followed by laboratory testing to gain a fundamental scientific understanding of potential contributing causes, including lead solubility, corrosion of lead pipe, and brass materials.

Field sampling. Field testing at a single site between 2003 and 2004 provided insight into the cause of the lead problem (Figure 3). Before spring 2004, lead concentrations had been relatively high at the test site in water samples collected after a consistent 1-h stagnation time and then 1-min flushing time. However, during routine springtime use of free chlorine as a disinfectant, lead levels dropped by a factor of 7.6 times compared with the previous sample obtained when chloramine was used. Lead levels then increased by a factor of 13.6 in a sample collected 10 days after the switch back to chloramine. During this time period, WASA also collected monitoring data and reported up to a tenfold drop in lead concentrations from lead service line samples (Cohn, 2004). The order of magnitude increase in lead with chloramine versus chlorine was consistent with that observed in Portland for pipe rigs with lead solder (Portland Bureau of Water Works, 1983). Although this type of full-scale data cannot be used to prove cause and effect, it did provide additional support for the idea that the switch from free chlorine to chloramines was key.

Public education materials distributed by USEPA and water utilities often recommend that consumers flush water

from the tap for time periods between 30 s and several minutes to minimize lead exposure. It is also common to recommend flushing until the water temperature changes before collecting volumes to brush teeth, drink, or cook (USEPA, 2002a). These well-intentioned instructions are based on the assumption that the "first-draw" lead samples (i.e., samples collected in the first litre flowing from the tap) usually contain the highest amount of lead and that lead levels will decrease with flushing. Consumers are often further informed that flushing is necessary ". . . any time the water in a faucet has gone unused for more than six hours" (USEPA, 2004).

In marked contrast to the conventional wisdom, lead levels were not worst in the first-draw samples at some homes in WASA but sometimes were worst after 1 min of flushing (Figure 4). One sample collected after 1 min of flushing was off the scale even after a 1:10 dilution, and although the concentration on the figure is reported at 1,250 µg/L, the level was greater than that. Samples of lead collected after flushing and measured by WASA (using standard USEPA sample handling and analysis procedures) were as high as 48,000 µg/L (Nakamura & Timberg, 2004). This provides indirect support for the high lead concentrations obtained after flushing using the field test kit (Figure 4). As points of comparison, lead levels >5,000 µg/L qualify a water sample as hazardous waste, and USEPA considers that lead levels >40 µg/L in drinking water pose an imminent and substantial endangerment to the health of children and pregnant women. The concentration of lead in the samples did not always return to below the action limit even after 10 min of flushing.

Another round of experiments was conducted at one sampling site, during which time a 1-L sample was collected from the tap after following the publicly recommended 1-min flush time. The time that water was allowed to sit in the pipes between sampling events was varied (Figure 5). Even after only 1-h stagnation, lead levels in the sample had built up to 140 µg/L, demonstrating clear problems well before the 6-h threshold cited in some public education materials.

These findings were of obvious public health concern for several reasons. First, consumers following the written guidance to minimize their lead exposure could actually markedly worsen their exposure to lead. In retrospect, problems with this advice could have been anticipated. USEPA has issued explicit instructions aimed at collecting samples from lead service lines: "Each service line sample shall be one liter in volume and have stood motionless in the pipe for at least six hours." . . . "[A]llowing the water to run until there is a significant change in temperature" is "indicative of water that has been standing in a lead service line" (USEPA, 2002b). In other words, the USEPA instructions to collect samples with high lead

