Appendix A IOCCT Designation Letter, USEPA 2004

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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By Federal Express

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August 3, 2004

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Gentlemen:

The United States Environmental Protection Agency Region III ("EPA") has primacy for the Public Water System Supervision ("PWSS") Program in the District of Columbia. The primacy agency is responsible for implementing the PWSS Program and the National Primary Drinking Water Regulations ("NPDWRs"), including designation of optimal corrosion control treatment ("OCCT") under the Lead and Copper Rule ("LCR") for public water systems. The NPDWRs define OCCT at 40 C.F.R. § 141.2 as "the corrosion control treatment that minimizes lead and copper concentrations at users' taps while insuring that the treatment does not cause the water system to violate any national primary drinking water regulations." The Preamble to the LCR states that the effect of corrosion control treatment on the waste water stream also may be considered in selecting OCCT. 56 Fed. Reg. 26460, 26480 (June 7, 1991).

On July 16, 1997, EPA conditionally designated an OCCT for the drinking water treatment and distribution system for the District of Columbia and required additional study. In February 2000, EPA designated the use of pH adjustment as the OCCT for the drinking water distribution system for the District of Columbia, which required the Washington Aqueduct to maintain a pH in the finished water between 7.7 and 8.5. On May 17, 2002, EPA revised its designation of OCCT with respect to the monthly pH goals.

On August 26, 2002, the District of Columbia Water and Sewer Authority ("DCWASA") submitted a final report to EPA Region III stating that, during the compliance period July 1, 2001 - June 30, 2002, the level of lead in first draw water samples from 53 residences served by the District of Columbia drinking water distribution system was 75 parts per billion ("ppb") at the 90th percentile. This monitoring result exceeded the lead action level of 15 ppb at the 90th percentile. On July 29, 2003, DCWASA reported to EPA Region III that, during the compliance period January - June 2003, the level of lead in the first draw water samples from 104 residences was 40 ppb at the 90th percentile. For the July - December 2003 compliance period, DCWASA reported that the level of lead in first draw water samples was 63 ppb at the 90th percentile. For the January -June 2004 compliance period, DCWASA reported that the level of lead in first draw water samples was 59 ppb at the 90th percentile.

On May 28, 2004, the U.S. Environmental Protection Agency Region III ("EPA") approved an interim modification of the OCCT for the drinking water distribution system for the District of Columbia. The interim modification consisted of an application of the corrosion inhibitor orthophosphate to the 4th High Pressure Zone of the District of Columbia drinking water distribution system. The 4th High Pressure Zone is hydraulically isolated from the remainder of the District of Columbia's drinking water distribution system, but is representative of the entire system in terms of component materials (lead service lines, unlined cast iron pipe, etc.). The purpose of the proposed partial system application was to assess, prior to any full system application, operational characteristics and any unanticipated effects. At the time EPA approved this interim modification, it was expected that, absent any unresolvable problems and subject to EPA's approval, the system-wide OCCT ultimately would be modified to include application of orthophosphate to maintain reduced levels of lead in the entire District of Columbia drinking water distribution system.

This letter modifies EPA's interim designation of the OCCT for the District of Columbia distribution system. The interim OCCT for the District of Columbia drinking water distribution system shall consist of the application of the corrosion inhibitor orthophosphate subject to the conditions and water quality parameters ("WQPs") set forth below. This designation is being considered an "interim" designation because it applies only to the passivation period. A final designation for maintenance of corrosion control will be issued once the system is passivated. The Washington Aqueduct will use an orthophosphate product in the form of phosphoric acid that meets ANSI/NSF Standard 60: Drinking Water Chemicals -- Health Effects. The Washington Aqueduct will apply an initial passivation dose that will continue until the lead level in the 90th percentile of tap water samples is equal to or below the 0.015 mg/l (15 ppb) lead action level, or until water quality results indicate the need to reduce the dosage earlier. The initial passivation dose should be designed to achieve a residual of $\geq$ 3.0 mg/L measured as orthophosphate in tap samples. Following initial passivation, it is anticipated that the Washington Aqueduct will apply a maintenance dose sufficient to achieve a residual of approximately 0.5 - 1.5 mg/L measured as orthophosphate in tap samples, or a dose sufficient to ensure lead levels remain equal to or below 0.015 mg/l (15 ppb) at the 90th percentile of tap samples.

The interim WQPs set herein apply to the initial passivation dose. The LCR contemplates that the primacy agency will establish final water parameters following passivation of the system. EPA will review monitoring results and system operation records after passivation has been reached and will establish final WQPs for the Washington Aqueduct and DCWASA for maintenance of corrosion control following passivation. EPA anticipates that it will establish final WQPs that will allow for smaller variations in the parameters than the interim WQPs for the passivation dose set forth in this letter.

The Washington Aqueduct is a wholesaler of water and has no distribution system of its own. The Washington Aqueduct sells water to a number of other water systems. DCWASA, Arlington County Public Works and the City of Falls Church are consecutive community water systems and provide no additional treatment to the water received from the Washington Aqueduct before they distribute it to their customers. The Washington Navy Yard is a consecutive community water system that purchases its water from DCWASA. The Anacostia Annex, the Naval Observatory and the Naval Security Station are consecutive non-transient, non-community water systems that purchase water from DCWASA. Ronald Reagan National Airport is a consecutive non-transient, non-community water system which has the capability of providing additional disinfection to the water it receives from the Washington Aqueduct. Thus, any treatment, including OCCT, applied by the Washington Aqueduct will affect all of its customer water systems. The public water systems affected are:

PWS Identification Number	Public Water System
DC0000001	Washington Aqueduct Division, U.S. Army Corps of Engineers
DC0000002	District of Columbia Water and Sewer Authority ("DCWASA")
DC0000003	Naval Station Washington – Washington Navy Yard
DC0000004	Naval Station Washington – Anacostia Annex
DC0000005	Naval Observatory
DC0000006	Naval Security Station
VA6013010	Arlington County Public Works
VA6013080	Ronald Reagan Washington National Airport
VA6610100	City of Falls Church Public Utilities

Background

Following DCWASA's report that it had exceeded the LCR lead action level in 2002, EPA recognized the need to conduct additional research into the cause of elevated levels of lead in the District of Columbia drinking water distribution system. (Arlington County and the City of Falls Church have not reported elevated lead levels in their drinking water distribution systems.) EPA contracted with an independent corrosion expert in May 2003 to research the cause of the increased lead levels. The expert presented a written report to EPA in October 2003. DCWASA developed a research strategy, which it presented to the Washington Aqueduct, Arlington County, the City of Falls Church and EPA in January 2004. EPA formed the Technical Expert Working Group ("TEWG") to address the problem of elevated lead levels in tap water in the District of Columbia in February 2004. The TEWG consists of representatives from EPA Region III, EPA Headquarters' Office of Ground Water and Drinking Water, EPA's Office of Research and Development, the Washington Aqueduct, DCWASA, the District of Columbia Department of Health, Arlington County, Falls Church and the Centers for Disease Control and Prevention.

The TEWG's Production Treatment Operations Team, led by the Washington Aqueduct and its contractor, developed a Desktop Study. The Desktop Study considered various treatment options, including maintaining a constant high pH at the Dalecarlia and McMillan water treatment plants using either quicklime (current practice) and/or sodium hydroxide (caustic soda), and feeding a corrosion inhibitor, such as orthophosphate, while maintaining a constant pH throughout the year of about 7.7. The Desktop Study reviewed the various reports and recommendations previously prepared for the Washington Aqueduct and/or EPA, conducted a telephone survey about treatment techniques employed by drinking water treatment and distribution facilities similar to Washington, D.C.'s, performed mathematical modeling of corrosion abatement strategies, and reviewed water treatment industry accepted corrosion control practices.

The TEWG and the Washington Aqueduct originally recommended introduction of orthophosphate as a corrosion inhibitor. The Desktop Study and its recommendations were reviewed by an Independent Peer Review Panel assembled by EPA's Office of Ground Water and Drinking Water in Washington, D.C. Based upon one of its members' greater familiarity with the use of zinc orthophosphate, the Peer Review Panel recommended the use of zinc orthophosphate. On April 30, 2004, EPA designated use of zinc orthophosphate for partial system application in the 4th High Pressure Zone.

On May 28, 2004, EPA modified its April 30, 2004 designation, and EPA designated use of orthophosphate (rather than zinc orthophosphate) for the partial system application of a corrosion inhibitor in the 4th High Pressure Zone. This modification was based on concerns raised by Arlington County regarding its wastewater treatment plant's ability to handle the anticipated added zinc load from any future full system application and on data suggesting that zinc orthophosphate and orthophosphate are equally effective in achieving corrosion control endpoints. For an explanation of EPA's considerations, *see* Letter from Jon M. Capacasa to Thomas P. Jacobus and Jerry N. Johnson (May 28, 2004).

Orthophosphate (in the form of phosphoric acid) is an approved and commonly used drinking water additive. Phosphoric acid, one of the three common forms of orthophosphate and the form proposed for the full system treatment by the Washington Aqueduct, is a proven corrosion inhibitor that is currently being used by the Washington Suburban Sanitary Commission for corrosion inhibition on Potomac River water. It also is used in a number of large distribution systems, including distribution systems in New York, Wisconsin and elsewhere. *See* The Cadmus Group, Inc., *Investigation of Potential Environmental Impacts due to the use of Phosphate-based Corrosion Inhibitors in the District of Columbia* (July 22, 2004) ("Cadmus Report"). As noted in TEWG's Desktop Study, orthophosphate "has been used for many years as a reliable, known and safe chemical additive that has been shown to reliably reduce lead and copper corrosion." *See* Letter from Jon M. Capacasa to Thomas P. Jacobus and Jerry N. Johnson (May 28, 2004).

EPA has considered the known studies and data. In addition, EPA has consulted with members of the TEWG, the Independent Peer Review Panel, other experts attending the recent Lead and Copper Rule Workshop, and regulators in states that have water distribution systems using orthophosphate and/or zinc orthophosphate. EPA has concluded that zinc orthophosphate and orthophosphate are likely to be equally effective in achieving corrosion control end points in the District of Columbia drinking water distribution system. It should be noted that the proposed application of orthophosphate will not immediately decrease lead levels in the tap water. It is expected that lead levels will decrease over the course of implementing the proposed treatment.

A measurable reduction of lead levels may take more than six months and possibly more than a year.

The partial system application to the 4th High Pressure Zone commenced on June 1, 2004. After reviewing the available data the Technical Expert Working Group reached consensus that there were no water quality monitoring results that would warrant delaying full system application of orthophosphate as a corrosion inhibitor. Although data from the 4th High Pressure Zone application have not yet shown a reduction in lead levels, this was expected based on experts' opinions and TEWG members' experiences elsewhere. Data did show some elevated numbers of heterotrophic plate count bacteria at several sample sites and elevated color and iron levels in about one third of samples taken from fire hydrants. These results can reasonably be expected during the start-up phase of a phosphate-based corrosion inhibitor treatment. There have been no customer complaints of red water in the 4th High Pressure Zone. The equipment installed to perform this temporary chemical feed has performed well. In summary, no results indicated unresolvable problems in connection with application of orthophosphate in the 4th High Pressure Zone, and no unexpected results from the water quality monitoring were seen. The TEWG's consensus, from its discussion on July 28, 2004, is that there is no reason to delay application of a full system treatment.

EPA considers this interim OCCT designation to be part of an ongoing process. Pursuant to 40 C.F.R. § 141.82(h), "[u]pon its own initiative or in response to a request by a water system or other interested party, [EPA] may modify its determination of the optimal corrosion control treatment ... where it concludes that such change is necessary to ensure that the system continues to optimize corrosion control treatment. A revised determination shall be made in writing, set forth the new treatment requirements, explain the basis for [EPA's] decision and provide an implementation schedule for completing the treatment modifications." EPA's interim OCCT designation is informed by its understanding that additional studies are being undertaken. For example, the TEWG is conducting pipe loop experiments to evaluate optimal treatment dose, pH and other factors. The Washington Aqueduct also is studying means to optimize pH stability. Other ongoing research includes: investigation into galvanic corrosion related to water meter replacement; flow-through pipe loop studies; lead corrosion behavior studies in household plumbing (lead profiling); pipe scale analysis; a study of lead leaching rates; and pipe loop studies to compare the relative effectiveness of zinc orthophosphate and orthophosphate in reducing lead levels. In addition, studies are planned on galvanic corrosion related to partial lead service line and water meter replacement and potential impacts on corrosion rates from electrical system grounding to home plumbing systems.

Conditions and Water Quality Parameters

The Washington Aqueduct will use an orthophosphate product that meets ANSI/NSF Standard 60: Drinking Water Chemicals – Health Effects. Based on the NSF certification, the application of orthophosphate is not expected to cause adverse human health effects. In addition, the application of orthophosphate is not expected to have an adverse effect on the Blue Plains Wastewater Treatment Plant or the Arlington County Water Pollution Control Plant. *See* Cadmus Report. Discharges of potable water from the drinking water distribution systems in the District of Columbia, Arlington County and the City of Falls Church to receiving streams through planned and unplanned events such as line flushing, water main breaks, combined sewer overflows, lawn watering, etc. are not expected to cause any adverse effects to the receiving streams.

The application of orthophosphate may cause temporary rust-colored or "red water" events in the tap water, a potential increase in total coliform bacteria due to breakdown of biofilm on the pipes, and an increase in calcium (lime) deposits in water mains and residential plumbing. Total coliform are indicator bacteria and any increase in total coliform bacteria caused by the application of orthophosphate does not present a human health risk. Information regarding these possible effects and what to do if there is "red water" was provided by EPA in two public information sessions conducted on April 27 and 29, 2004, by DCWASA in a public information session conducted May 24, 2004, and by the TEWG's fact sheet, which is posted on the District of Columbia Department of Health's website. EPA, DCWASA, the District of Columbia Department of Health and the Washington Aqueduct will continue with outreach programs designed to inform consumers of steps that should be taken as a result of the application of orthophosphate. DCWASA has informed EPA that DCWASA intends to send a letter to its customers informing of them of the application of orthophosphate and the steps that should be taken if they experience discolored water. EPA and the TEWG are scheduling additional public information meetings as well.

DCWASA, with support from Washington Aqueduct contractor flushing crews, will proceed with a unidirectional water main flushing program as quickly as possible to complete flushing the entire DCWASA distribution system prior to the onset of freezing weather. During this and all subsequent water main flushing events, DCWASA shall implement best management practices (in addition to dechlorination) to minimize discharges associated with water main flushings to storm sewers and receiving streams. Such best management practices shall include, but not be limited to, exercising best efforts to avoid conducting line flushings in combined sewer overflow ("CSO") service areas during or immediately after storm events and identifying and monitoring relevant CSOs during line flushings to determine whether the line flushings are associated with any discharges from CSOs.

No later than December 1, 2004, or within ten (10) days of completing a study to analyze pH control (whichever is sooner), the Washington Aqueduct shall submit to EPA a study analyzing methods of pH control designed to achieve the WQP goals set forth herein.

Monitoring

Pursuant to 40 C.F.R. § 141.82(f), EPA is required to set WQPs for water supplies implementing corrosion control treatment. The interim WQPs and WQP goals set forth herein apply both to water entering the distribution system and to water quality as measured in tap water samples from the distribution system collected pursuant to 40 C.F.R. § 141.87 and this letter. The Washington Aqueduct will be responsible for monitoring and achieving the WQPs for water entering the distribution system. DCWASA will be responsible for monitoring and achieving the WQPs in the distribution system. The interim WQP for orthophosphate in water entering the distribution system is set as a range to account for the possibility that the Washington Aqueduct may need to adjust treatment for a short period of time to respond to temporary conditions in the distribution system (such as red water). The pH values for waters entering the distribution system are expressed as a range to allow the Washington Aqueduct to make adjustments to consistently attain WQPs in the distribution system. The interim WQP goals will serve as targets which both the Washington Aqueduct and DCWASA should strive to achieve.

Along with the typical parameters required of systems using a phosphate-based corrosion inhibitor, EPA is requiring that DCWASA monitor for and report supplemental parameters in the distribution system to help determine whether the application of orthophosphate causes any unexpected water quality changes. Because the purpose of monitoring for and reporting the supplemental parameters is to assist EPA, DCWASA and the Washington Aqueduct in evaluating and fine-tuning operations, the requirement is for monitoring and reporting, and no numeric values have been assigned to the supplemental parameters.

The Washington Aqueduct shall conduct monitoring for WQPs according to the requirements in 40 C.F.R. § 141.87. DCWASA shall conduct monitoring for WQPs according to the requirements in 40 C.F.R. § 141.87, with the following modifications. With respect to frequency, DCWASA shall monitor for WQPs monthly at all sample locations. DCWASA also shall monitor all locations selected pursuant to 40 C.F.R. § 141.87 for all parameters set forth below, including those parameters designated as “monitor and report.” DCWASA’s compliance with the numeric interim WQPs established herein shall be assessed based upon monitoring conducted at the locations selected pursuant to 40 C.F.R. § 141.87.

In addition to monitoring at the locations selected pursuant to 40 C.F.R. § 141.87, DCWASA also shall monitor at least twenty-five (25) additional or “supplemental” locations to provide additional information on any changes in the water chemistry during the passivation period. Monitoring at the supplemental locations shall consist of monitoring and reporting for all parameters set forth below, including pH, orthophosphate, free ammonia nitrogen and nitrite/nitrate nitrogen. Although DCWASA must monitor and report parameter values for these twenty-five supplemental locations to comply with 40 C.F.R. §§ 141.82 & 141.87, compliance with the numeric interim WQPs for pH, orthophosphate, free ammonia nitrogen and nitrite/nitrate nitrogen will not be assessed based on the data from these supplemental locations. Monitoring at the supplemental locations shall be conducted in accordance with a supplemental monitoring plan described below.

Prior to the full system application of orthophosphate, DCWASA shall develop and submit to EPA for review a supplemental water quality monitoring plan. This plan shall identify at least twenty-five (25) additional or “supplemental” sample locations beyond those required by 40 C.F.R. § 141.87. The additional or “supplemental” sample locations shall be representative of dead-end and low flow areas of the distribution system confirmed using DCWASA’s calibrated hydraulic model. The supplemental water quality monitoring plan also shall include monitoring for all parameters listed below at all sampling locations, both those identified in the supplemental water quality monitoring plan and those identified pursuant to 40 C.F.R. § 141.87.

Reporting

The Washington Aqueduct and DCWASA shall report WQP monitoring data as required by 40 C.F.R. §141.90 with the modifications below. WQP reports are due to EPA within ten (10) days of the end of each monthly monitoring period. Where the tenth day falls on a weekend or holiday, reports are due the first business day thereafter.

DCWASA shall also report to EPA data collected under the supplemental WQP monitoring plan within ten (10) days of the end of each monthly monitoring period. Data for the parameters identified below as "monitor and report" will be used by EPA, the Washington Aqueduct, and DCWASA for evaluating and fine-tuning operations.

At this time, EPA is setting interim WQPs and WQP goals for the passivation period. As stated above, once the distribution system is passivated, EPA will establish more refined WQPs to be achieved in connection with maintenance of corrosion control. EPA anticipates that the WQP goals provided herein will form the basis of the more refined WQPs associated with the maintenance of corrosion control that will be established by EPA following the initial passivation period.

Interim Water Quality Parameters for the Passivation Period

For water entering the distribution system during passivation period
(These apply to Washington Aqueduct):

	InterimWQPs	WQP Goals
pH	7.8-7.9 ± 0.3	7.8 ± 0.1
Orthophosphate	1.0-5.0 mg/l*	3.0 mg/l*

*dose necessary to reach this residual in tap samples

For water samples from the distribution system during passivation period
(These apply to DCWASA):

	Interim WQPs	WQP Goals
pH	7.7 ± 0.3	7.7 ± 0.1
Orthophosphate residual in tap samples	1.0-5.0 mg/l	3.0 mg/l
free ammonia nitrogen	0.5 mg/l	0.2 mg/l
nitrate/nitrite nitrogen	0.5 mg/l	≤ 0.1 mg/l

Supplemental Parameters	
free chlorine	monitor & report
total chlorine	monitor & report
temperature (○C)	monitor & report
alkalinity	monitor & report

Calcium hardness as CaCO3	monitor & report
Calcium dissolved hardness	monitor & report
iron	monitor & report
aluminum	monitor & report
total dissolved solids	monitor & report
oxidation-reduction potential	monitor & report
sulfate	monitor & report
color	monitor & report
heterotrophic plate count bacteria	monitor & report
total coliform bacteria and fecal coliform or E. coli testing of total coliform positive samples	monitor & report
free ammonia	monitor & report
total ammonia nitrogen	monitor & report
dissolved PO4	monitor & report
total PO4	monitor & report

Thank you for your efforts to help secure a long term solution to elevated lead levels in the District of Columbia drinking water distribution system. If you or your staff require additional information, please contact Rick Rogers, Water Protection Division, EPA Region III at (215) 814-5711.