FIGURE 7 Representative lead leaching data from lead pipes in different waters after two days (A) and after nine days (B)
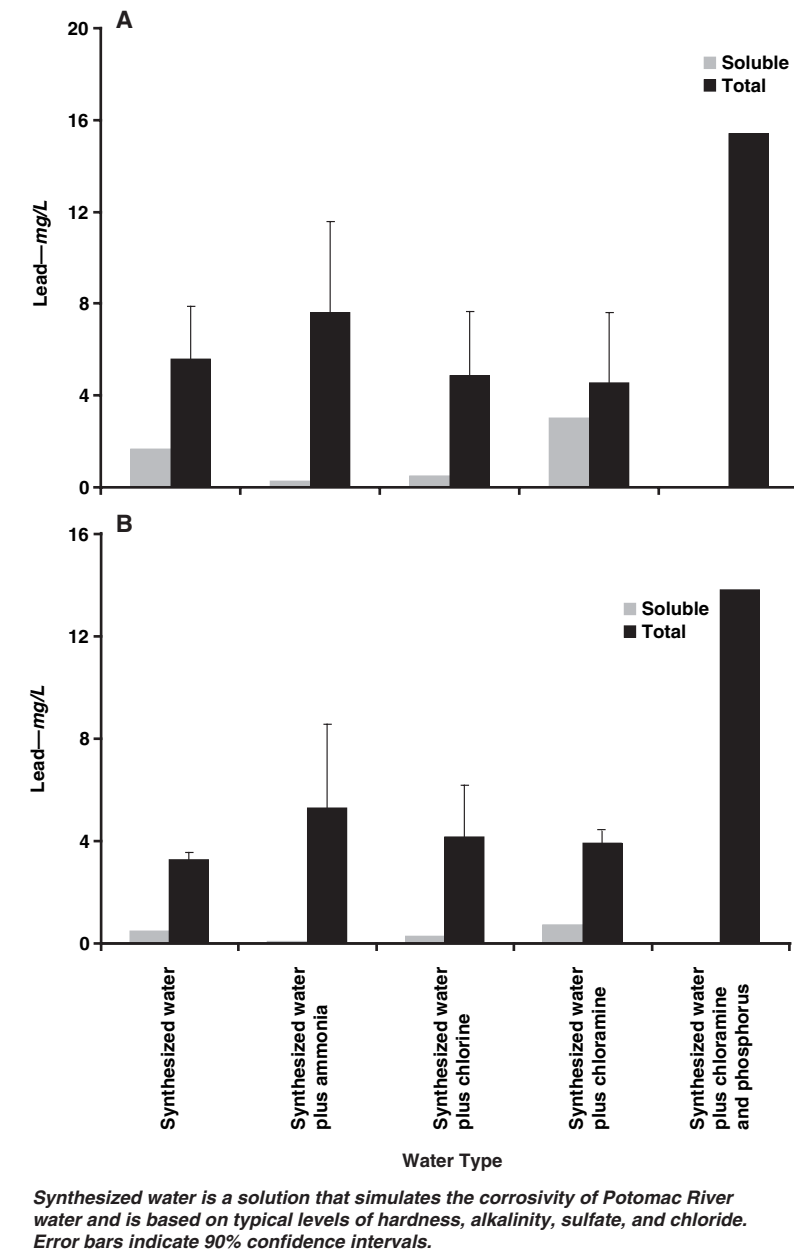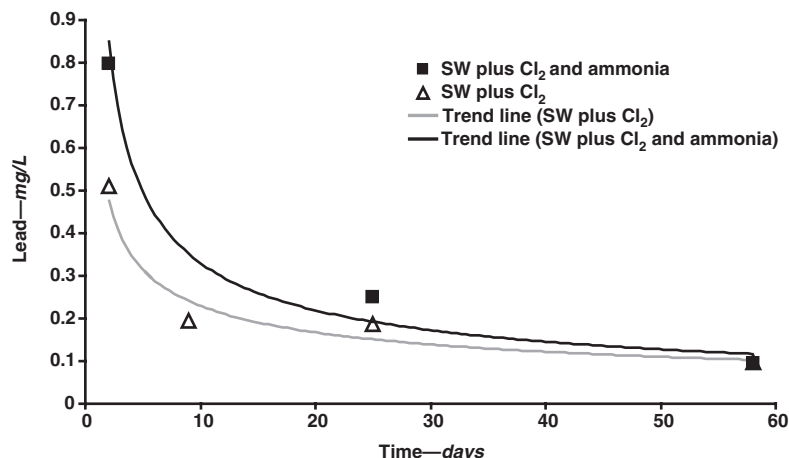

Synthesized water is a solution that simulates the corrosivity of Potomac River water and is based on typical levels of hardness, alkalinity, sulfate, and chloride. Error bars indicate 90% confidence intervals.

FIGURE 8 Decrease in lead leaching from brass sample 4 over time

■ SW plus Cl₂ and ammonia
△ SW plus Cl₂
— Trend line (SW plus Cl₂)
— Trend line (SW plus Cl₂ and ammonia)

Cl₂—free chlorine, SW—synthesized water

FIGURE 9 Lead leached from brass hose bibs after 58 days

■ SW
■ SW plus ammonia
■ SW plus Cl₂
■ SW plus Cl₂ and ammonia
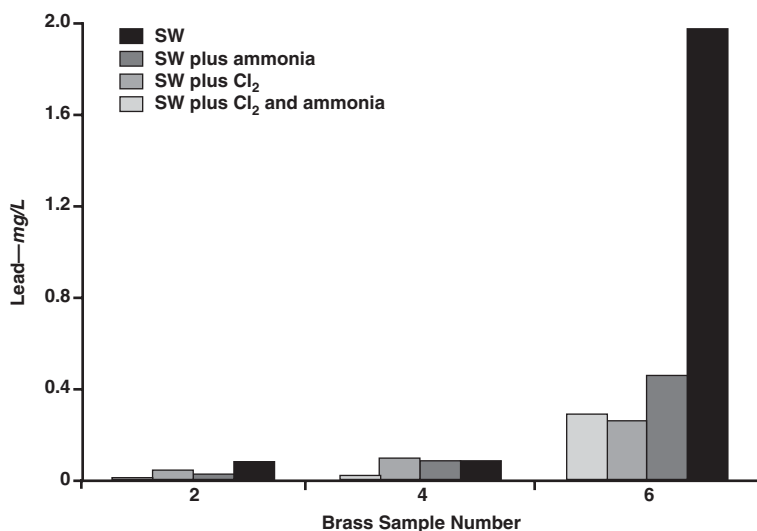
Cl₂—free chlorine, SW—synthesized water

levels are completely indistinguishable from the USEPA advice given to customers regarding collection of their drinking water.

Clearly, the advice to collect drinking water after flushing briefly or until water temperature changes should never be distributed to consumers in homes with lead services when a corrosion problem arises, unless extensive sampling confirms that the technique is producing water with acceptable levels of lead. Collection of lead profiles by WASA at the instruction of the authors proved the standard USEPA flushing advice could be harmful in many cases. In late March of 2004, nearly three-and-a-half years after the switch to chloramine, the utility publicly recommended 10 min of flushing and use of a lead filter

before collection of drinking water in homes that had a lead service line (Nakamura & Goldstein, 2004).

The second public health concern relates to Centers for Disease Control (CDC) instructions for assessment of childhood lead poisoning cases (CDC, 2004). The CDC correctly notes that poisoning from water is unlikely if lead concentrations are at or near the 15 ppb USEPA action limit. However, to assess lead in drinking water, CDC recommends examination of 90th-percentile lead values posted by USEPA on the Internet. If the listed 90th-percentile value in the community is below the action limit, "no additional testing is necessary, unless no other sources of a child's elevated blood lead level can be found." If testing of water is done, it is almost always a first draw sample.

CDC is therefore relying on reported USEPA 90th-percentile lead values to represent the potential health threat from drinking water in individual homes, which is unacceptable given that 10% of homes could have first draw lead at any concentration above the action limit. These higher lead values are of greatest interest in a case of lead poisoning. Moreover, the first draw sample tested by CDC could contain much less lead than the water consumers are actually drinking by following recommendations (Figure 4). Consequently, if lead services were to cause a case of childhood lead poisoning, the published CDC protocol would have little likelihood of identifying drinking water as the source.

A recent study in Germany (Fertmann et al, 2004) attempted to measure average lead concentration in drinking water, and a correlation was established between blood lead and average lead in drinking water. Consumers with drinking water lead concentrations above 10 µg/L and who switched to bottled water reduced their blood lead levels by 37% during the study. US public health officials should strongly consider collection of multiple drinking water samples and use of average lead concentration when assessing cases of childhood lead poisoning. Use of 90th-percentile USEPA LCR concentrations to assess lead exposure from drinking water is highly misleading.

The sampling site depicted in Figure 5 did not have a lead service line. This suggests a significant problem with solder or brass materials in the system under at least some

circumstances. In 2002 and 2003, WASA spent $36 million replacing 110,000 water meters in the system with new devices containing 5–7% lead (Nakamura, 2004). Recent research (Dudi, 2004; Dudi et al, 2004) suggests that standards for such devices are not always sufficiently protective of public health. As of May 2004, it was uncertain if the new meters were a significant source of lead in the water in Washington, D.C.