Sincerely,

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cc: Hugh J. Eggborn, Director, Office of Water Programs, Culpepper Field Office, Virginia Department of Health,
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Appendix B Oxidant/Disinfectant Chemistry and Impacts of Lead Corrosion

Oxidant/Disinfectant Chemistry and Impacts on Lead Corrosion

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Background

In response to continued elevated lead levels throughout the District of Columbia's distribution system, a collaboration was begun with the District of Columbia's Water & Sewer Authority (WASA) and Water Resources Division of U. S. Environmental Protection Agency's (USEPA) Office of Research and Development in late winter of 2004 to investigate the causes of the sudden increases in lead release. Lead levels had been slightly above the Action Level in 1991 through 1994. Although increases in pH and the addition of orthophosphate were investigated in pilot studies and desktop corrosion studies at that time, the 90th percentile lead levels dropped to below 0.012 mg/L throughout the mid- to late 1990s. This coincided with a program of increased flushing and considerably elevated free chlorine dosages (often as high as 4 mg/L) to provide improved control of biofilms and bacterial regrowth. However, by 2000, concern with the upcoming increases in stringency of disinfection byproduct regulations led to a decision to change to chloramination in an attempt to keep trihalomethane (THM) levels below the new standards. The change was made in November of 2000, and in the next Lead and Copper Rule (LCR) monitoring round, the 90th percentile lead level surprisingly was found to have jumped to over 0.07 mg/L. Subsequent LCR 90th percentile results have remained over 0.04 mg/L. The general history of lead levels is illustrated in Figure 1, keeping in mind that some sampling periods are represented by some different monitoring sites in the site pool, and there were also differences in the number of sampling sites required.

Although there was considerable skepticism that chloramination could have been the cause of the sudden elevation of lead levels, some apparent increases of lead and copper release and attack on brass had been reported before in several investigations (Larson et al., 1956; James M. Montgomery Consulting Engineers, 1982; Francis, 1985a, 1985b; James M. Montgomery Consulting Engineers, 1985; Schock, 1999). In fact, reviews of general aspects of the redox chemistry of disinfectants and consideration of the different chemical behavior of metals in their different common valence states (eg. Fe, Mn, Cu, Pb) do suggest that any substantial change in the oxidation/reduction potential (ORP) could substantially alter the behavior of pipe scales and

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the potential for corrosion byproduct or contaminant release (AWWARF-TZW, 1996; Schock, 2000; Schock & Holm, 2003).

While most water treatment and water chemistry specialists are very familiar with the radically different solubilities and scale formation properties of ferrous iron versus ferric iron, or cuprous copper versus cupric copper, there is much less realization of the same potential behavior of lead. Potential-pH diagrams for the lead system going back many years have a prominent stability field for the highly insoluble lead dioxide (PbO_s) solid (Delahay et al., 1951; Pourbaix et al., 1966; Pourbaix, 1973; Schock, 1980, 1981; Schock & Wagner, 1985; Schock et al., 1996; Schock, 1999). Thus, an analogy can be drawn between the Pb(IV)-Pb(II) redox couple and the Fe(III)-Fe(II) redox couple. The higher valence state forms oxide or oxyhydroxide scale phases of much lower solubility than those of the lower valence state. In the case of lead, however, the ORP required for the transformation of Pb(II) to Pb(IV) is much higher than for the ferrous to ferric iron transformation. Because of typical free chlorine dosages, consumer dislike of chlorinous tastes and odors, normal water residence times, and the usual pipe wall and bulk water oxidant demands, such highly oxidizing conditions will not be common amongst public water systems in the United States.

USEPA analyses of scales from lead pig-tails and service lines in the late 1980's and early 1990's verified that one or both of the common polymorphs of PbO_2 (plattnerite and scrutinyite) were present in varying degrees on the pipes from several different water systems (Schock et al., 1996). Thus far, of more than 85 lead pipe specimens obtained from 34 water systems, at least 16 specimens representing 9 systems have either α-PbO_2, or β-PbO_2, or both present in clearly identifiable quantities. More samples may have trace amounts that are hard to positively confirm. Usually, the PbO_2 exists in the form of patches or a thin surficial layer at the water boundary. PbO_2 comprises nearly the entire scale material in the pipe samples from WASA and Cincinnati, and the majority of the scale material in some Oakwood, OH specimens. In Madison, WI, it formed a rather distinct surficial layer in contact with the water. The presence of PbO_2 is associated with waters of persistently high ORP. The elevated ORP could be caused by any of several mechanisms. For example: pristine low-NOM ground waters with little bulk oxidant demand allowing significant persistence of free chlorine; waters that very effectively passivate iron and remove its oxidant demand (such as hard waters with high buffering intensity); waters with low oxidant demand resulting from oxidative treatments such as greensand filtration (enabling the stability of high ORP); and many other possible scenarios. An additional cause can be the use of very high dosages of free chlorine to combat biofilm problems or to overcome corrosivity towards iron and its pipe wall demand.

More pipe analysis investigations by the U. S. Environmental Protection Agency in 2000 and 2001 revealed much more evidence for the importance of tetravalent lead compounds as very large primary components of lead service line scale material, particularly those in Cincinnati, Ohio and Madison, Wisconsin (Schock et al., 2001). In the Cincinnati pipe, representing long periods of relatively high disinfectant concentrations, followed by a combination of granular activated carbon and free chlorine treatment, essentially the entire scale was composed of the two PbO_2 polymorphs, with only traces of basic lead carbonate. It is not known when the PbO_2 scale formed in the Cincinnati pipe, as there were no historical scale analyses during several earlier treatment schemes. For the distribution system area where the Cincinnati pipe specimens were obtained, it has employed elevated pH (8.5 to 9.2) since the 1980s for corrosion control. The lead service line specimens from Madison had a thin layer of PbO_2 at the water interface, with $PbCO_3$ making up the bulk of the underlying scale. An important amount of tetravalent lead scale material was also found in pipe from Oakwood, Ohio (another pH 7 high alkalinity water where greensand filtration for iron removal is employed). Taken in combination, these observations finally provide a reasonable hypothesis to explain the apparent anomaly observed in many field studies in which high alkalinity waters did not tend to produce nearly as high levels of lead release as would be expected from the knowledge of lead solubility chemistry and bench-scale tests (Dodrill & Edwards, 1994; Dodrill, 1995; Dodrill & Edwards, 1995; Edwards et al., 1999).

Pipe Scale Analyses Results

Lead service line specimens from residential homes in the District were shipped to the WSWRD, U. S. Environmental Protection Agency lab in Cincinnati, with their ends sealed to preserve humidity and moisture. The specimens were cut longitudinally with a band saw having a fine metal-cutting blade, and were photographed with a stereomicroscope at 6 to 66 X. Figures 2 and 3 illustrate some of the specimens from the WASA system that were analyzed, and how they compare to similar scales composed of large amounts of tetravalent lead compounds from other water systems.

Scale was removed and analyzed by X-ray powder diffraction using the same procedures as described previously (Schock et al., 2001). When lead carbonate and hydroxycarbonate solid phases are present, the positive identification of PbO_2 can be somewhat problematic, because some of the significant diffraction peaks of β-PbO_2 and α-PbO_2 overlap with some of the peaks from PbO (litharge) and $PbCO_3$ (cerussite). While the d-space accuracy of the carefully-calibrated diffractometer should be more than sufficient to positively identify the phases of interest, the naturally-formed solids tend to have lattice distortions and peak broadening from small crystallite sizes. Both of these factors complicate the positive identification of PbO_2 polymorphs.

Therefore, to confirm the existence of tetravalent lead phases and corroborate the XRD results, the Pb pipe scales were additionally analyzed by X-ray absorption near edge (XANES) and X-ray absorption fine structure (XAFS) spectroscopies. For XANES and XAFS studies, a thin layer of a Pb scale was smeared onto Kapton tape and folded back on itself. Pb (13035 eV) L_{III}-XANES and XAFS data were collected at Sector 20-BM (Pacific Northwest Consortium - Collaborative Access Team (PNC-CAT)) at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. The electron storage ring operated at 7 GeV. Three scans were collected at ambient temperature in fluorescence mode with an Ar-purged Lytle detector. A 0.5 mm premonochromator slit width and a Si(III) double crystal monochromator detuned by 20% to reject higher-order harmonics was employed. The beam energy was calibrated by assigning the first inflection of the absorption edge of lead metal foil to 13 035 eV. Reference samples of PbO (massicot), $PbCO_3$ (cerussite), $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite), $Pb_5(PO_4)_3Cl$ (chloropyromorphite), $Pb(NO_3)_2$, β-PbO_2 (plattnerite), and Pb_3O_4 were commercially obtained for comparison with the XANES and XAFS spectra. The phase identities were confirmed by XRD. The collected scans for a particular sample were averaged, the data were then normalized, and the background was removed by spline fitting using WinXAS 2.0 (Ressler, 1998).

Because the scales were very thin and tenaciously adherent to the pipe surfaces, only small amounts (tens of milligrams) were available for analysis. Subsamples have also been sent by USEPA to the U. S. Geological Survey laboratory in Denver, for digestion and elemental analysis to investigate general scale chemistry and to try to help identify some of the other trace compounds present in the diffraction patterns.

Figures 4 and 5 show examples of the XRD and XANES patterns that confirmed that the WASA lead pipes are coated with a thin and uniform layer of α- and β-PbO_2.

Discussion

Conventional lead corrosion control theory, which is normally based on divalent lead chemistry, would predict solubility behavior approximately as represented in Figure 6. This was done using the LEADSOL computer program (Schock, 1980; Schock et al., 1996) with some representative concentrations for chloride, sulfate and total inorganic carbon. Figure 7 illustrates the difference in trends and order of magnitude of solubility for tetravalent lead as opposed to divalent lead.

Trying to model Pb(IV) solubility is full of difficulties, as there is little relevant data appropriate to potable water systems. Some of these issues have been addressed previously (Schock et al., 2001). Due to lack of stability constant data and speciation data, the model followed suggestions of Pourbaix (1966) as a first approximation. Only PbO_3^{2-} and PbO_3^{4-} complexes were included. The accuracy of the thermodynamic data and the proper species to choose for the aqueous model is highly questionable. However, even if considerably off, it still strongly argues that tetravalent solubility is remarkably lower than in well-treated systems working with divalent lead scales. Using the existing tentative aqueous solution model for Pb(IV), tetravalent lead solubility is predicted to be at its lowest level at a pH even below neutrality. Hence, the solubility minimization trend with pH is intriguingly opposite that of Pb(II) in the normal pH range for controlling corrosivity to metallic materials, approximately pH 7 to 10.

No specific information on identified Pb(IV) orthophosphate or carbonate-containing solids has been uncovered so far. Whether or not orthophosphate interacts with tetravalent lead is also hard to determine reliably, because of conflicting published interpretations of experimental results from lead-acid battery performance investigations (Voss, 1988). At very high phosphoric acid concentrations, some evidence has been found for some stable Pb(IV)-orthophosphate complexes or poorly-crystalline materials (Amlie & Berger, 1972). Some research suggests that orthophosphate facilitates reversibility of oxidation and reduction by surface sorption and modification of the PbO_2 phases, while other research suggests that the orthophosphate could bind with Pb(II) and reduce the formation of $PbSO_4$ (Bullock & McClelland, 1977; Bullock, 1979a; Bullock, 1979b, 1980; Voss, 1988). The high acidity and extremely high concentrations of sulfuric and phosphoric acids present in such systems cannot be directly applied to estimate the relative impacts at concentrations thousands of times lower in drinking water solutions. One of the most interesting aspects of the literature, however, is that PbO_2 solids may readily function as semiconductors (Greninger et al., 1975). Thus, there is likely considerable electrochemical reversibility and ease of electron transport between the water and the underlying lead metal of the pipe, making responses of the scale to changes in ORP rather fast and measurable.

The critical role that the concentration and type of disinfection plays in the formation and solubility of passivating films on lead service line piping is clarified by Figure 8. The top figure is a simple potential-pH diagram for 1 mg/L free chlorine, showing the speciation of the chlorine system and the high ORP necessary for free chlorine stability. These fields are considerably above the thermodynamic water stability boundary. The bottom two graphs show the comparison of ORP values obtained using different concentrations of monochloramine solution and free chlorine in recent USEPA laboratory studies by James, et. al. (2004). Note the ORP produced by monochloramine concentrations are far lower than those produced by the same concentration of free chlorine. Referring to the potential-pH diagram for lead (Figure 9), it can be seen that free chlorine at high dosages can produce sufficiently high ORP to form PbO_2. These experimental data are in good agreement with values extracted from the research literature in papers relating to virus inactivation studies or breakpoint chlorination studies (Schock et al., 1996).

There are some uncertainties in the PbO_2 field boundary because of the imprecision and possible inaccuracy of the tabulated free energy of formation data, although it is qualitatively consistent with the analyzed scale material and the solubility behavior in the actual lead piping. The boundary would shift upward (higher ORP needed) if the PbO_2 material is less soluble than predicted by the published data. However, there is clearly a straightforward mechanism that can readily explain the sudden rise in dissolved lead release (as well as some particulates) when the ORP is lowered. In the pH range of normal operation (high 7's to low 8's), divalent lead solubility is considerably higher than the Action Level, and observed lead levels in targeted samples representing water in direct contact with the lead service lines for "overnight" standing periods were in an amazingly similar range (100 to 200 µg/L) to that predicted by the solubility model. Unfortunately, specific lead service line sample data was not available from the late 1990's when the 90th percentile values were very low and the ORP was very high from the use of free chlorine. However, given the first-draw relationships to the service line concentrations in the current sampling (post-chloramination), the lead levels were probably very low during that time period, consistent with tetravalent lead solubility trends. Note that of 5 second-draw sample collections in 1997-2000, the 90th percentile for the second-draws were equal or lower than the 90th percentiles for the first draws in 3 cases and only slightly higher in the other two cases. Since the change to chloramination and the lead scale destabilization, the 90th percentile of the second draw samples has always been at least approximately 50% higher than the 90th percentile of the first draw samples, and has generally been 2 to 4 times the Action Level.

Two other lines of investigation further corroborate the operation of the Pb(IV) to Pb(II) conversion mechanism as being the cause of the sudden increase in lead levels. During April of 2004, the normal springtime seasonal switch to 1 month of free chlorine residual (4 mg/L) was made. After 3 weeks of going back to free chlorine, several lead profiles were conducted in residential homes containing lead service lines that previously had lead profiles conducted during chloramination. In all cases, lead levels decreased substantially over that time frame (Figures 10 & 11), showing the reversibility of the lead redox reaction.

Support is also provided by data from the exhumed pipe section used in one of the "stagnation" loop tests described by Thomas et, al, (2004), shown in Figure 12. After equilibrating with the chloramines "control" condition, the disinfection was changed to hypochlorite solution (dashed reference line). The lead concentrations immediately began to drop. After about a month of operation at approximately 5 mg/L free chlorine dosage, the dosage was approximately doubled (solid reference line). As was demonstrated in the USEPA laboratory experiments (Figure 13), the ORP did not change significantly by the additional free chlorine addition. Lead levels continued to nearly linearly decrease. It is hard to tell from the data if the trend was beginning to reduce in slope after about 3 weeks of this elevated ORP when approximately 10 mg/L (as PO_4) was added to test its effect (dot/dashed line). Therefore, it is not possible at this time to unambiguously determine if the apparent stabilization is caused by interference with the oxidation of existing Pb(II) solids in the scale to PbO_2, or not. In comparison to the "control" experiment with chloramine only (not shown), the lead concentration after 2 months of return to free chlorine was more than a factor of 15 times lower. Interestingly, the total lead concentration in the control loop is similar (particularly within modeling uncertainty) or slightly higher than that predicted by the diagram in Figure 6, and the dissolved lead concentrations in orthophosphate-dosed chloraminated loops were mostly between approximately 45 and 80 μg/L, again consistent with model trend predictions, though slightly higher.

The plausibility of relatively rapid (months) formation of PbO_2 under drinking water conditions (DIC = 10 mg/L, free chlorine residual, pH 6.5 – 10) from the addition of lead chloride to water has been proven in bench experiments at USEPA (Lytle & Schock, 2004). The PbO_2 evolved from a hydrocerussite or cerussite precursor phase, and when the ORP decreased after the chlorine residual was reduced or lost, the PbO_2 decomposed. The phase transformations were observed to follow the expected trends, i.e. decreasing dissolved lead concentration during PbO_2 formation, and increases back to the carbonate phase equilibrium values after oxidant depletion and reversion. The induction period for PbO_2 formation varied with pH, but was generally only a few weeks. Decomposition after the loss of sufficient ORP was similarly only a few weeks in duration.

Future Research Needs

More lead pipe specimens will be collected and analyzed from both the service line removal program, and also from the laboratory test systems, to get an even better understanding of the scale transformations taking place.

The field data and the chemical models show that high ORP conditions will mitigate the lead solubility problem caused by the breakdown of the PbO_2 passivating scale. However, if the maintenance of high ORP conditions through free chlorine are not desired for other reasons, there is relatively little firm information upon which to base the development of an alternative treatment strategy that would be as effective against lead release.

The viability of different alternate treatment schemes are totally dependent upon the exact reaction pathway of the chemical reduction/breakdown pathway of the PbO_2, and the relative rates of the breakdown reaction(s) versus the rates of formation reactions for divalent lead compounds. For example, the breakdown of PbO_2 could follow any of several reaction paths to release lead into solution, such as (but not confirmed to be)

$$PbO_2(s) + 4H^+ \rightleftarrows Pb^{2+} + 4H_2O \tag{1.1}$$

or

$$PbO_2(s) + 2H^+ + 2e^- \rightleftarrows PbO(s) + H_2O \tag{1.2}$$

$$PbO(s) + 2H^+ \rightleftarrows Pb^{2+} + H_2O \tag{1.3}$$

Pb(II) oxide and hydroxide are both extremely soluble at any drinking water pH, so other precipitation reactions would have to be operative to limit lead levels. Once in solution, the activity of the free lead ion will be governed by the amount of complexation, primarily by bicarbonate, carbonate, and hydroxide ions (Hunt & Creasey, 1980; Schock, 1981; Schock & Gardels, 1983; Schock et al., 1996; Schock, 1999). The free lead ion can then react with carbonate or orthophosphate in the water to precipitate one of the conventional passivating solids. For example:

$$3Pb^{2+} + 2H_2O + 2CO_3^{2-} \rightleftarrows Pb_3(CO_3)_2(OH)_2(s) \tag{1.4}$$

$$5Pb^{2+} + 3PO_4^{3-} + H_2O \rightleftarrows Pb_5(PO_4)_3OH(s) \tag{1.5}$$

$$3Pb^{2+} + 2PO_4^{3-} \rightleftarrows Pb_3(PO_4)_2(s) \tag{1.6}$$

Presumably, these reaction rates would necessarily be very dependent upon pH and the activities of the passivating and complexing ligands, such as bicarbonate and orthophosphate. Unfortunately, kinetic information for these dissolution and precipitation reactions is almost completely lacking, making *a priori* estimates of lead levels and time to achieve them very unreliable. If the existing scale dissolves faster than the released aqueous lead(II) species can re-precipitate into a sufficiently insoluble passivating film, then prolonged elevated lead levels will persist, until all of the prior scale is converted. If the precipitation reactions are as fast or potentially faster than Pb^{2+} ions are released from the PbO_2 breakdown, and if the scale material adheres to the pipe surface, then the lead concentrations in the pipes will stabilize in the usual timeframes typified by the experiences of many other water systems that have successfully used pH/carbonate adjustment or orthophosphate passivation.

The current hardness of the water and the use of lime for pH adjustment essentially precludes the pH/alkalinity/TIC adjustment approach, because the necessary pH (over 9 based on theory and the experiences of other water systems) could not be achieved without major scaling problems in the filters and distribution system. Supplemental softening or some kind of carefully balanced threshold sequestration would be needed. The remaining alternative approach, using orthophosphate dosing, needs to be investigated to determine empirically what the relative rates of divalent lead passivation reactions are in comparison to the breakdown of the existing pipe scale. As noted above, if the reaction of the Pb(II) released from the breakdown of the PbO_2 scale with orthophosphate in the water (equations 1.5 and 1.6) is equal to or faster than the rate of dissolution and release into the water, then it should be possible to achieve sufficiently low lead levels in the water relatively quickly. If it is not, there is not a good basis to estimate the length of time it would take to achieve complete conversion of PbO_2 to the passivating divalent lead phosphate solids.

Very basic questions pertaining to Pb(IV) chemistry are critical to answer to provide important information necessary for revisions to lead corrosion control guidance, and to properly evaluate disinfection alternatives. These fundamental questions include:

- What are the solubility constants for the α-PbO_2 and β-PbO_2 polymorphs?
- What factors govern the formation of one polymorph as opposed to the other?
- What are the important aqueous complexes of Pb^{4+} (e.g. PO_4, SO_4, Cl, HCO_3, CO_3, OH^-)?
- What are the stability constants of those complexes?
- What reaction pathways are taken for formation and breakdown of PbO_2 phases?
- Are there other important Pb(IV) solid phases for drinking water conditions?

Little is known about the passivation mechanism for exposed soldered joints and brass devices. Whether or not PbO_2 solids can form and be stable on these kinds of surfaces is another important question, because of its relevance to the origin of lead concentrations caught in 1-liter first-draw samples.

Several studies to shed light on some of the aspects of tetravalent lead chemistry are currently underway at WASA and at USEPA. Corrosion control is intimately interrelated with other finished water quality objectives, for consumer satisfaction and regulatory compliance. Therefore, these recent discoveries of the importance of Pb(IV) chemistry in some water systems support the idea that more resources need to be mobilized quickly to gather the information needed to provide timely guidance for water systems confronted with needing to evaluate complex and costly major treatment upgrades to meet new regulatory requirements.

Disclaimer

Any opinions expressed in this paper are those of the author(s) and do not, necessarily, reflect the official position and policies of the EPA. Any mention of products or trade names does not constitute recommendation for use by the EPA.

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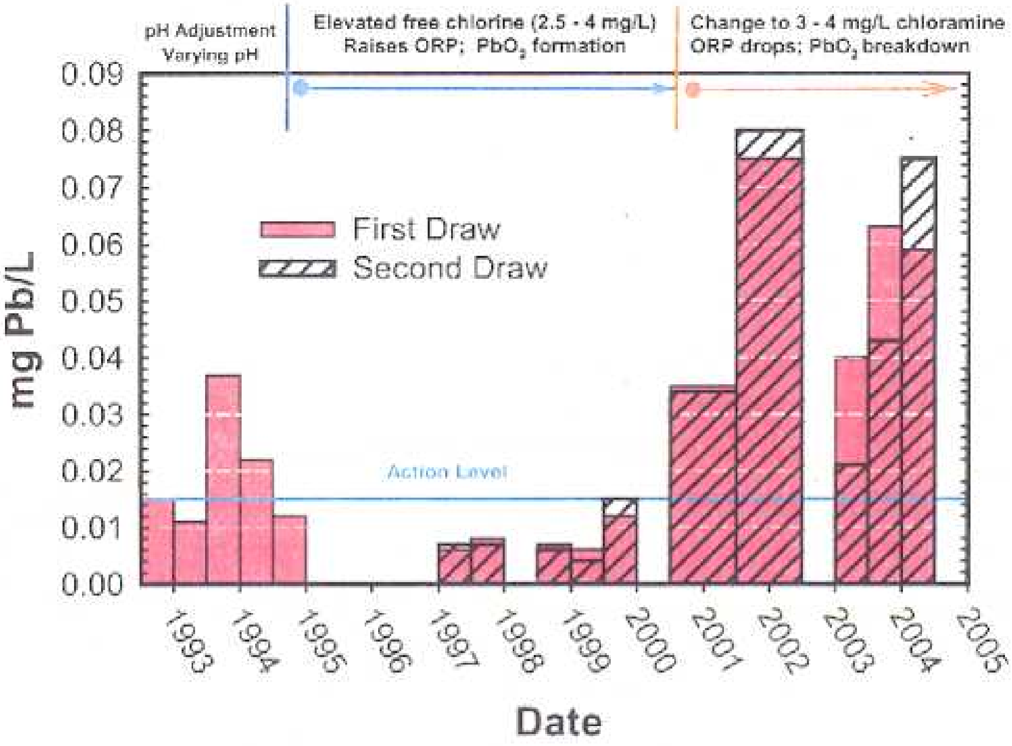


Figure 1. DC WASA lead history timeline.

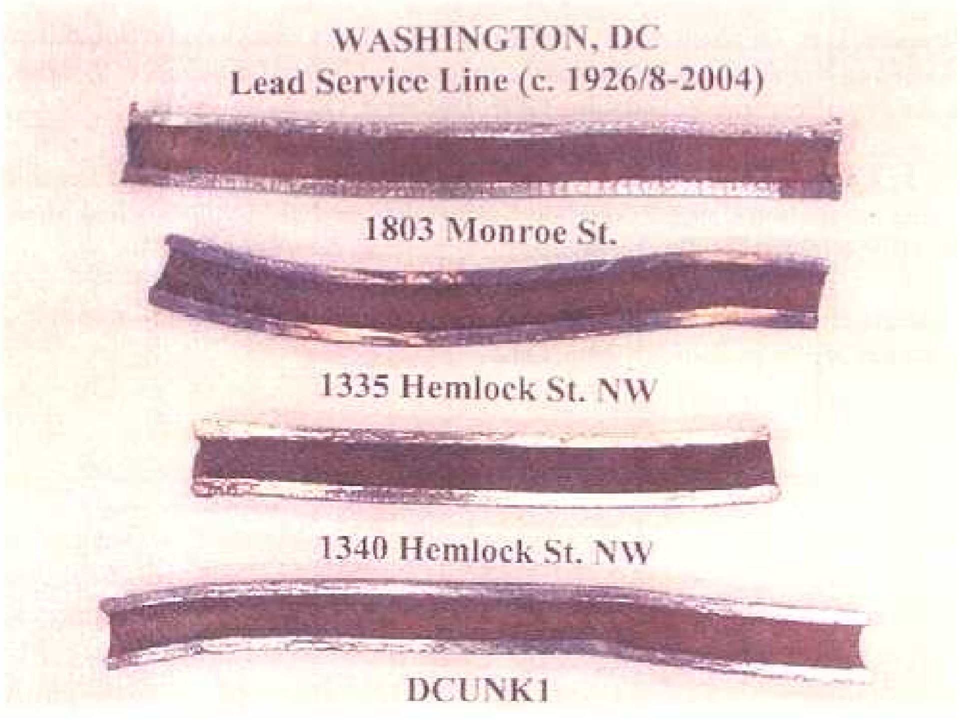


Figure 2. Lead service line scale from 4 different locations in WASA distribution system.

Figure 3. Comparison of similar PbO_2-rich scales in two other water systems, showing the similarity to the DC-WASA pipe scales.

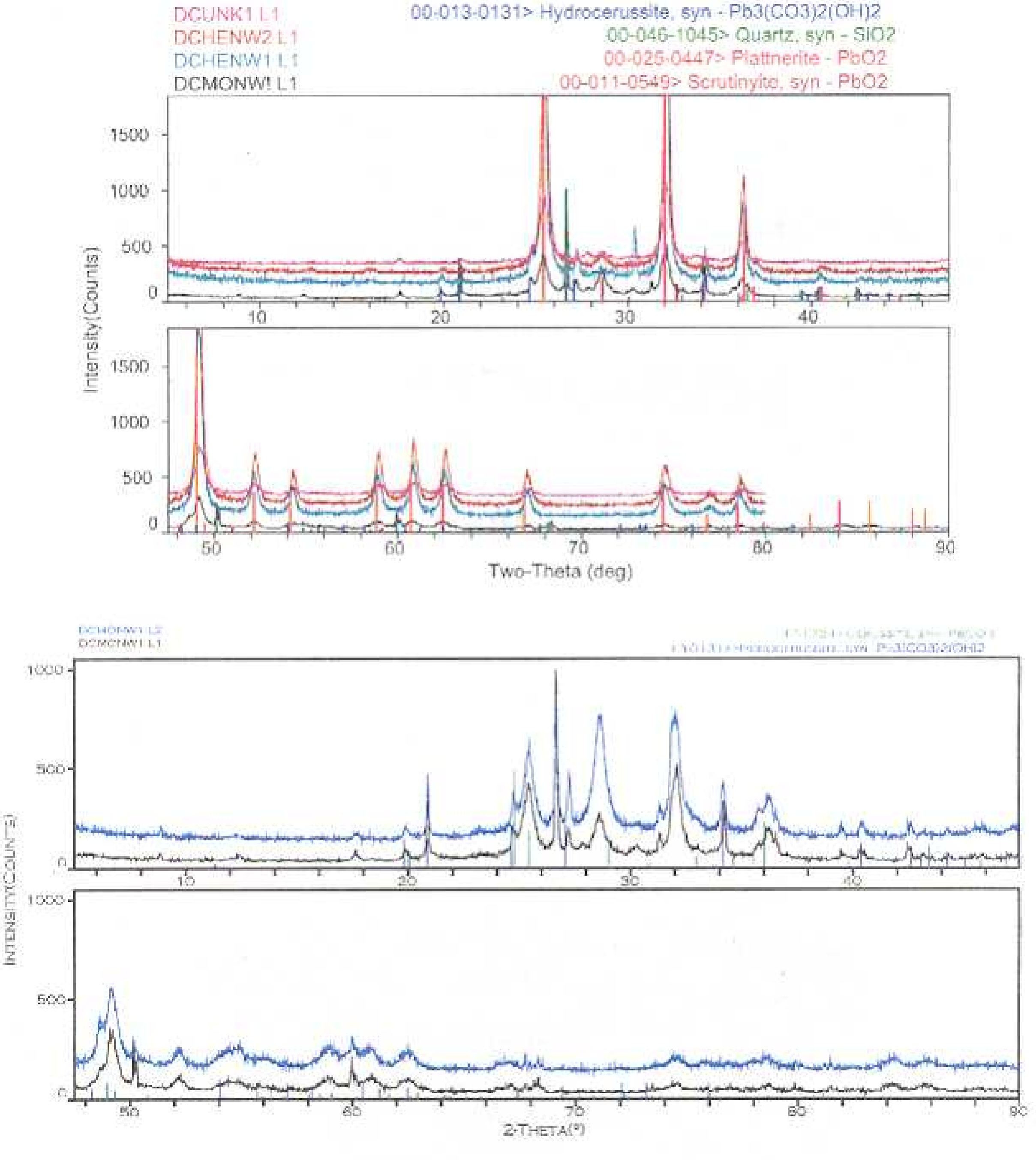


Figure 4. X-ray diffraction patterns of lead service line specimens from the WASA system. (Top) Predominance of plattnerite and scrutinyite phases in four samples and similarity of mineralogical compositions in the different locations. Hydrocerussite and quartz are minor phases on some specimens. (Bottom) Reference lines for cerussite and hydrocerussite for two scale layers (L1 nearest water), showing potential peak overlap for $PbCO_3$ with PbO_2 and the minor amount of $Pb_3(CO_3)_2(OH)_2$ present. Large peak near 27° is quartz (SiO_2).

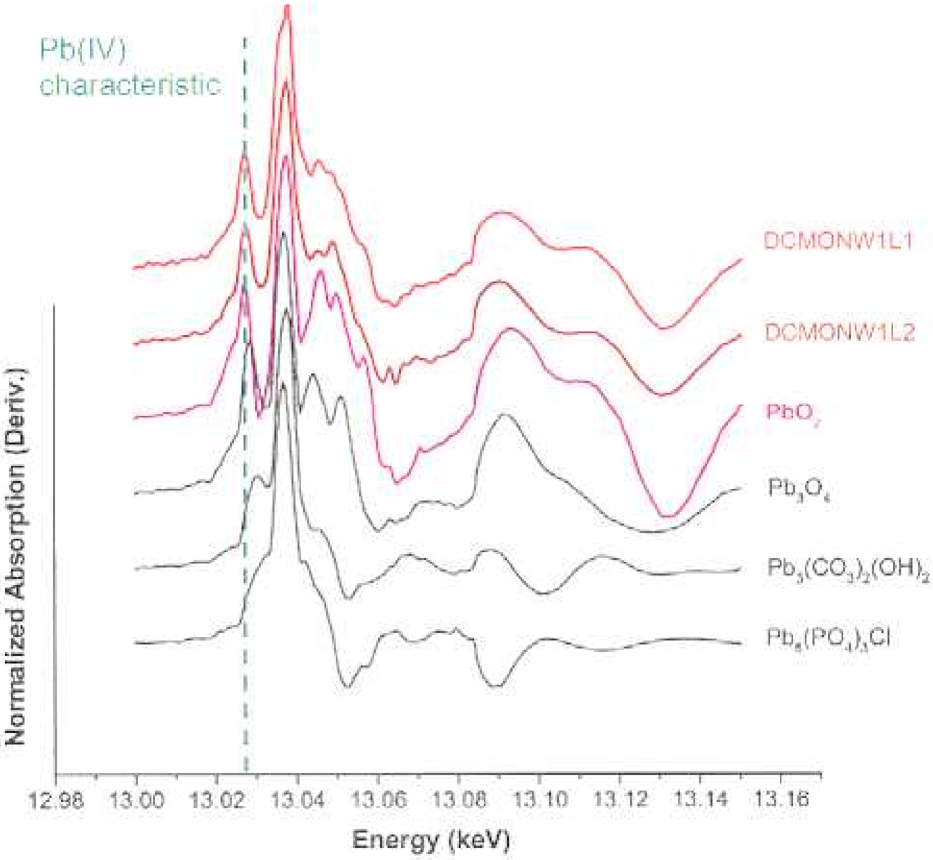


Figure 5. XANES spectra example showing uniformity of scale sample from 1083 Monroe St. NW (two layers scraped) and similarity to reference spectrum for β-PbO_2.

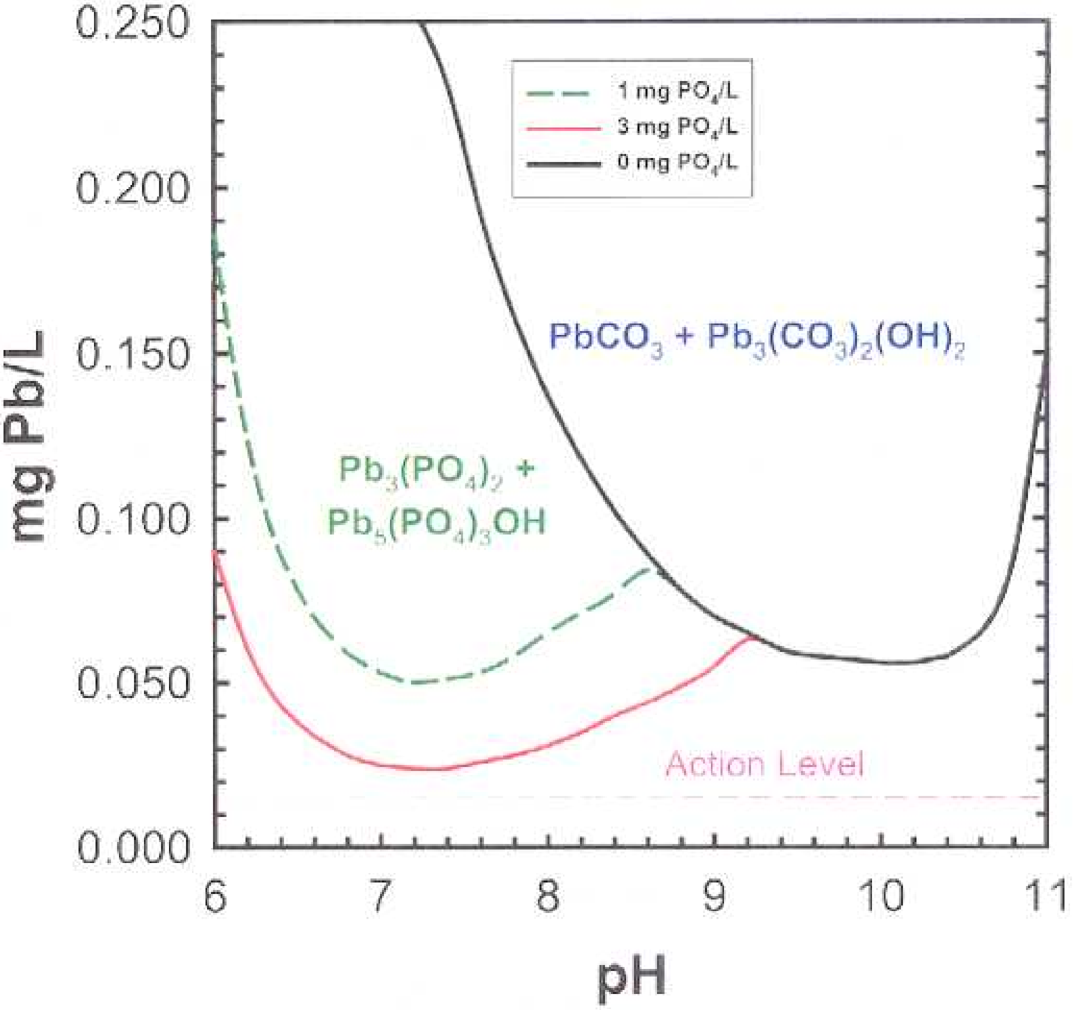


Figure 6. Solubility diagram for the impact of orthophosphate on Pb(II) species for DIC = 18 mg C/L, $Cl^- = 31$ mg/L, $SO_4^{2-} = 44$ mg/L, 0.005 M ionic strength, and 25°C.

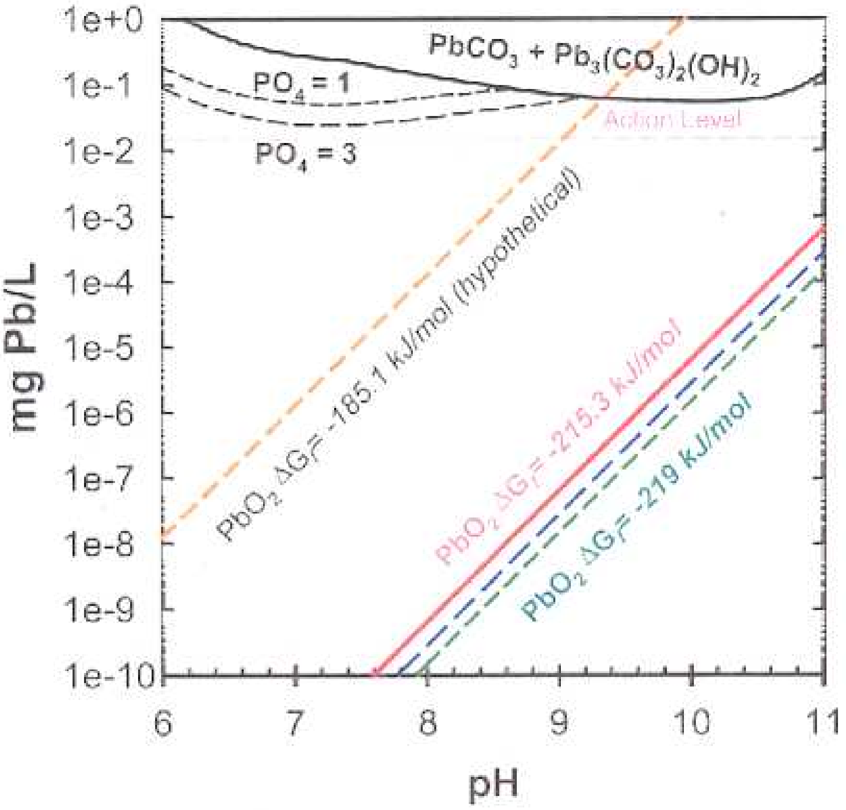


Figure 7. Computed solubility diagram for PbO_2, using several tabulated Gibbs free energy of formation values to compute the solubility constants. Shown also is the relationship to divalent lead solubility for the same water.

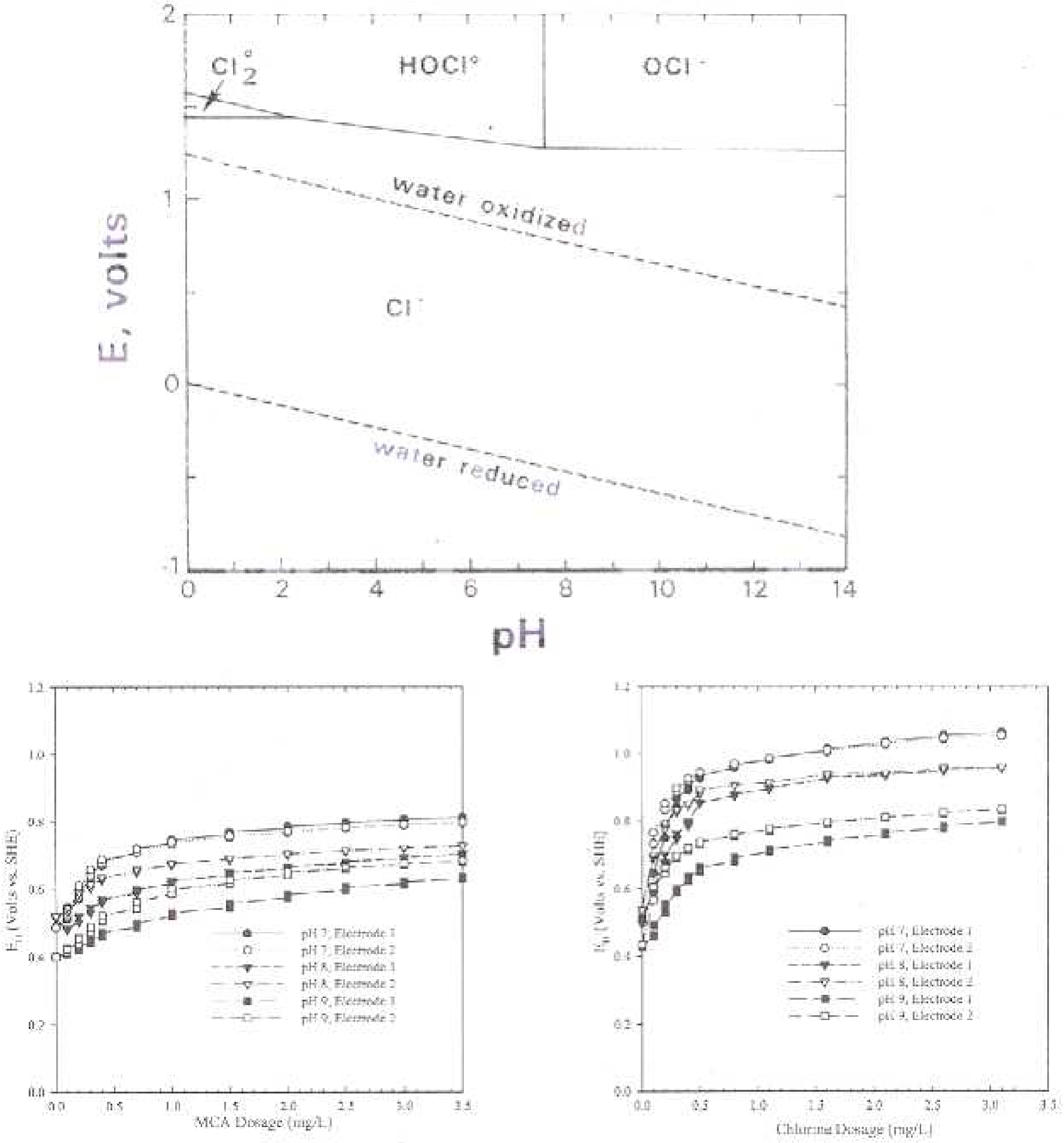


Figure 8. (Top) Potential-pH diagram for 1 mg/L free chlorine, showing the speciation of the chlorine system and the high ORP necessary for free chlorine stability, and the relationship to the water stability boundary. (Bottom) Comparison of ORP values obtained using different concentrations of monochloramine solution (left) and free chlorine (right) in USEPA laboratory studies by James, et. al. (2004). Note the consistently much lower ORPs produced by chloramines.