Lead solubility in the presence of no oxidant, free chlorine, and chloramines. The solubility of lead was studied as a function of time, pH, and oxidant type (chlorine and chloramines) in water. To provide simple photographic evidence of the dramatic effect of chlorine on lead solubility, tests were conducted using the highest level of lead reported in the WASA monitoring data (48,000 µg/L Pb). In solutions maintained at pH 5.5–8.5, red–brown-colored solids formed when chlorine was dosed (see photo p. 71). In contrast, no solid at all formed at pH 5.5, and a white solid formed at pH 8.5 in the systems dosed with no oxidant or with chloramines. The obvious implication is that a different type of low-solubility lead solid was rapidly formed in the presence of chlorine.

Experimental results for soluble and total lead concentrations at the end of 48 h were representative of trends obtained at shorter time periods (Figure 6). Soluble lead was ~4.4–6 times lower in the presence of chlorine at pH 7.5 and pH 9.0 than in comparable systems without oxidant or with chloramine (Figure 6, part A). A less significant effect was observed at pH 8.25, but chlorine still reduced solubility relative to the other two conditions at this pH. The soluble lead concentrations in the water without chlorine were relatively consistent with expectations based on carbonate chemistry and Pb^{+2} precipitation, whereas those in the presence of chlorine were well below those expectations (Schock, 1989; Schock & Gardels, 1983). Qualitatively, in the presence of 10 mg/L chlorine, the red–brown solids began to form in the chlorinated water at pH 7.5 in the first 24 h but required about 36 h to form in the same water at pH 8.25 and took even longer (48 h) at pH 9.0. Thus, kinetics of the solid formation seemed slower at the higher pH in this water, perhaps because of the predominance of the weaker oxidant OCl^- at higher pH.

After 48 h, phosphate was spiked into all of the samples with soluble lead concentrations (shown in Figure 6, part A). Soluble lead was decreased by phosphate dosing in all systems within 1 h, in some cases by as much as a factor of 10 (Figure 6, part B). The greatest reductions were observed in the system originally dosed with chlor-
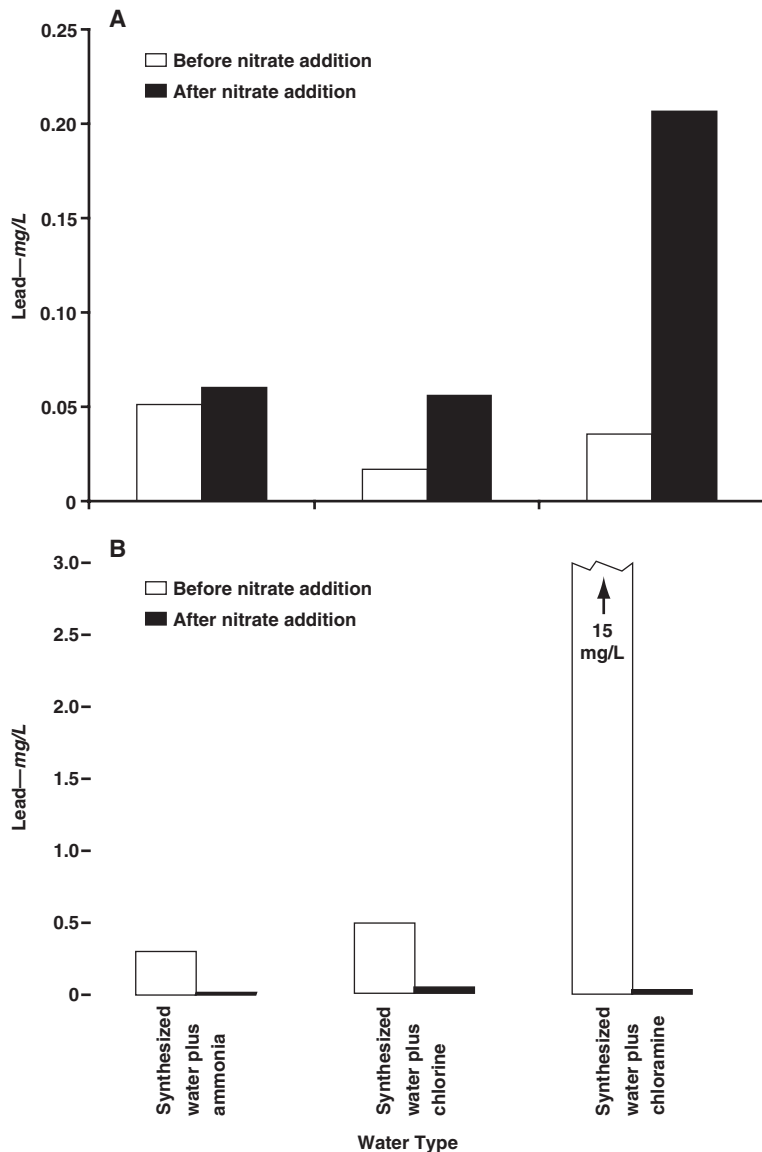
FIGURE 10   Effect of nitrate on lead leaching in brass hose bibs exposed to synthesized water in absence of oxidants
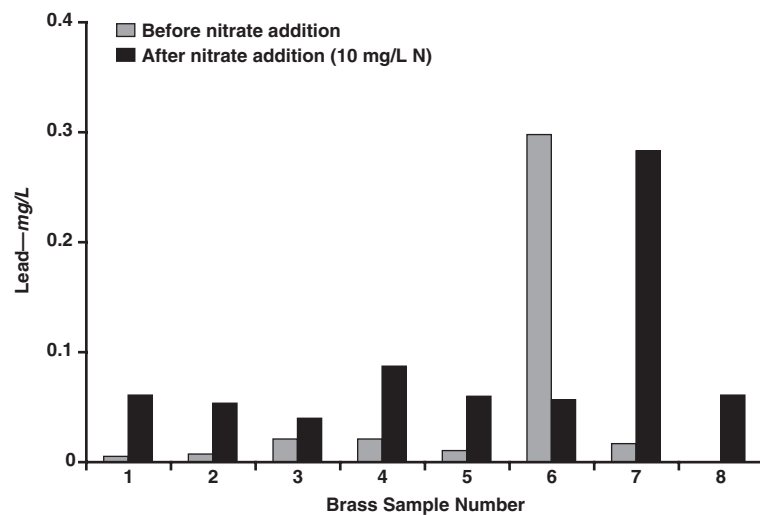
amine. In the companion experiment in which phosphorus was dosed at the start (before the red-colored solids formed), soluble lead also dropped, but red–brown solids did not form at any pH during the test, even though the level of chlorine was unchanged (Figure 6, part C). Thus transformations of solids from one type to another depend on water quality, disinfectant type and dosage, and sequence of chemical addition, as has been noted previously for copper solids (Edwards et al, 2001; Powers & Edwards, 2001). In the specific context of lead solubility, Schock and colleagues hypothesized that very insoluble PbO_2 could form under highly oxidizing conditions and further identified the presence of this solid on lead pipes in chlorinated systems (Schock et al, 2001; Schock et al, 1996). In light of these results, it is considered highly likely that the low-solubility red–brown solids formed in these tests were at least partially comprised of Pb(IV) oxides.

Although the data are not shown, measurements of total lead in the experiments (soluble lead plus any particulate lead in suspension) indicated that the red–brown lead solid had a strong affinity for polycarbonate labware. In one case, for instance, significantly more than 80% of the lead solid that formed in the presence of chlorine stuck to the labware, but nearly none of the lead solid that formed without any oxidant or in the presence of chloramine did so. The dosing of phosphate tended to cause detachment of these lead solids that were attached to the labware. It is uncertain whether this observation has any relevance either to the ability of these solids to stick to pipe walls, sampling containers, or to any practical aspect of lead contamination of drinking water. However, it is possible that phosphates could detach and disperse particulates, which is consistent with trends in par-

FIGURE 11 Effect of nitrate on lead leaching from different hose bib types in the presence of chloramine: A—sample 1, B—sample 6

acidified to pH 1.9 with nitric acid, only 2% of these solids had dissolved.

Even 1 ntu of this red lead solid was usually undetectable by visual observation and yet was responsible for >1,000 μg/L of lead in samples. This raises an obvious concern that innocuous "red water" reports invariably attributed to iron might actually be due to the presence of high concentrations of lead solids under rare circumstances. Utilities should be vigilant for such incidents and should not assume red water is harmless, because it may contain high levels of lead as well as other contaminants (Schock & Holm, 2003; Davis, 2000; Reiber et al, 1997).