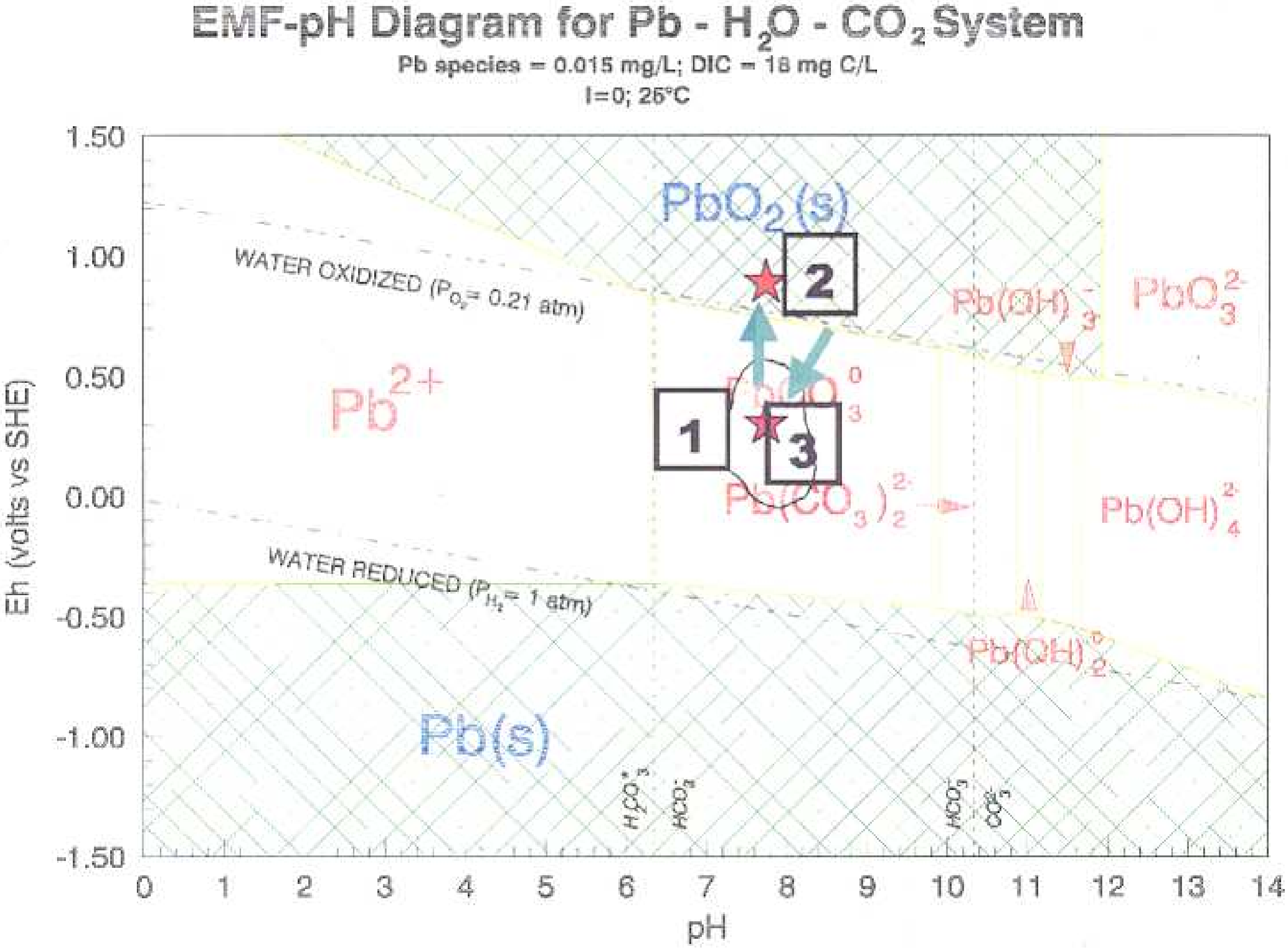
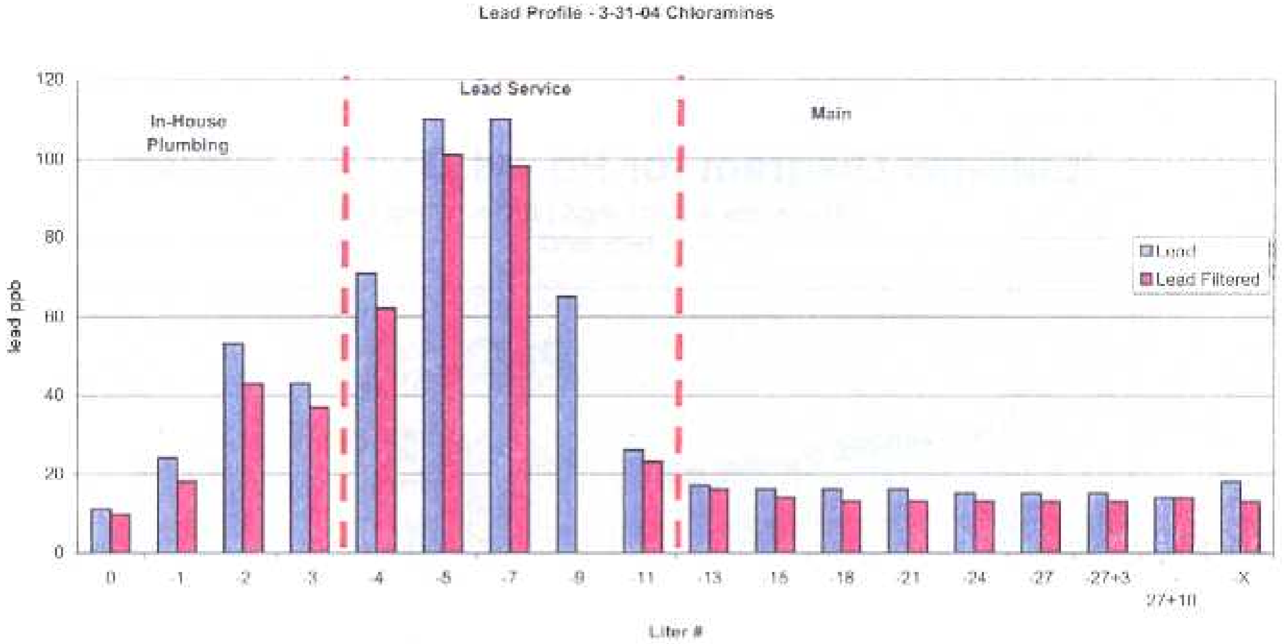


Figure 9. Potential-pH diagram for the lead system corresponding to DC-WASA water, showing how the sequence of treatment changes over the past decade formed and then destabilized the PbO_2 passivating film. (1) represents the initial conditions of the early 1990's where there were some lead release problems. The initiation of high free chlorine residuals and flushing in 1994 moved the system chemistry to approximately point (2). The change to chloramines secondary disinfection in 2001 moved the ORP back into approximately the area of (3).



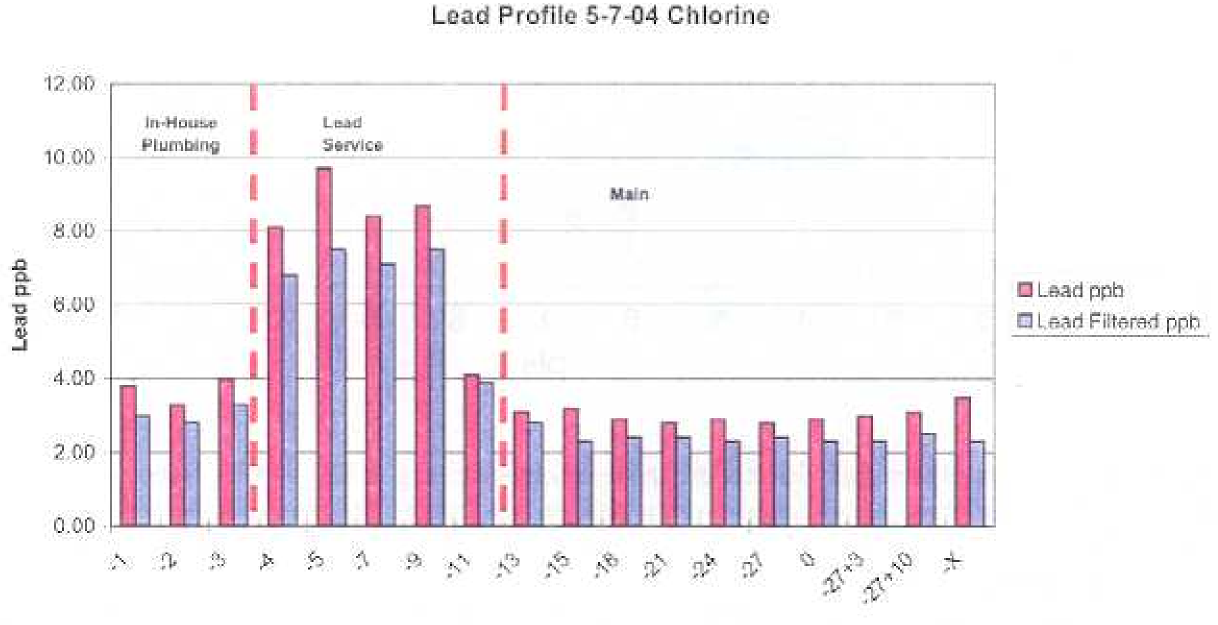


Figure 10. Lead profile conducted at the same home during chloramine (top) and chlorine. The x-axis represents the liter number taken from the tap into the main (i.e. 1 = first draw, 2 = 2nd liter, 27 = 27th liter. 27+3 represents 3 minutes after the 27th liter was taken, X = water hammer). Lead profile procedures taken from *Edwards, Giani et al 2004)*

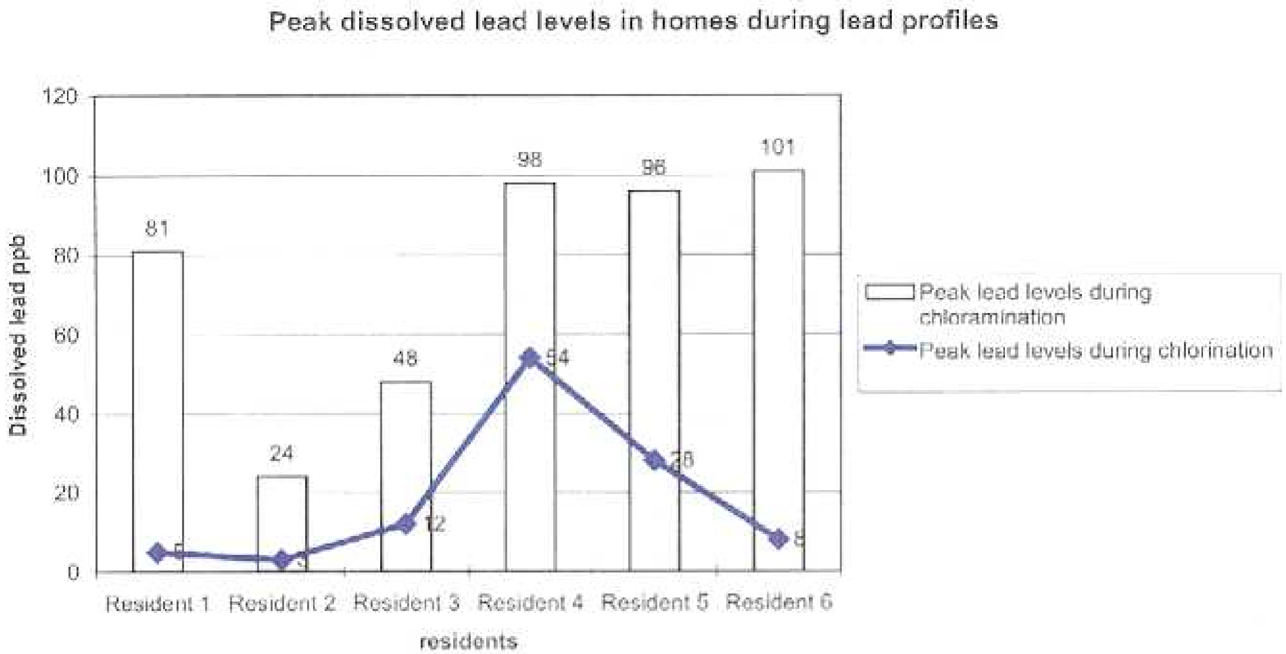


Figure 11. Peak dissolved lead concentrations taken from 6 residential homes during chloramination and chlorination.

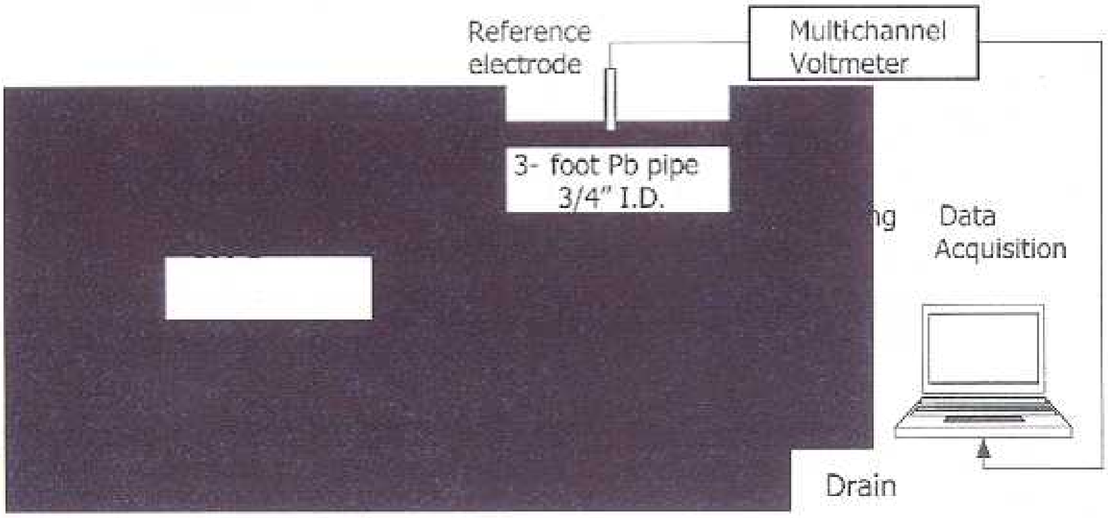


Figure 12. Stagnation loop setup diagram.

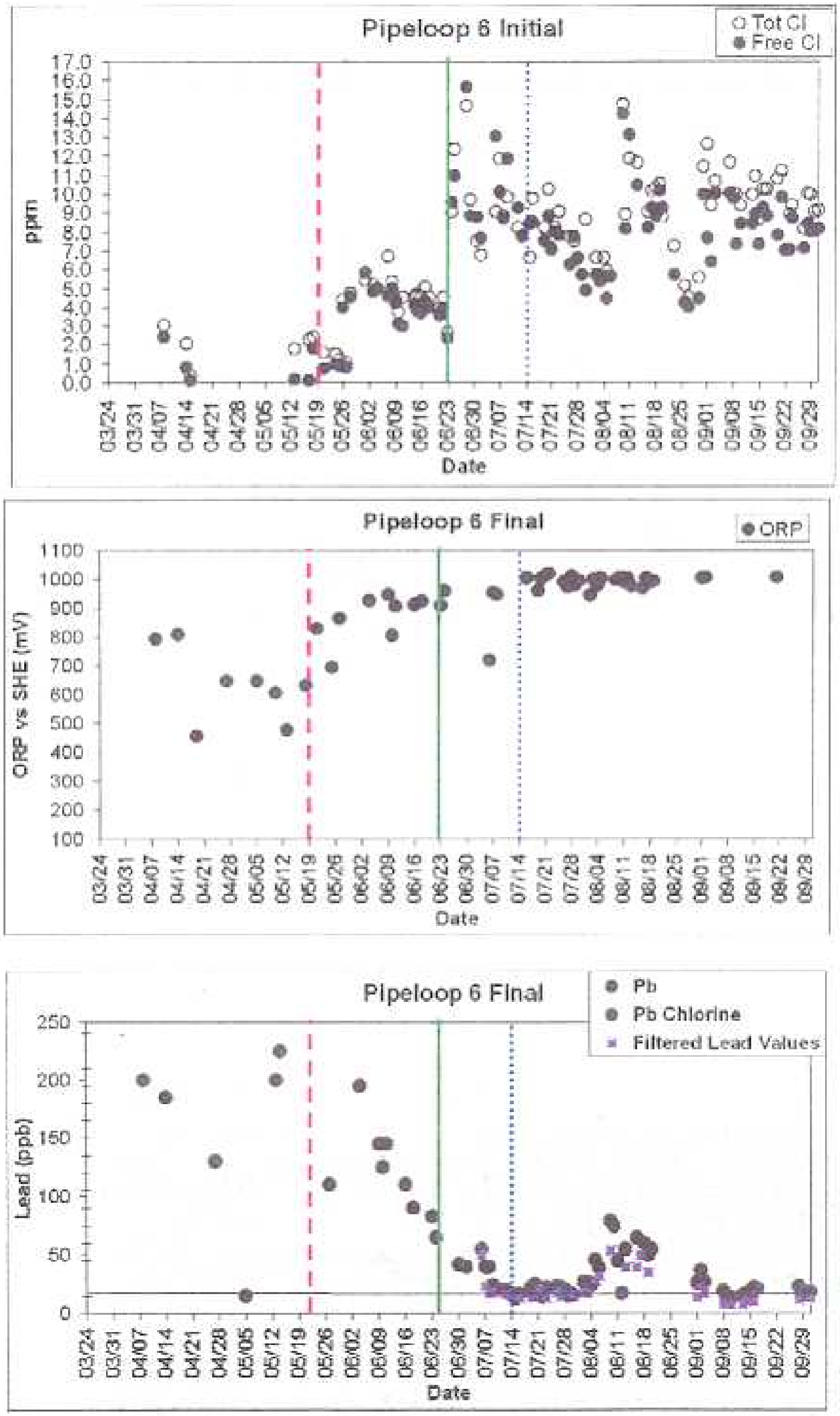


Figure 13. Laboratory "stagnation loop" data for actual removed pieces of service line, testing the effects of free chlorine and subsequent orthophosphate (10-15 mg/L as PO_4) addition on redox potential and lead release. The magenta reference line indicates the end of the conditioning period of exposure to chloraminated water, before shifting to free chlorine (top graph). The green line represents a boost in free chlorine concentration, and the blue dotted line represents the introduction of the orthophosphate dosing.

Appendix C Galvanic Corrosion and Grounding Effects Study

Final Report

Effects of External Currents and Dissimilar Metal Contact on Corrosion from Lead Service Lines

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Finalized November 2006

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Executive Summary

This study set out to investigate two basic issues and has largely succeeded at resolving both. The first issue was whether grounding or impressed currents have a significant and prolonged impact on the electrochemistry and corrosion of lead service lines (LSLs) in a water distribution system, or, for that matter, on any metal plumbing appurtenance that may be hydraulically and electrically connected to a household service line used as an electrical ground. The second principal issue was to characterize the electrical impacts associated with galvanically-coupled copper and lead service lines to determine if replacing a portion of a lead pipe with copper piping might cause accelerated lead release. Both issues relate to the potential for accelerated corrosion on LSLs leading to the release of metals in drinking water. Both have relevance to the DC WASA corrosion control program and LSL replacement program.