In the presence of 5% nitric acid or hydroxylamine, the red–brown lead particles were rendered completely soluble. Strong nitric acid digestions were used throughout this research but are not required by USEPA for LCR sampling. It is very likely that the resistance of the undissolved red–brown lead solids to acid dilution would interfere with lead detection during conventional LCR sampling and analysis. To support this idea, in a few field samples both strong nitric acid digestion and conventional acidification to pH <2 were conducted; in some cases, lead levels were 500% higher when the stronger digestion was used than with the conventional USEPA procedure. Thus, there is a large potential to "miss" lead that is actually present in samples. Similar problems have recently been documented for Cr(III) (Parks et al, 2004). A clear area of future research would be to determine whether the lead solids formed in the presence of free chlorine might be less bioavailable to humans.

Lead leaching from pure lead pipes. For samples collected from the pipes after 2, 9, and 30 days of exposure, there were no significant differences at 90% confidence in total lead leaching from synthetic Potomac water with no amendments, with ammonia, with chlorine, or with chloramine (Figure 7). The water from the lead pipe receiving chloramine did consistently have a larger soluble fraction of lead (66%) than did the other waters (3–30%). An additional month of testing did not show a significant difference in lead leaching in waters with or without nitrate. Thus, the direct effect of chloramine on lead leaching from pure lead in short-duration experiments in this type of water was relatively small, consistent

ticle stability reported for iron particles in the presence of phosphate (Lytle & Snoeyink, 2002).

Several other critical observations should be of interest to utilities and public health professionals. First, the red–brown lead particulates were difficult to distinguish from the iron particulates that cause "red water" (see photograph, page 71). Some red solids that collected from the WASA system during fieldwork for this study were pure lead oxides. When samples of pure red–brown lead solids were acidified to pH <2.0 according to conventional USEPA procedures before analysis (Parks et al, 2004), the red–brown solid did not dissolve. In fact, even after two months of holding time in the presence of water

with previous findings (Lin et al, 1997; Davis et al, 1994; Portland Bureau of Water Works, 1983).

Duplicate samples were run for pure lead pipes receiving both chloramine and phosphate. Surprisingly, this combination consistently had the highest total lead leaching of all waters tested (Figure 7). Unfortunately, soluble lead measurements were not made for this sample. When a paired *t*-test was conducted, matching data for lead leaching from water with chloramine plus phosphate versus other waters collected at the same time, lead leached from the water containing both chloramine and phosphate was highest overall at >90% confidence. This finding seems to be contrary to other reports for phosphate effects on lead leaching (Lin et al, 1997), but numerous differences in methods could explain these conflicting results. If nothing else, it is clear that phosphate is not always beneficial in the context of mitigating lead leaching. Resolving such discrepancies should be the focus of future research.

These preliminary results suggest that chloramine does not cause serious problems with leaching from pure lead pipes relative to the testing in the same synthesized water with chlorine. The authors propose three possible explanations for the discrepancy in this result versus observations at WASA. The first is that PbO_2 solids of the type found on pipes by other researchers (Schock et al, 2001; Schock et al, 1996) may be involved and that the problem in Washington may occur only in older lead pipe samples that had preexisting PbO_2 solids (Renner, 2004). Such solids may not be present on the new pipes used in this work or previous studies (Lin et al, 1997; Portland Bureau of Water Works, 1983). Another hypothesis is that the high lead values might result from the presence of nitrifying bacteria growing on lead pipes (as discussed earlier in the literature review). A third possibility is that the worst problems might be manifested only when lead materials are galvanically coupled to copper pipe as discussed in Dudi (2004) and suggested by Portland Bureau of Water Works (1983). In most practical situations, lead materials are galvanically connected to copper pipe. A combination of these three possibilities could also be operative. Given that the water industry has used free chlorine and lead pipe for more than 100 years, it seems remarkable that fundamental direct reactions between chlorine and lead were only discovered by Schock and colleagues in 1996–2001 and then further documented in this research. Clearly, this subject merits additional study.

Lead leaching from brass devices. The corrosion chemistry of brass is complex, with a great deal of variation in lead leaching among the alloys and production methods (Lytle & Schock, 1996). To attempt to capture the range of possible effects, this research studied eight types of brass hose bibs for lead, copper, and zinc leaching. The brass devices in question contained 2–8% lead. Manufacturers of these devices were contacted to obtain information regarding alloys and manufacturing practices; as

of August 2004, however, this information had not been shared with the authors.