The specific objectives of the research were to establish under controlled laboratory conditions the absolute magnitude of the electrical impacts on LSLs associated with both grounding and galvanic coupling under a variety of pipe geometries and water chemistries. This research did not intend to explore grounding currents in an existing home or to replicate actual distribution system conditions where a partial lead service line replacement (PLSLR) had occurred. Rather, the goal was to demonstrate whether or not grounding currents or galvanic coupling could generate lead release. If a meaningful impact could not be demonstrated under conditions designed to exacerbate lead release, then it would be unlikely that a PLSLR as practiced in the DC WASA system (where conditions would be much less challenging than in the laboratory) would produce accelerated metal release. If positive effects were found, the study would then serve as a foundation for further testing.

All the LSL pipe sections used in these tests had been removed recently from residences in the DC WASA distribution system.

In brief, this study has shown that grounding and/or impressed currents moving along LSLs, end eventually leaving the pipe to ground, have no meaningful impact on internal pipeline corrosion and do not contribute to metals release. Therefore, we believe the long-debated controversy about whether or not grounding currents generate accelerated corrosion and metal release can now be considered closed. Also, while the study found that galvanic impacts can be substantial on unpassivated, newly-exposed lead surfaces, the magnitude of galvanic impacts on aged and passivated LSL surfaces and on new copper surfaces is minimal, and, in the long term, likely to be inconsequential. Therefore there is now a basis for discounting concerns relative to the long-term impacts associated with PLSLR.

A caveat that must be attached to these finding is that testing was restricted to waters with low mineral content similar to the water distributed within the DC WASA system; galvanic impacts in systems having water with a substantially higher mineral content could be more extensive and possibly more prolonged.

The significant conclusions to be drawn from this study are as follows:

- Well-aged DC WASA LSL specimens – including those that have been exposed to an orthophosphate inhibitor – are exceptionally well passivated and highly resistant to electrical perturbations of any kind.
- When a well-passivated LSL is coupled to a new length of copper tubing (as in a partial LSL replacement) the area of galvanic influence is very limited. The actual reach of the galvanic current is partially a function of the water quality, but is likely limited to the first inch of the LSL.
- A conventional plumbing dielectric junction removes even the minor corrosion risks associated with galvanic coupling. Any break in electrical continuity between the copper and LSL lines effectively eliminates the potential for significant galvanic effect.
- A chlorine residual (free or combined) does elevate the galvanic effect on the LSL/copper couple by accelerating the cathodic current exchange process. The impact overall, however, is largely limited to the galvanic influence on the copper service line. The overall impact on the LSL surface is nearly imperceptible. Interestingly, water conductivity has a more important effect on the galvanic process than chlorine residual.
- Impressed currents, whether AC or DC, on LSLs or copper service lines (including grounding type currents), have no impact on the internal corrosion of the household service lines (or any other plumbing appurtenance for that matter). There is no acceleration of corrosion associated with the conventional practice of electrical system grounding to household water systems.

Background

In theory, it is conceivable that replacing a portion of a lead line with a new copper service line could create a strong galvanic couple with an initial Cu/Pb electromotive difference in the 400 - 500 mV range (Reiber, 1991). If a significant portion of the remaining section of lead service line were shifted in the anodic direction by even a fraction of this amount, there would be a substantial acceleration of the corrosion rate and associated metal release rates.

In a similar sense, for well over a decade, there has been substantial conjecture within the drinking water industry that electrical currents impressed, or, more often, shunted onto water service lines as a result of grounding practices in individual homes, create a similar scenario. Supposedly these impressed currents shift the surface potential of the corroding pipeline surface, generating accelerated corrosion and metal release, and in some cases producing other corrosion-related problems such as localized pitting. There are few texts on distribution system corrosion that do not cite impressed currents as a potential cause of the interior pipeline corrosion (Bell, 1996; AWWARF, 1996). The suggestion has been made that these currents may be responsible for some of the abnormally high lead release levels observed in isolated homes. By extension, it could be assumed that if grounding currents are important, then perhaps a portion of the randomness associated with observed lead levels may be related to the presence of different magnitudes of grounding currents.

It is important to note that while the proposed mechanisms of galvanic and/or impressed current influence are plausible, and that some limited evidence is supportive, it has not been demonstrated that either grounding currents or galvanic coupling meaningfully increase LSL corrosion rates. Moreover, partial LSL replacement in the DCWASA system has not resulted in observed increases in lead release (Wujek, 2004). In fact, the recent DC WASA experience relative to LSL replacement suggests that in the long term PLSLR does not exacerbate lead release rates, but rather reduces overall household drinking water lead concentrations in proportion to the amount of LSL replaced. While this evidence appears strong, for several years there has been a debate on the potential galvanic effects associated with replacing a portion of old LSLs with new copper tube, or for that matter coupling any lead-containing alloy to a dissimilar metal.

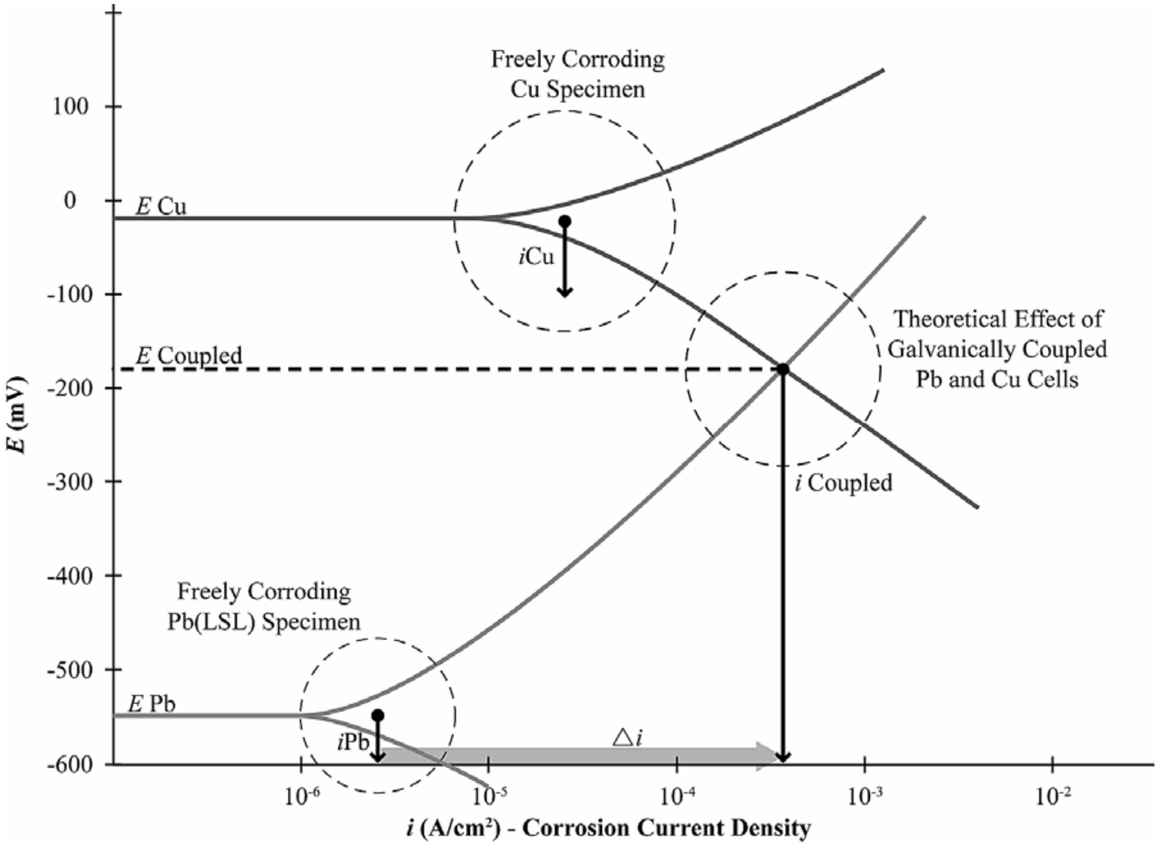

Figure 1. Polarization (Evan's) diagram of coupled lead and copper surfaces.

Theoretically, the coupling of a new copper surface to a lead surface should produce a substantial galvanic impact. The Evan's Diagram above illustrates this point. The diagram presents the observed polarization behavior of uncoupled copper and lead surfaces, as well as the theoretical polarization behavior of the surfaces that would occur if they were coupled. The uncoupled surfaces are unscaled and unpassivated, and hence represent practical worst-case scenarios. Relative to lead, the coupling of the two surfaces results in a theoretical initial increase in the anodic (lead) exchange current (Δi, corrosion current density) of approximately two orders of magnitude, which of course would have a profound impact on corrosion and metal release rates if it were sustained at this level.

What cannot be discerned from the above representation is how long that accelerated current exchange can be sustained after the initial coupling. In a practical sense, since all of the existing LSLs in the DC WASA system are well passivated after many decades of service, the more important question becomes how passivation of the lead and/or copper surfaces affects the galvanic current. A large portion of this modest study focuses on that question.

Research Protocol

Electrochemical Measurements

At the core of this study was the search for the substantial electrochemical impacts that, theoretically, should be associated with the galvanic and impressed currents imposed on the LSLs. The principal measure of these impacts would be a significant shift in the electrochemical potential of the interior surface of the LSLs away from the freely corroding surface potential. Surface potential can be directly and accurately measured using straightforward electrochemical tools (AWWARF, 1996).

This research did not attempt to create laboratory conditions that exactly replicate field conditions. Instead, the goal was to demonstrate whether or not extremes of grounding currents or galvanic coupling could affect the LSL electrochemistry. It was also beyond the scope of this work to define how differences in passivation states of copper tubing, or quality of plumbing fabrication may influence the respective current impact. Testing was generally short-term, inexpensive and designed to answer the simple question, "Can grounding and/or galvanic currents under a worst-case scenario meaningfully contribute to lead corrosion and metals release?"

The study used a series of electrochemical cells which allowed the mounting of sections of LSLs under flow conditions and the placement of electrodes capable of quantifying shifts in surface potential. In most cases the electrode of choice was a calomel electrode (Hg/Hg_2Cl_2), selected because of its stability and resistance to external electrical noise. This electrode, coupled with a sensitive potentiostat, can measure surface potential shifts of a millivolt or less. This is an important analytical factor, since the shifts in surface potential theoretically resulting from the galvanic and impressed currents were thought to be hundreds of millivolts or greater.

The surface potential measurement is sensitive, easy to use, and allows speedy measurements, but its principal advantage is that it is influenced only by the electrochemistry of the metal surface and the water in contact with that surface. It is not substantially or directly influenced by the mechanical stability or chemical solubility of the corrosion scale covering the surface – unless the rapid loss of that scale is changing the underlying electrochemistry. The surface potential measurement reflects the corrosion conditions of the underlying metal, which, in this case, is the factor most directly influenced by application of the galvanic and/or impressed currents in question. At the same time, the limitation of this electrochemical testing is that it tells us very little about the stability or changing mineralogic makeup of the corrosion scale. Nonetheless, relative to the issue of galvanic and impressed currents, electrical perturbation will precede any long-term change in the nature of the corrosion scales.

The short-term tests used in this study did not readily lend themselves to standard metal release monitoring used in other aspects of the DC WASA corrosion-control optimization studies (Giani et al, 2005). While monitoring of metal-release rates was attempted, it was found that the physical cutting and manipulation of LSL sections generated frequent, but irregular, particulate release. The individual tests, which generally ran for periods of only a few days each, did not provide sufficient time to condition and stabilize the scales on the different test sections.

Galvanic Coupling Experiments

The original approach to the galvanic coupling research was to utilize polarization cells mounting individual sections of LSLs and copper tubing. These cells could be connected in a hydraulic series, with the electrical connections between the individual cells manipulated at will. Because the pipe specimens of each cell were not in direct contact, these cells were referred to as ***indirectly coupled***. The importance of the indirectly coupled cells relates primarily to the ability to control cathode/anode ratios. It is critical to the appreciation of the galvanic couple concern to understand that it is not the contact of dissimilar metals, per se, that creates the corrosion risk, but rather the fact that the cathodic surface (the more electropositive metal), if present in abundance, can affect a shift in the surface potential of the anodic surface. The greater the cathode/anode ratio the greater the potential shift, and the greater the area of anodic impact. Any meaningful shift in the anodic surface in a more positive direction generates a higher corrosion rate on that surface.

A second approach to galvanic testing utilized longer segments of LSLs and copper pipe coupled together in a manner similar to an actual PLSLR. Because these pipe specimens are in direct contact, this type of testing is referred to as ***directly coupled*** pipe specimens. This form of testing yielded more useful results about the nature of the galvanic couple formed between copper and LSL sections.

Indirectly Coupled Cells.

Recirculation pipe loops with individual cells holding LSL and copper pipe sections were fabricated with acrylic polarization cells and vinyl connecting tubing. The schematic presented in Figure 2 shows the arrangement of the individual cells, hydraulics and electrical connections. In this arrangement the cells are hydraulically connected in series, and electrically connected via external circuits that can be configured as needed. The arrangement offers the opportunity to manipulate cathode/anode ratios, measure the current flow between cells, evaluate metal release and, most importantly, accurately assess the surface potential of the individual pipe sections, all while controlling flow and water quality conditions. Figure 3 presents a photo of such a loop in operation.

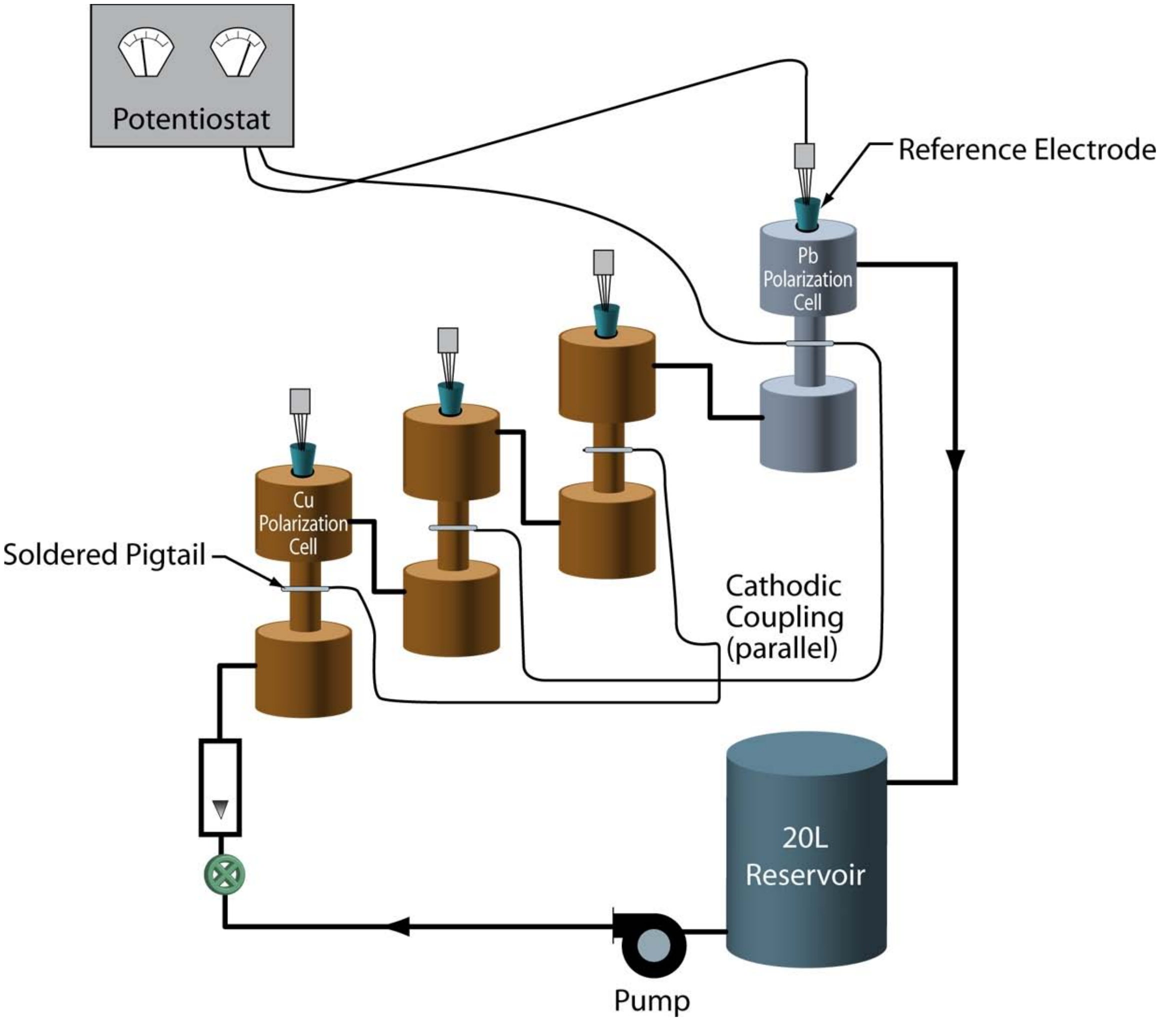

Figure 2. Schematic of a typical pipe rig configuration using indirectly-coupled cells

Figure 3. Photo of a pipe rig with indirectly-coupled cells in operation.

Evan's Diagram.

The data presented in the Evan's diagram of Figure 1 was prepared using results obtained from an indirectly-coupled pipe rig of a type similar to that in Figure 2. In that test a single LSL section was coupled to a single copper pipe section of comparable internal surface area (20 cm^2). Originally, both the LSL and copper surfaces were abraded and then polished (300 grit wet jeweler's paste) so as to represent truly unscaled and unpassivated surfaces. This attempt to create an unpassivated LSL surface generated a surface potential of approximately -400 mV (vs. SCE), which is not substantially different than the surface potential of a passivated LSL. Discussions with Michael Schock (US EPA – ORD) suggested that a truly unpassivated lead surface should be closer to -500 mV (vs. SCE), rather than the -400 mV measured.

Revisiting the techniques used to remove the LSL corrosion scale, a milling machine with high speed de-burring tool was used to ream out the interior of the short LSL sections, exposing bare metal with the assurance that no corrosion scale or passivation layer remained. Surface potential measurements on these specimens were approximately -550mV (vs. SCE) when first exposed to water flow. Owing to the electroactive nature of the pure lead surface, the absolute magnitude of the measurement quickly began to decrease as the surface began to passivate in the presence of water.

The rapidly changing electrochemical nature of a bare lead surface makes it difficult to accurately assess the surface potential of a truly unpassivated specimen. The data presented in the Evan's diagram of Figure 1 is probably best described as a partially passivated LSL surface.

Other experiments conducted to define the character of an unpassivated LSL surface were, at best, only partially successful. The most substantial observation is the speed with which an unscaled lead surface will begin to passivate. Although we have not tried to quantify the rate of passivation, we note that an unpassivated LSL section within a matter of weeks will take on the character of a passivated LSL section having decades of exposure, and it will do this in a low mineral content water very similar in chemistry to that distributed by DC WASA. Moreover, it is clear that while orthophosphate corrosion inhibitors can over a substantial period of time enhance the passivation of LSL surfaces (based on on-going metal release pilot studies), these surfaces will effectively passivate absent orthophosphate or other specific corrosion inhibitors (Reiber and Giani, 2005). It is the nature of the lead surface to quickly form an effective passivation layer, which is why LSLs are still found in service even after a century of exposure to drinking water flows.

Cathode/Anode Ratio Effects.

Using the indirectly coupled cell rig, the effect of coupling passivated LSL sections to unpassivated copper sections quickly became apparent. Figure 4 presents the results of coupling a single LSL section (20 cm^2 internal surface) to multiple copper pipe sections of equivalent surface area. At most, the electrical perturbation of the passivated LSL was a few millivolts, regardless of how many copper sections were electrically coupled to it.

A substantially different observation was made when a relatively unpassivated LSL section (mechanically reamed) was coupled to the same copper pipe sections as above. The unpassivated LSL surface was substantially influenced by the galvanic coupling – producing an anodic shift of approximately 100 mV at a cathode/anode ratio of three. Clearly, galvanic coupling is important on relatively unpassivated surfaces, yet largely irrelevant to passivated LSL specimens.

While this experiment evaluated the macro effects of galvanic coupling, it is not unreasonable to extrapolate these macro observations to the micro surface chemistry associated with leaded brasses. The question has been raised (Korshin, 2005) as to whether brasses having any lead inclusions will accelerate corrosion of the lead by virtue of the intrinsic galvanic couple created by a surface with very small lead anodes surrounded by the much more abundant and more electropositive copper/zinc alloy (brass). The macro galvanic coupling experiment described above would suggest that cathode/anode ratio is largely irrelevant to the corrosion of a passivated lead surface.

Hence, it seems likely that lead corrosion on an aged brass surface is unlikely to be influenced by the more electropositive alloy surrounding it.

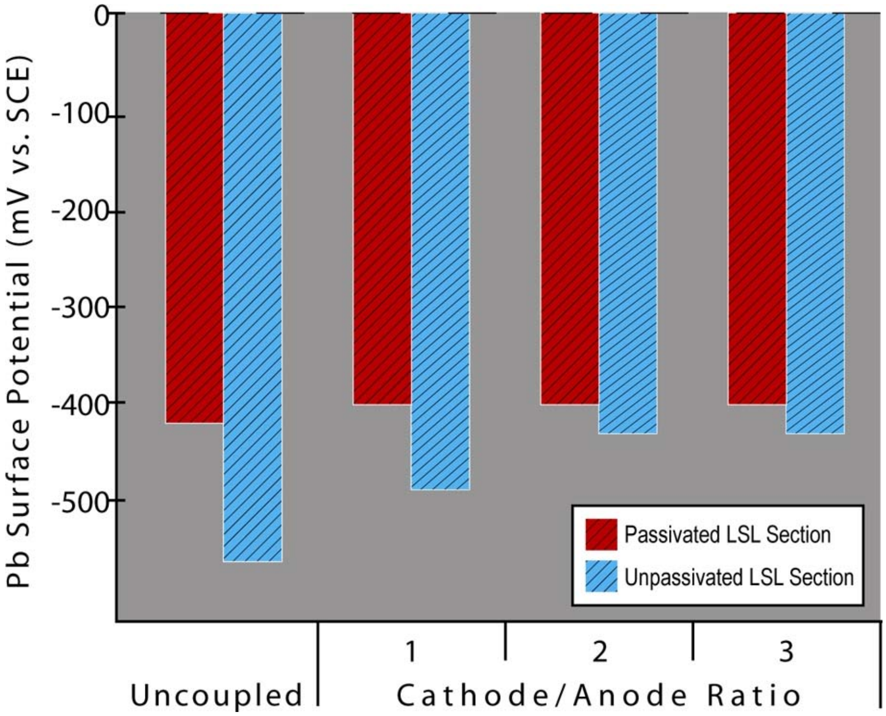

Figure 4. Effect of cathode/anode ratio on LSL surface potential.

Directly Coupled Pipe Sections.

Following the test with indirectly coupled pipe sections, the study attempted to quantify galvanic effects by directly coupling copper tubing sections and DC WASA LSL sections. New ¾-inch diameter copper tubing was selected to ensure as high a galvanic driving force as possible. To ensure electrical coupling, the end of the LSL was grooved to accept the end of the copper tubing, which mated directly with the LSL. A hydraulic seal was achieved by mounting both the copper and LSL sections between compressive headpieces. Holes placed at strategic locations along the copper and LSL sections allowed for the placement of reference electrodes capable of reading the surface potential on the pipe opposite to those locations. To simulate operational service, water was circulated through the pipe sections while the surface potentials were recorded. Figure 5 presents a schematic of a directly coupled cell. Figure 6 presents a picture of a small coupled pipe cell used for one portion of this testing.

The LSL pipe sections used in these tests were recently removed (July, 2005) from residences in the DC WASA distribution system. As such, they had been exposed for a period of almost one year to the phosphoric acid corrosion-control mitigation strategy implemented in the summer of 2004. The passivated LSL sections described in this section were used as received. An attempt was made to create unpassivated LSL sections for this testing by polishing the interior of relatively long sections of the LSLs by forcing a tightly wadded plastic abrasive sheet (Scotch-Brite) back and forth along the length of the LSL section. This was at least partially successful and did remove a portion of the very adherent and very protective passivating layer on the aged LSL sections. Because of the length of the test sections it was not possible to use a mechanical reaming tool as was done in the indirectly coupled cell testing. Although the specimen geometry did not allow for a rigorous polishing, the effort did produce a substantial change in the surface electrochemistry that was evidenced in subsequent testing. For purposes of this discussion, partially polished LSL sections are referred to as unpassivated.

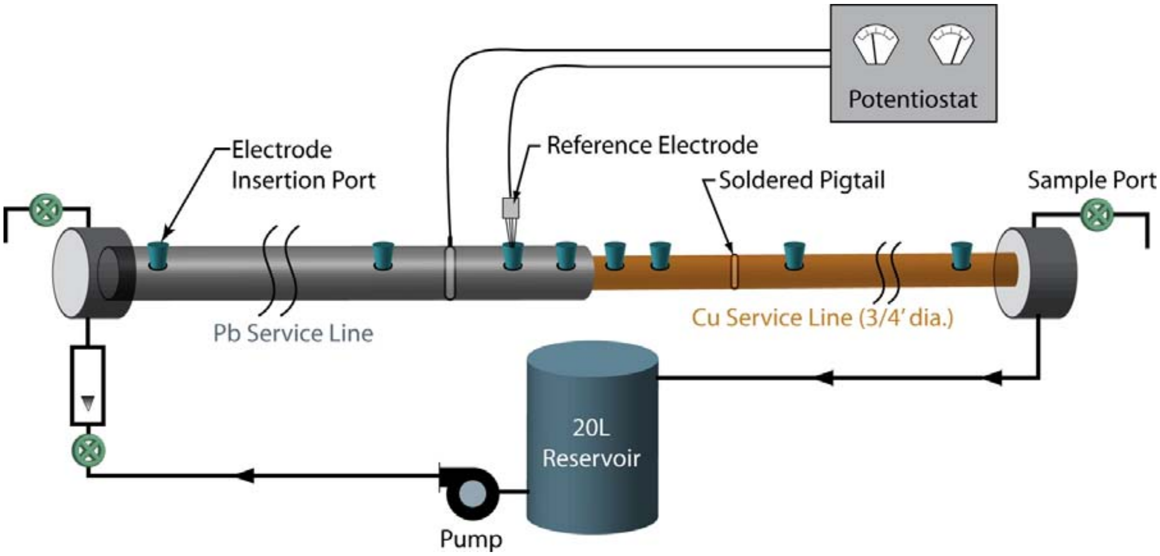

Figure 5. Schematic of a test rig showing the direct coupling of LSL and copper pipe sections

Figure 6. Photo of directly coupled LSL and copper sections used in a portion of this study

Figure 7 presents a comparison of the surface potentials measured along passivated and unpassivated LSL sections connected to equivalent lengths of copper tubing in a directly coupled cell. The comparative results are significant at two levels: first and foremost, as in the testing in the indirectly coupled cels described earlier, direct coupling of new copper tubing to well-passivated LSL sections has almost no discernible electrochemical impact on the LSL. Secondly, coupling to an unpassivated LSL section shows the converse, and is in fact strongly influenced by the connection to the copper tubing. This second point underscores the earlier observations that an unscaled and unpassivated LSL section is highly electroactive, but that once it is passivated it is remarkably polarization resistant.

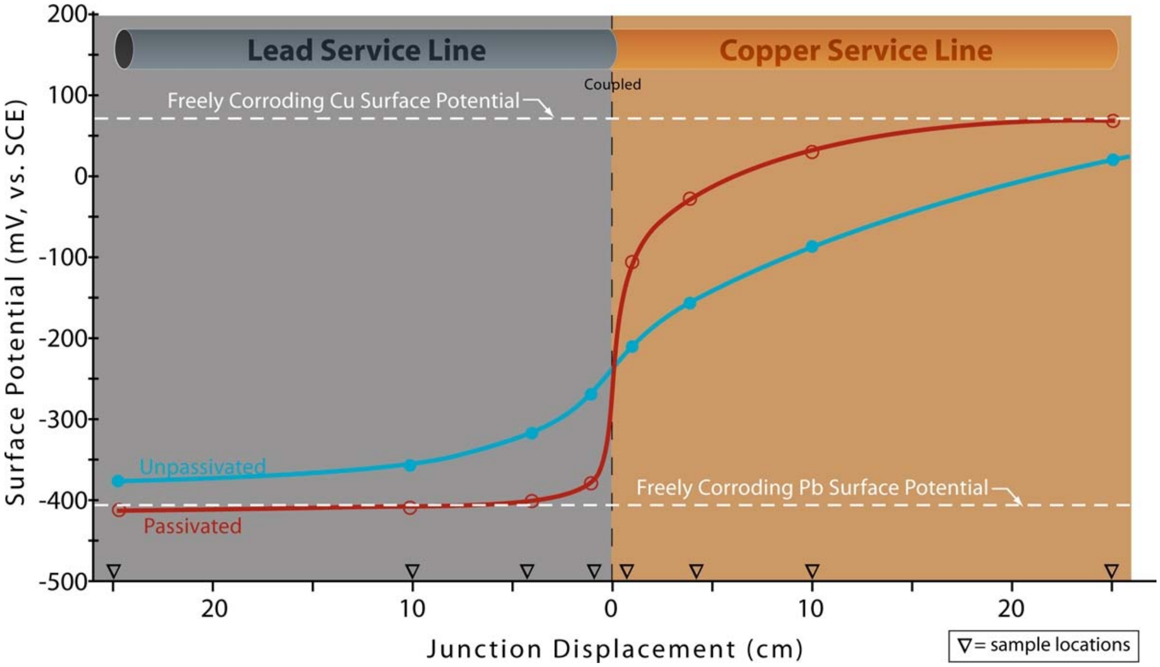

Figure 7. Surface potential along the length of coupled LSL and copper service lines

Water Quality and Galvanic Impacts.

The directly coupled cell approach was used to assess the impact of important water chemistry changes including chlorine chemistry and concentration, and the impact of water conductivity. The baseline water chemistry used in this testing was a simulated DC WASA water having similar pH, alkalinity, hardness and conductivity profiles.

Figure 8 shows the effect of chlorine concentration on the galvanic impacts on a passivated LSL section. An increasing free-chlorine residual elevates the galvanic effect by accelerating the cathodic current exchange process on the copper pipe, however, the impact overall is limited to the copper service line, while the impact on the passivated LSL surface is nearly imperceptible.

Figure 9 shows the comparative effect of equal concentrations of free and combined chlorine relative to galvanic coupling using a passivated LSL sections. The test shows no meaningful difference in galvanic impact on either the lead or copper surfaces. (*Note: While the DC WASA lead solubility issues were the result of redox chemistry impacts associated with the change from free to combined chlorine, the test used here is capable of discerning only fundamental changes in surface electrochemistry, and tells us nothing about solubility of the existing corrosion scales*).

Figure 10 shows the impact of increasing conductivity levels on the galvanic impact relative to a passivated LSL section. Conductivity increases were brought about by the simple addition of NaCl to the recirculating water in the test rig. Interestingly, water conductivity has a more important effect on the galvanic process than chlorine residual, or chlorine type. The area of galvanic influence on the LSL specimen is marginally expanded as the conductivity of the electrolyte (water) increases, while the area of influence on the copper service line is substantially expanded. This would appear to be because the higher conductivity lessens the resistance of the electrolyte circuit (water), expanding the "reach" of the galvanic current. (*Note: DC WASA distributes a low conductivity water (< 100 microSiemens), which, in part, explains the minimal galvanic impacts observed*.)

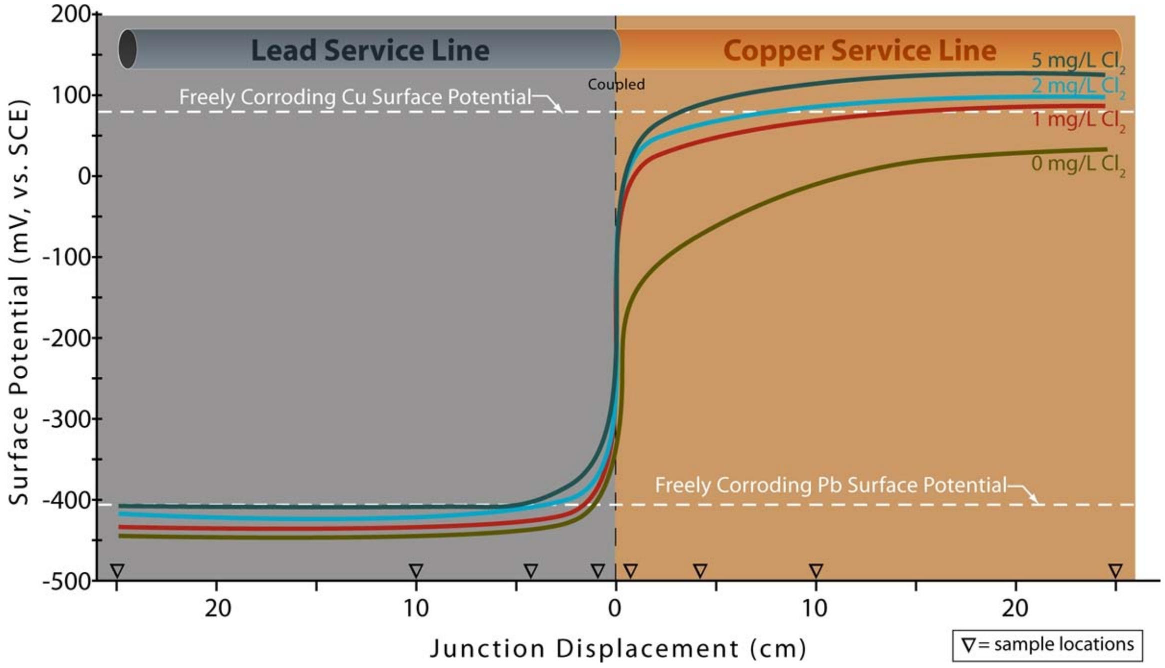

Figure 8. Effect of chlorine concentration on galvanic impacts relative to passivated LSL specimen.

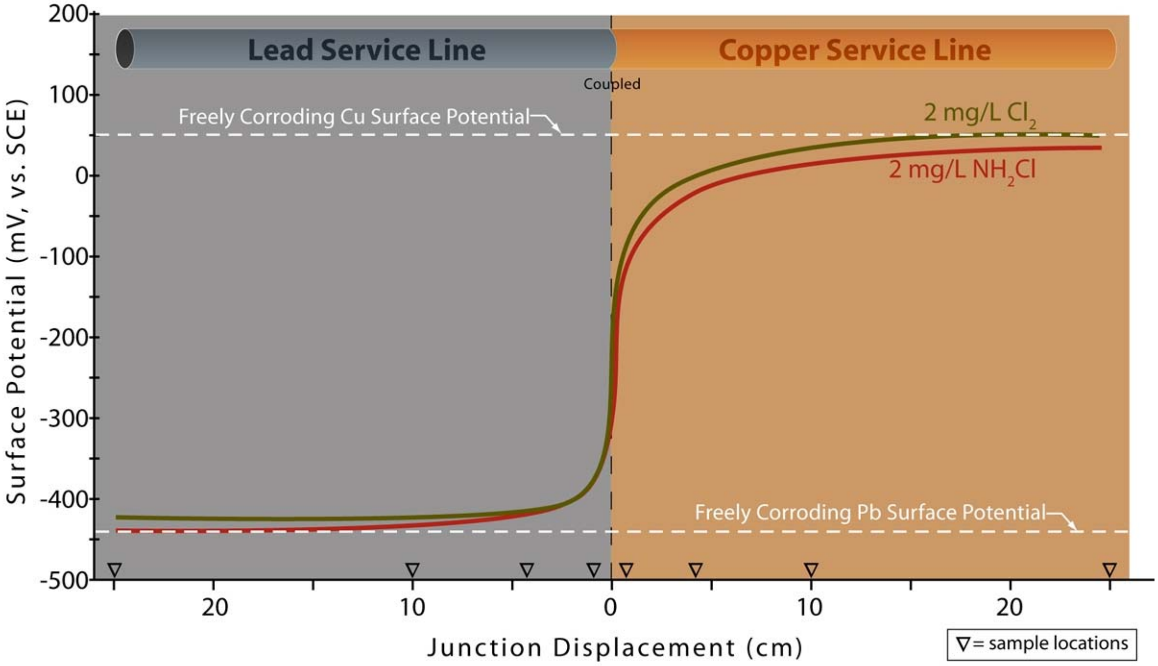

Figure 9. Comparative effect of free versus combined chlorine on galvanic impacts relative to passivated LSL specimen.

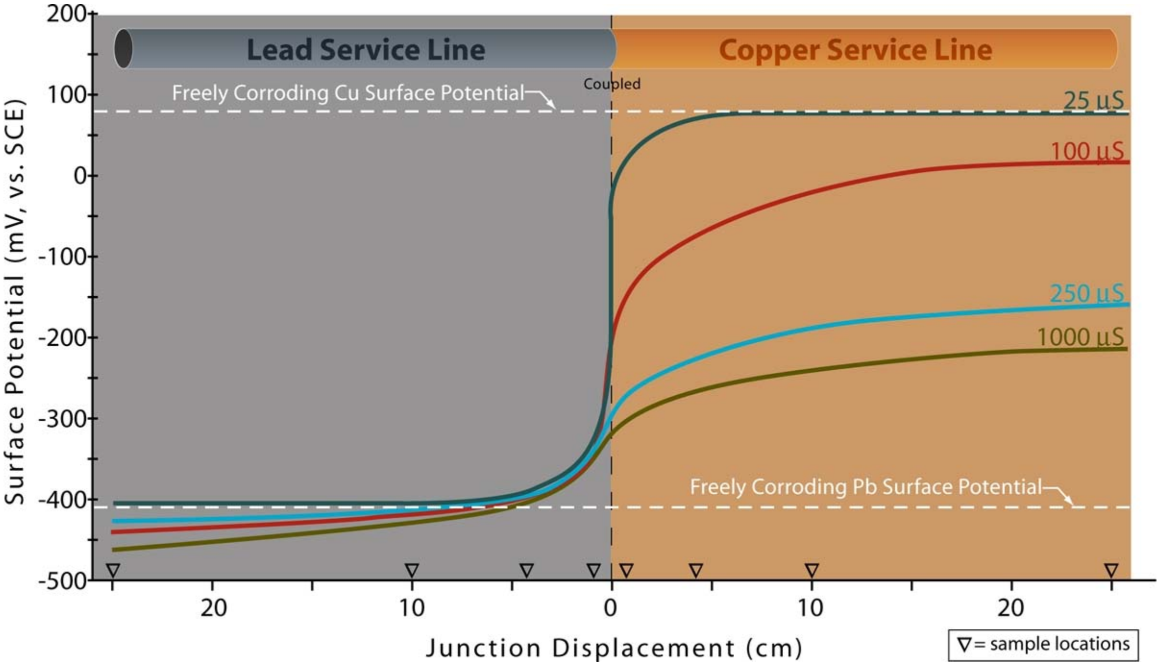

Figure 10. Effect of conductivity on galvanic impacts relative to passivated LSL specimen.

Dielectric Insertion.

A dielectric is an insulating device that prevents direct electrical contact between dissimilar metals, and hence avoids at least some of the problems associated with galvanic coupling. Although not always used, it is generally considered good plumbing practice to use a dielectric when different metal plumbing materials are to be connected. It is standard policy for DC WASA to use dielectric couplers when performing partial LSL replacements (DC WASA, 2004).

Figure 11 shows the effect of inserting a dielectric coupler between the passivated LSL and copper sections of the directly coupled test rig. While in the previous water quality testing it was shown that the galvanic effect of the direct coupling was largely limited to the copper line and had little effect on the LSL, the insertion of a dielectric removes any galvanic impact from either surface. This is a particularly important finding, and along with the general polarization resistance of passivated LSL sections, explains why the partial LSL replacement program in the DC WASA system has not exacerbated lead conditions, but rather has helped to reduce household lead levels.

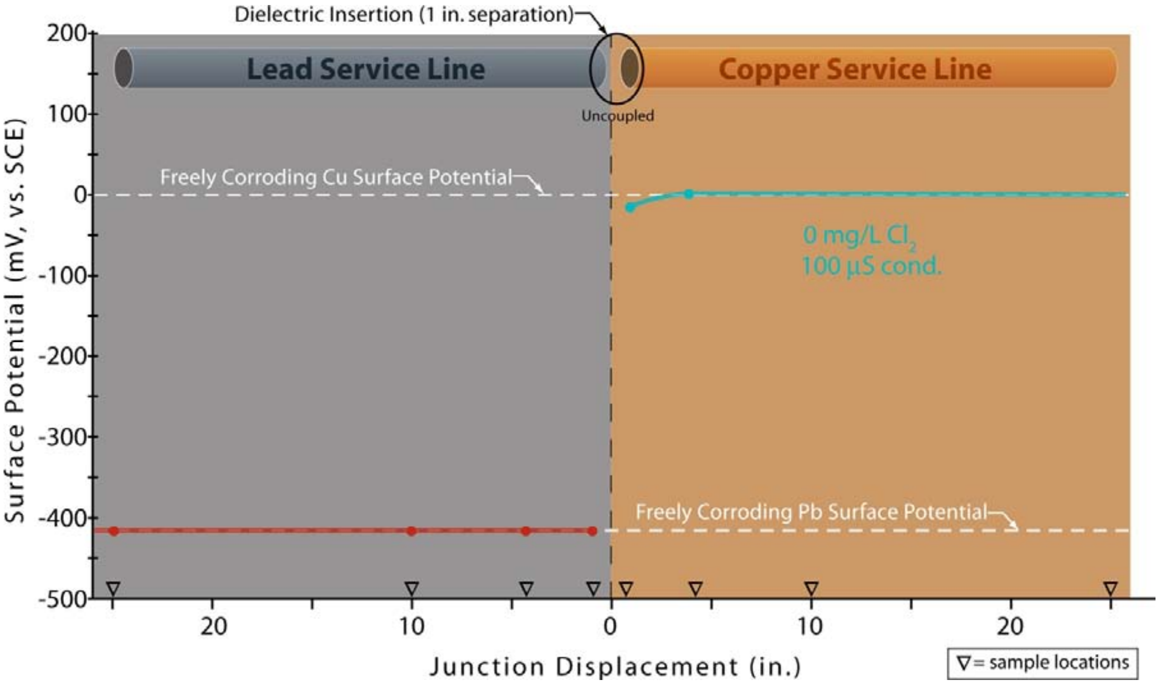

Figure 11. Effect of inserting a dielectric between the passivated LSL and copper sections on galvanic impact.