For the eight devices studied, two types of responses were observed for chloramine when nitrate was not present. In the typical response (found for seven of eight samples), lead leaching started out high and decreased exponentially with time over the 58 days of testing (Figure 8). Chloramine typically increased lead leaching compared with the same water with chlorine. However, paired *t*-testing indicated that this difference was only significant at the 85% confidence level for two of the brass samples over the duration of this study phase. This low confidence is partly attributable to the low number of samples collected, because the tendency was usually very consistent. A different response was observed for sample 6, which sometimes had 33 times more lead than did the other brass samples exposed to the same water (Figure 9). Lead leaching from sample 6 was very erratic, even after two months.

After 58 days, the experiment was continued but with the addition of 10 mg/L NO_3-N to all waters. Sampling after four days indicated a startling result: lead leaching dramatically increased for seven of eight brass samples in water without any oxidant present (Figure 10). Limited sampling showed that a significant amount (up to 15%) of the nitrate was being converted to ammonia during stagnation in the pipes, a trend that is commonly noted for nitrate oxidation (corrosion) of iron metal (Westerhoff, 2003). Thus, nitrate can also oxidize (corrode) brass as would be expected based on previously published results (Uchida & Okuwaki, 1998). Exceptional behavior was noted for sample 6, in which lead leaching decreased markedly in response to the higher nitrate (Figure 10). The net result is that sample 6, which had been leaching the most lead by far of the eight brass samples, was suddenly leaching nearly the same amount of lead (Figure 10) as the other devices.

In the presence of chloramine, lead leaching also increased in the presence of nitrate, as typified by the 500% increase observed for brass sample 1 (Figure 11). But again, sample 6 was the exception, with lead leaching plummeting if nitrate was present in synthesized Potomac water with ammonia, chlorine, or chloramine (Figure 11). In addition, the long-term effects of nitrate may differ from the short-term effects; after nitrate exposure was continued for two months, water dosed with chloramine often leached less lead than the same water dosed with chlorine (data not shown). Given the limited amount of lead in the alloy, lead can be selectively leached from the surface. It is therefore conceptually possible that for brass, a water producing very high lead leaching in the short term could eventually produce very low lead leaching over the long term because of lead depletion from the surface.

These results confirmed the concept that lead leaching from brass devices can be a complex function of brass type, exposure time, and water quality (Lytle & Schock, 1996). Nonetheless, ammonia, nitrate, and chloramine clearly can exert a strong influence. In light of early work

documenting high rates of brass failure in the presence of chloramine, more fundamental research is needed.

SUMMARY AND CONCLUSIONS

• A switch to chloramine from free chlorine can trigger dramatically higher total lead leaching in real circumstances. Possible mechanisms for this effect include the following: (1) Free chlorine can reduce lead solubility compared with waters with chloramine or oxygen as an oxidant. (2) Under at least some circumstances, chloramines can attack brass and can significantly increase lead leaching. (3) A galvanic connection between lead pipe–lead solder to copper pipe may be involved; effects of chloramine on leaching from new lead pipe alone do not appear to be significant. (4) Bacteria such as nitrifiers may couple biological and chemical reactions to exacerbate lead leaching.

• Some public education materials routinely distributed to consumers in cases of lead corrosion problems need revision. Specifically, consumers with lead service lines should not be instructed to let water run until the temperature changes or for a time period of seconds to a few minutes before they collect samples for drinking—especially when a corrosion problem is occurring. The lead concentration in pipes can increase to harmful levels in a period far shorter than 6 h of stagnation.

• The low-solubility red–brown-colored solid produced in the presence of chlorine complicates the conventional wisdom regarding lead bioavailability, LCR monitoring, and handling of "red water" complaints. Red water can be a serious health concern in unusual cases, and certain forms of lead in drinking water are poorly quantified using conventional USEPA-approved sample handling and analytical procedures.

• Until additional experience and understanding are obtained, utilities serving systems with either lead services or lead pipes in consumers' homes are urged to exercise considerable caution and diligence when switching from free chlorine to chloramine. Indeed, any change that could affect redox in the distribution system should be carefully tested before full-scale implementation. Monitoring should also be in place to confirm that problems with brass failures and lead leaching from solder/brass are not triggered by the disinfectant changeover. Problems with brass may be harder to detect because of the limited amount of lead in the alloy.

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• With many utilities switching to chloramine as a residual disinfectant or considering a changeover in the near future, additional research on chloramines and all types of material degradation is needed. It is clear that in some waters, few problems will result from such a changeover, but there is ample reason to believe that in other instances serious problems will occur. In some cases, decades could pass before adverse effects on infrastructure longevity would come to light, unless a utility was actively evaluating infrastructure degradation.

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