Grounding and Impressed Currents

Does a current flowing in the pipe wall, and exiting the pipe via an external connection (a typical electrical-system grounding scenario in many older households), change the electrical character of the internal pipe surfaces? If it does, a variety of corrosion and water quality impacts are to be expected, including accelerated metal release. However, a clear absence of a measurable electrical change on the internal surface would mean the grounding circuit is irrelevant to the internal corrosion processes.

That is the question that was addressed by this portion of the study which focused on investigating the interior LSL surfaces relative to simulated grounding currents. The objective was to demonstrate under controlled conditions whether it was possible to create a grounding scenario that accelerates internal corrosion, and to extrapolate its relevance to household plumbing practices.

Although this topic has been previously researched, there is still considerable debate about the impact of externally imposed grounding currents on the electrochemistry of domestic plumbing. The bulk of available research has focused on copper tubing – largely ignoring grounding impacts on LSLs. While some research has suggested an important internal corrosion role for grounding currents (Bell, 1998), other laboratory simulations and field tests have discounted them relative to copper release and associated water quality effects (AWWARF, 1996).

At first glance, it seems intuitive that imposing a (grounding) current on a buried pipe would change the surface potential of the internal and external surfaces. Certainly, as the current is dissipated to ground, the surface potential of the external surfaces does change. However, internally, unless some portion of the grounding current is lost to the electrolyte (water in the pipe), these surfaces will show no change in surface potential relative to the water contacting them. In effect, imposing an external current on the pipeline changes the potential of all surfaces (internal and external) and everything in contact with the pipe. Internally, however, the surface potential relative to the electrolyte (which determines corrosion rates) may not change since the electrolyte potential has also been shifted an amount equal to the internal surface.

Impressed Current Experiments

A flow-through recirculation loop consisting of DC WASA LSL segments, new copper tubing, water reservoir, flow control and pumping hardware was employed for this testing. As in the previous galvanic work, the LSL segments were modified to accept high impedance reference electrodes penetrating the pipe wall at multiple locations along its length. The electrodes monitor surface potential on the interior of the pipe relative to the electrolyte, yet allow for pipeline pressurization. Internal surface potential along the pipeline was monitored, while different current forms, amperages, voltages and grounding scenarios were applied to the test pipes. Figure 12 presents a schematic of the test rig.

Quantifying the actual interior surface potential change vis-à-vis the electrolyte (water) of these pipes was key to assessing grounding current impacts. Any meaningful change in the corrosion condition of the internal surface could be assessed by measuring any substantial change in surface potential, which could be monitored with a high degree of accuracy (+/- 0.1 mV). Table 1 presents a summary of the basic electrical testing profile used in this examination.

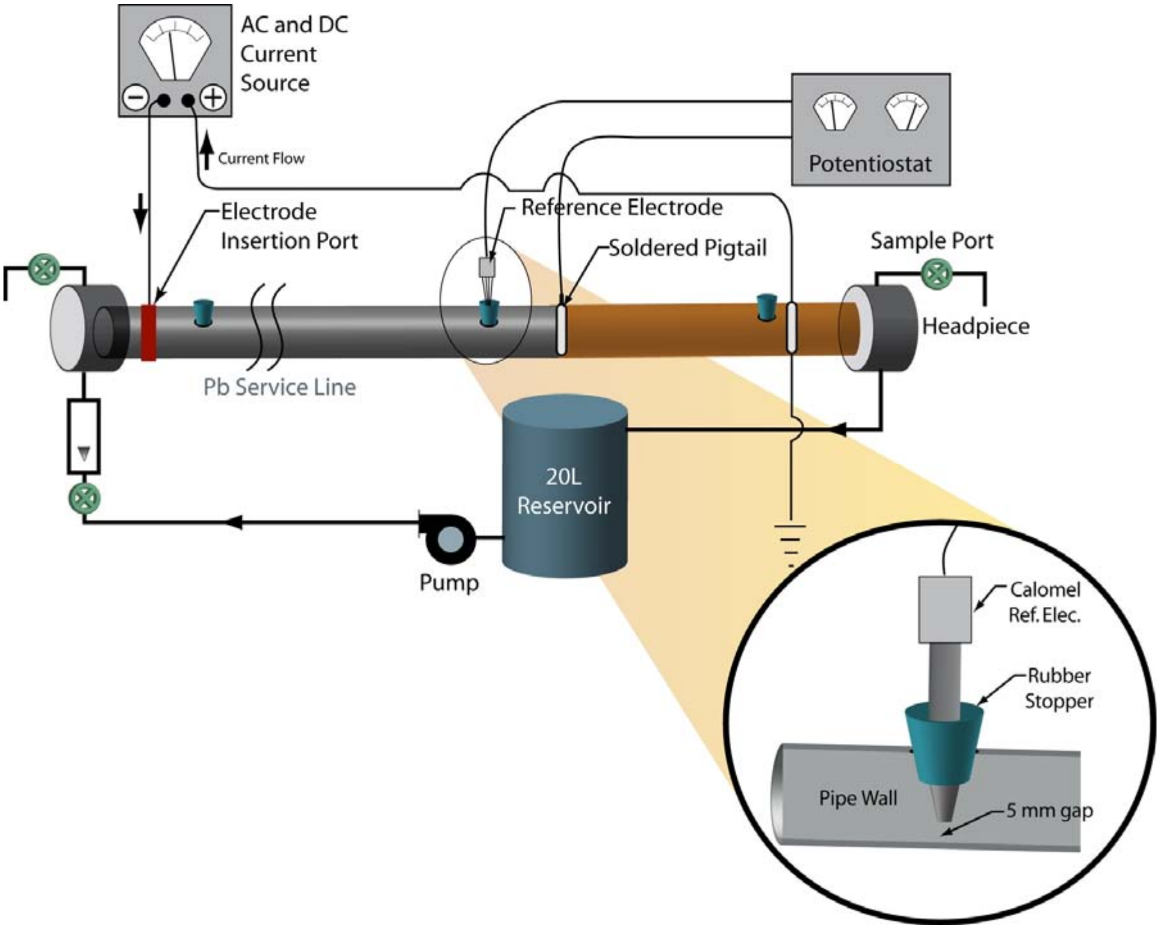

Figure 12. **Schematic illustration of impressed current test rig**

Table 1. Grounding Currnet Testing profile

Impressed grounding current forms	• Full wave AC • DC
Voltage range	0 – 120 Volts AC, 0 - 12 Volts DC
Current range	0 – 20 Amps AC, 0 – 6 Amps DC
Grounding scenarios	• Single-point ground • Multi-point ground along pipe length • Variable resistance reservoir ground: *By providing a current path from the pipe wall through the electrolyte to ground, it was possible to dissipate some of the applied external current to the interior surface of the pipe.*

With the test rig in operation, the actual assessment could be conducted quickly, generally requiring no more than a few hours per test condition. The testing proceeded from impressing direct currents at minor voltages and amperages to upwards of a 12-Volt current at up to six amps of current flow. Attempts to measure the impact of the impressed current on the interior surface potential were made at different locations along the pipe rig. Different grounding scenarios were tested in conjunction with the impressed current in an attempt to force the impressed current to flow the full length of the pipe samples, as well as to force as much of the current to transfer to the water flow as possible. (*Presumably, current transfer from pipe wall to water creates a corrosion cell*). The most rigorous of the grounding protocols involved adding a ground to the recirculation water reservoir in parallel with the pipe rig ground, thus allowing a direct current path from the pipe wall to the recirculating water.

Following the DC testing, alternating currents were imposed on the pipe rig using a standard 120-Volt (breakered at 20 amp) wall-type circuit. Grounding scenarios similar to the DC testing were employed. A summary of actual results from this testing is straightforward: impressed currents, whether AC or DC, had no meaningful impact on the surface potential of the pipe rig regardless of voltage or amperage. Figure 13 summarizes the results of the highest voltage DC and AC tests, demonstrating that these impressed currents did not meaningfully shift the interior surface potentials of the test specimens.

Impressing an AC current, however, does create substantial electrical noise, making it difficult to measure a stable potential. Yet, while the noise effect expanded the range of variability by about 5 mV, the baseline potential did not shift. There is an electrochemical argument to be made about the capacitive effect of an AC current applied across a corrosion scale, yet, if the corrosion potential of the interior surface does not change vis-à-vis the water, capacitance is irrelevant.

From this testing we conclude the obvious: currents flowing in pipe walls take the path of least resistance to ground, producing no change relative to the corrosion potential of the internal surface, whether it be a copper or lead service line.

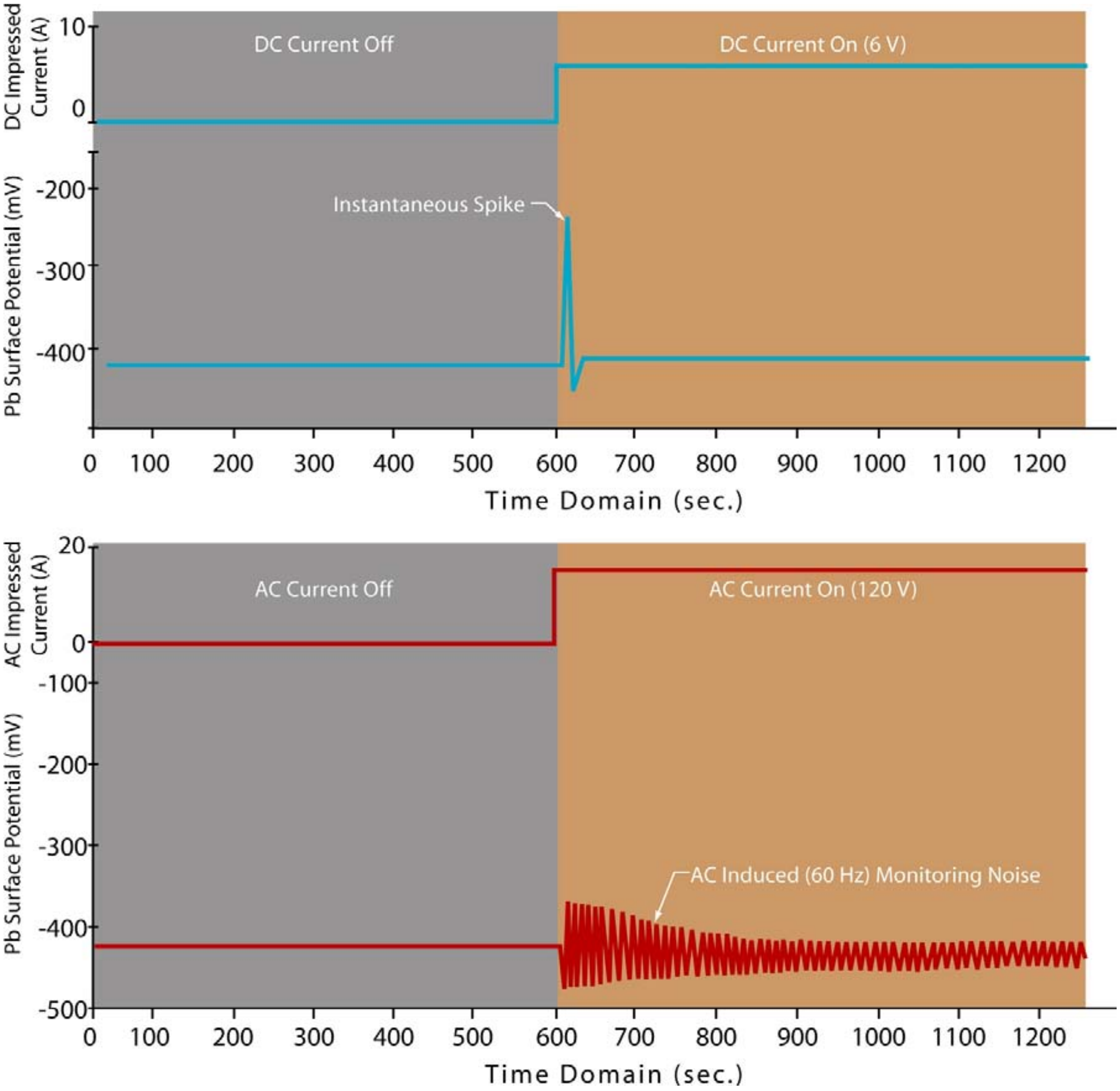

Figure 13. Impressed current impacts (separate DC and AC tests) on surface potential of an LSL coupled to copper tubing.

Observations and Conclusions

This study has shown that grounding and/or impressed currents moving along LSLs, and eventually leaving the pipe to ground, have no meaningful impact on internal pipeline corrosion and do not likely contribute to metals release. Secondly, while the study found that galvanic impacts can be substantial on unpassivated lead surfaces, the magnitude of the impact on aged and passivated LSL surfaces (as well as on copper service lines) is so minimal as to be inconsequential. The study provides a strong basis for discounting claims and concerns relative to accelerated metal release associated with PLSLR. Moreover, we believe that the long-debated controversy about grounding currents impacts can now be considered closed.

The most significant observations to be drawn from this study are summarized below.

Passivation.

Lead is a highly electroactive metal, and in pure form oxidizes extremely rapidly. An unscaled lead surface, even under natural environmental conditions, has an exceedingly high initial corrosion rate. Fortunately, lead also passivates strongly and quickly. Observations in this study suggests that meaningful passivation on LSLs can be achieved within a matter of days. Well-aged DC WASA LSL specimens – especially those that have been exposed to an orthophosphate inhibitor – are exceptionally well passivated and highly resistant to electrical perturbations.

Lead Electrochemistry.

Passivated LSL specimens are highly polarization resistant – meaning that it takes an exceptional surface perturbation to affect the underlying corrosion rate. The actual degree of polarization resistance expressed as a Tafel Value is in excess of 500 - 600 mV per decade of current shift. Overall, this explains, at least in part, why the galvanic coupling has little apparent effect on passivated lead surfaces.

Area of Galvanic Influence.

When coupled to a new length of copper tubing (as in a partial LSL replacement) the area of galvanic influence on a well-passivated LSL is likely limited to less than the first inch of LSL pipe in the immediate vicinity of the coupling. The galvanic area of influence on an unpassivated LSL specimen is larger, but likely limited to the first few inches of pipe in the vicinity of the coupling. As the LSL passivates, the area of galvanic influence decreases rapidly. The period of transition can be as short as a few days under normal distribution system conditions.

A potential reason why galvanic impacts do not generate a more significant corrosion response relates to the respective geometries of the anodic and cathodic surfaces of the pipeline couple. Because sequential pipelines (LSL to copper tubing) are connected at only a single location, only a small portion of the LSL is polarized by the galvanic current. And, given the relatively rapid rate at which both copper and lead surfaces passivate, the duration of the polarization is relatively brief. Hence even the meager galvanic effect, is short-lived.

Cathodic Effect of Copper Pipe.

The cathode/anode ratio on a well-passivated LSL surface is unimportant relative to the galvanic effect. This means that even an exceptionally long length of copper pipe connected to a partial LSL does not elevate the galvanic effect. (It had been argued that long lengths of copper service line connected to short LSL sections would exacerbate the galvanic effect.)

Water Quality and Galvanic Impacts.

A free-chlorine residual does elevate the galvanic effect by accelerating the cathodic current exchange process. Conversely, chloramine has a lesser galvanic impact than free chlorine. The impact overall, however, is largely limited to the galvanic influence on the copper service line. The overall impact on the LSL surface is nearly imperceptible.

Interestingly, water conductivity has a more important effect on the galvanic process than chlorine residual. The area of galvanic influence on the LSL specimen is marginally expanded as the conductivity of the electrolyte (water) increases, while the area of influence on the copper service line is substantially expanded. This is because the higher conductivity lessens the resistance of the electrolyte circuit (water), expanding the “reach” of the galvanic current.

DC WASA distributes a low conductivity water (< 100 microSiemens), which, in part, explains the minimal galvanic impacts observed.

Dielectric Effects.

While galvanic impacts relative to DC WASA PLSLRs are likely minimal, any break in electrical continuity between the copper and LSL lines effectively eliminates the potential for a galvanic effect. In short, a conventional plumbing dielectric junction removes even the minor corrosion risks associated with galvanic coupling.

Impressed Current Effects.

Impressed currents (AC or DC) on LSLs and copper service lines, including grounding type currents, have no impact whatsoever on the internal corrosion of the household service lines (or any other plumbing appurtenance for that matter). There is likely no acceleration of corrosion associated with the conventional practice of electrical system grounding to household water systems.

References

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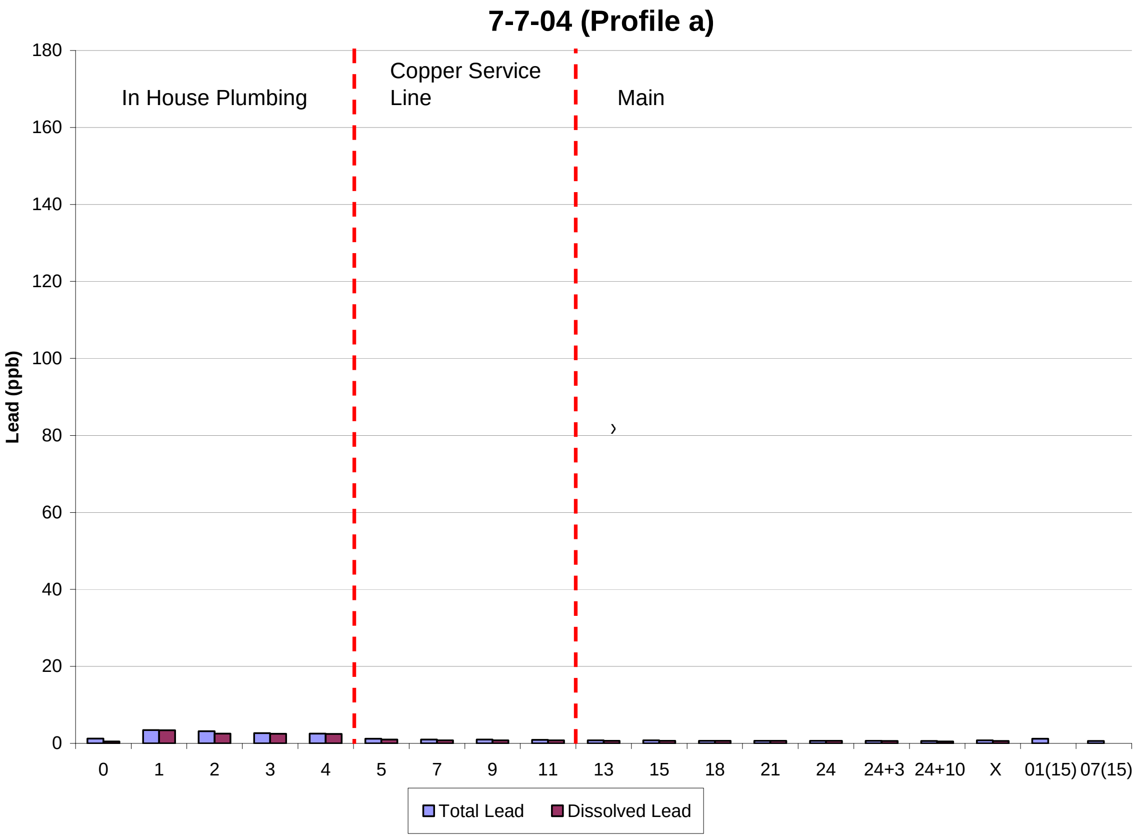
Appendix D Lead Profile Results

D.1 Total and Dissolved Lead Profile for a Residence Without a Lead Service Line, Before Orhtophosphate Application



D.2 Total and Dissolved Lead Profiles from Samples Drawn Prior to Initiation of Orthophosphate Treatment Program

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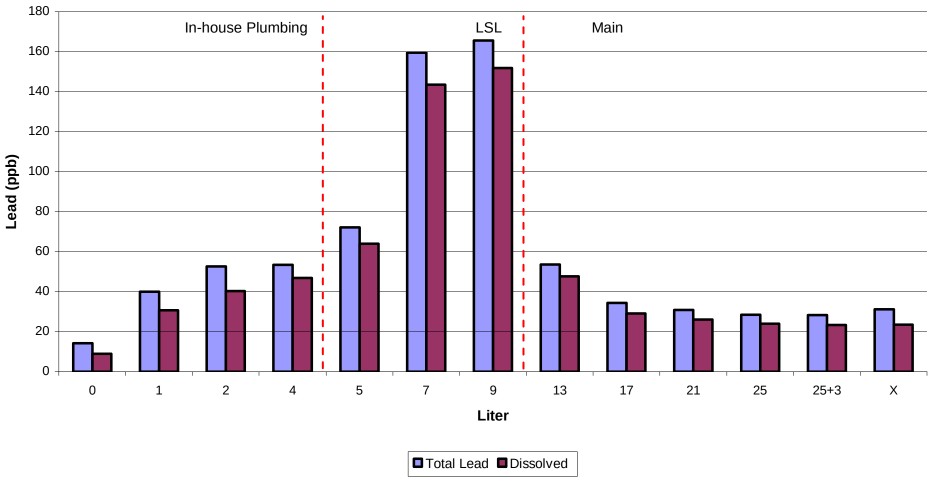

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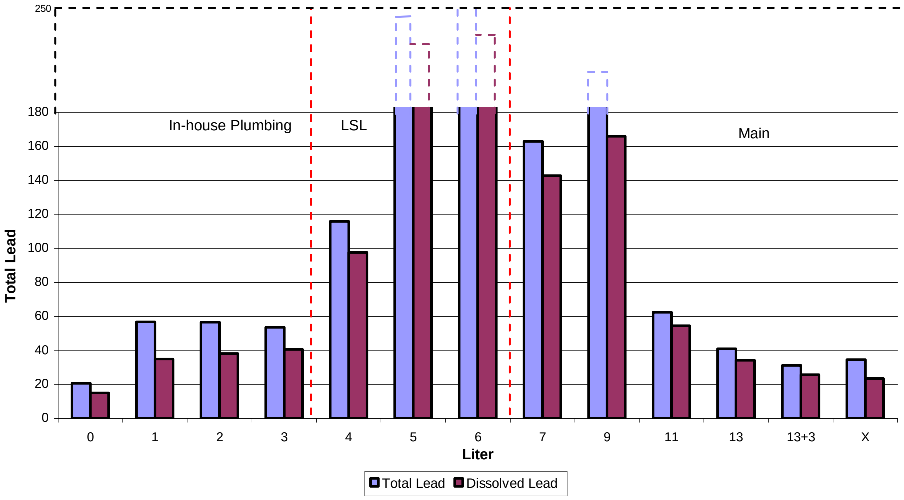

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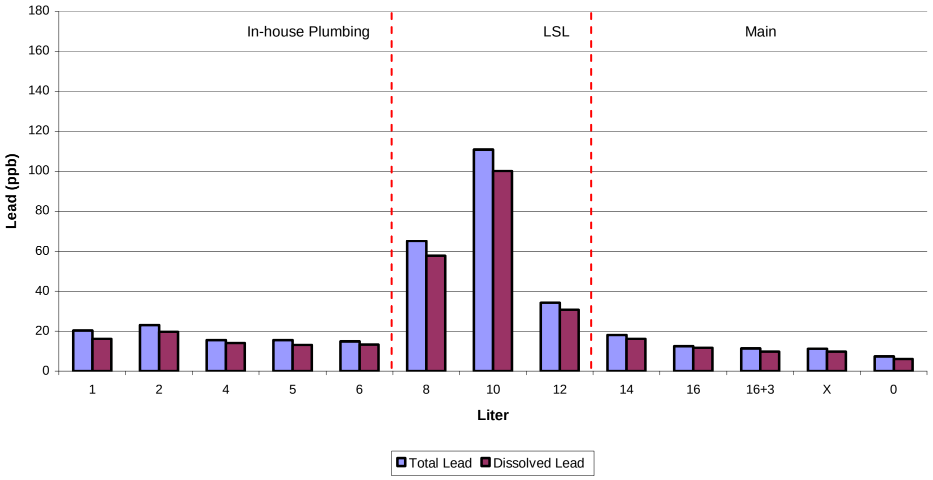

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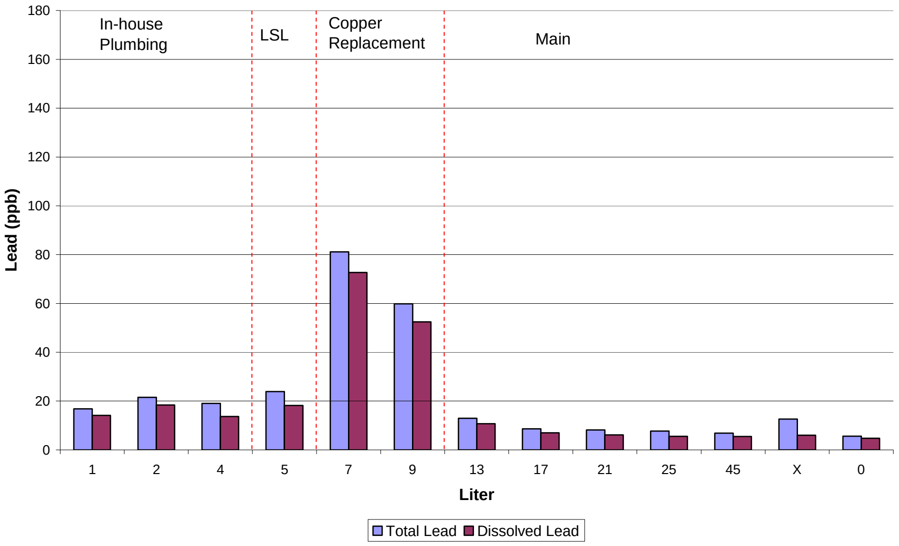

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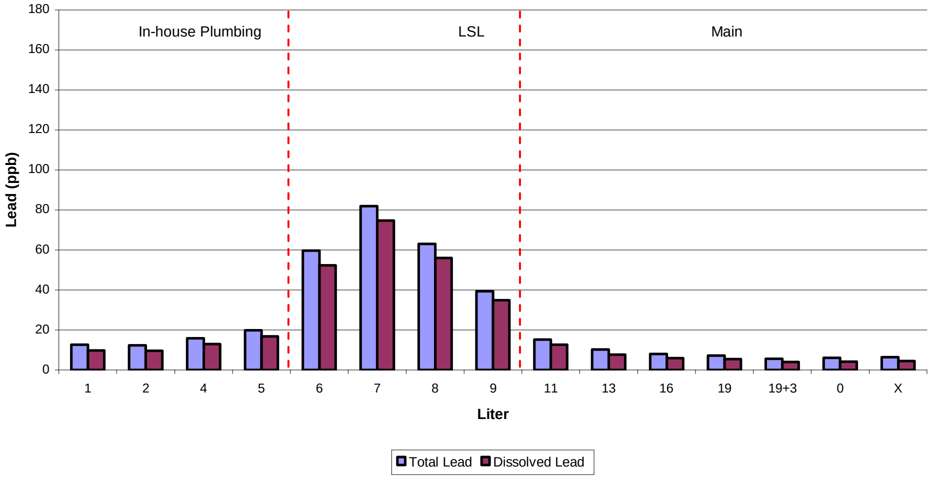

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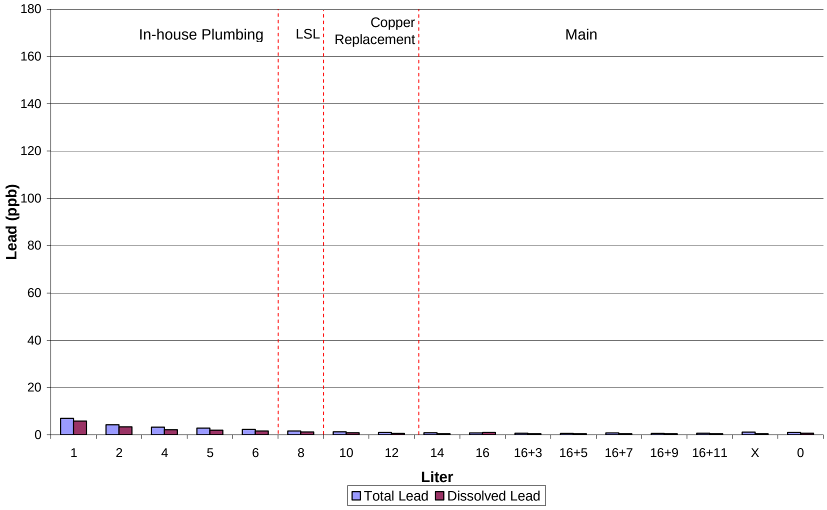
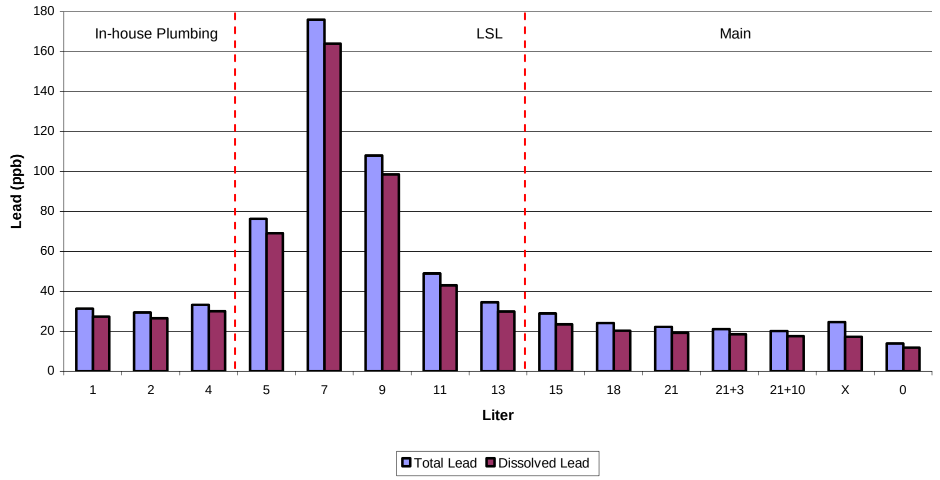
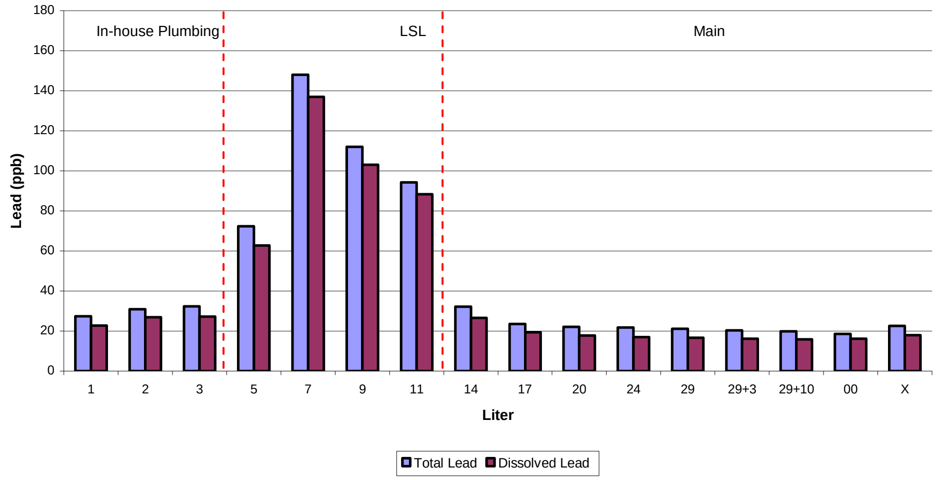


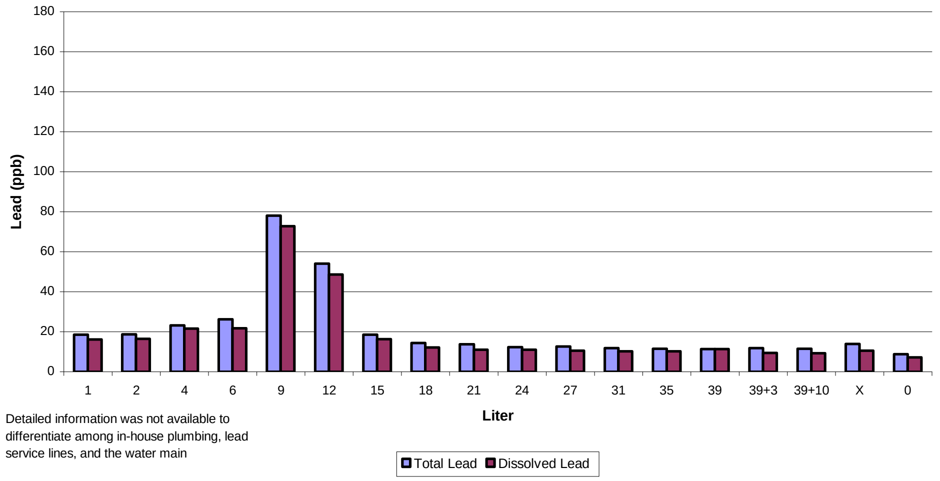
3-2-04 (Profile No. 7)



3-9-04 (Profile No. 8)

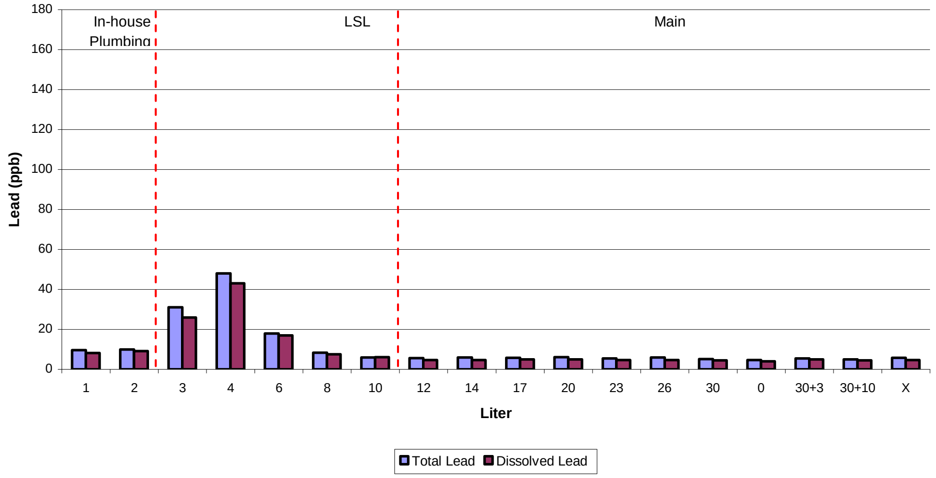


3-16-04 (Profile No. 9)



Detailed information was not available to differentiate among in-house plumbing, lead service lines, and the water main

3-24-04 (Profile No. 10)



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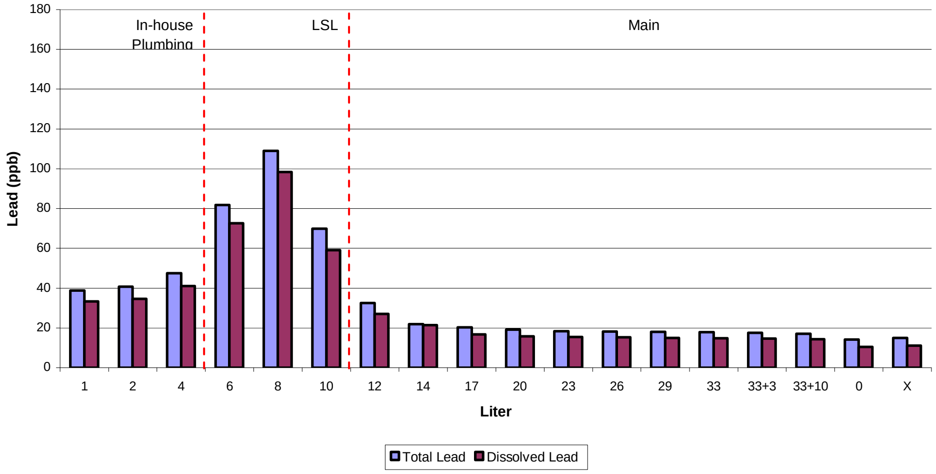

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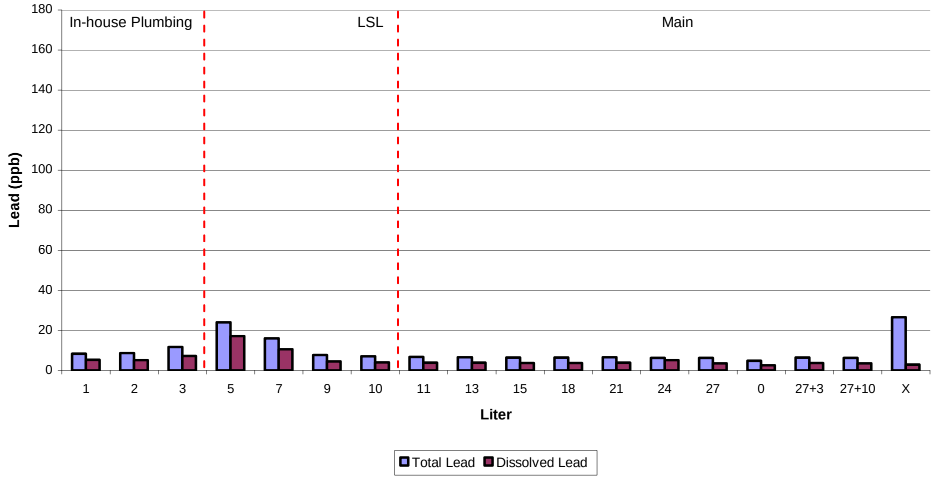

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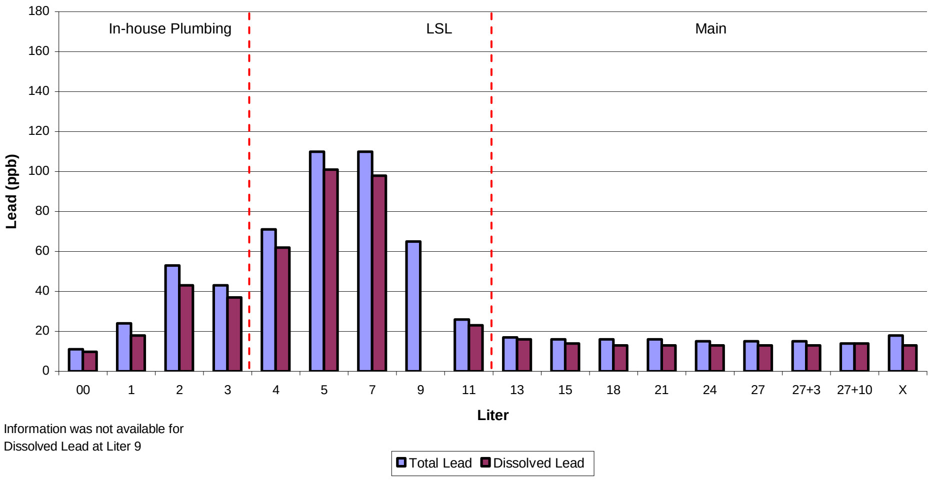
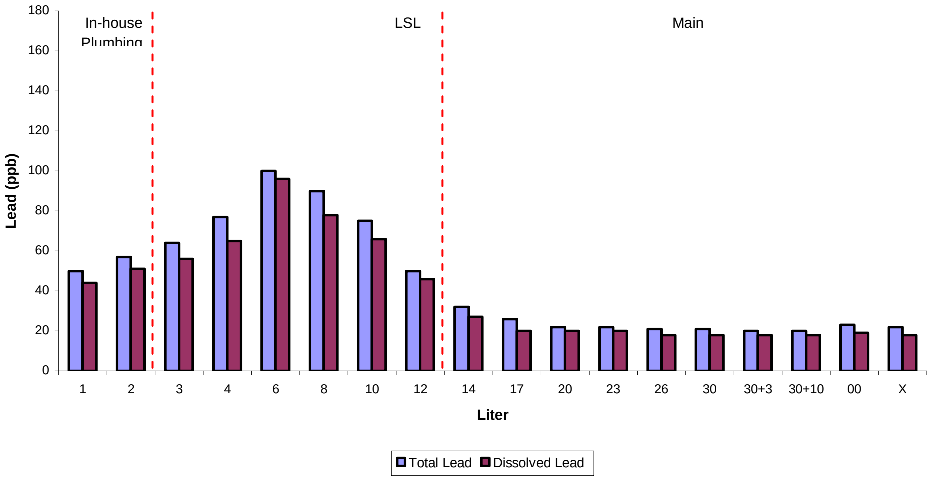


Information was not available for
Dissolved Lead at Liter 9

4-1-04 (Profile No. 14)



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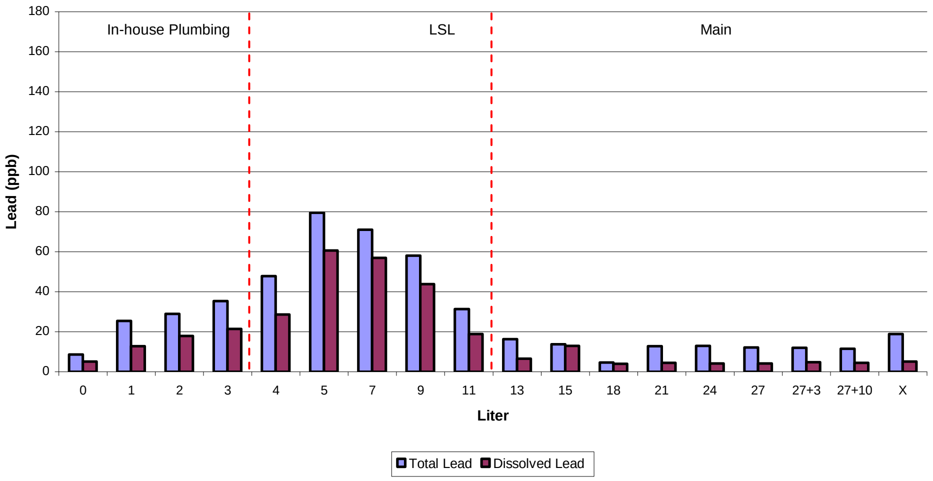

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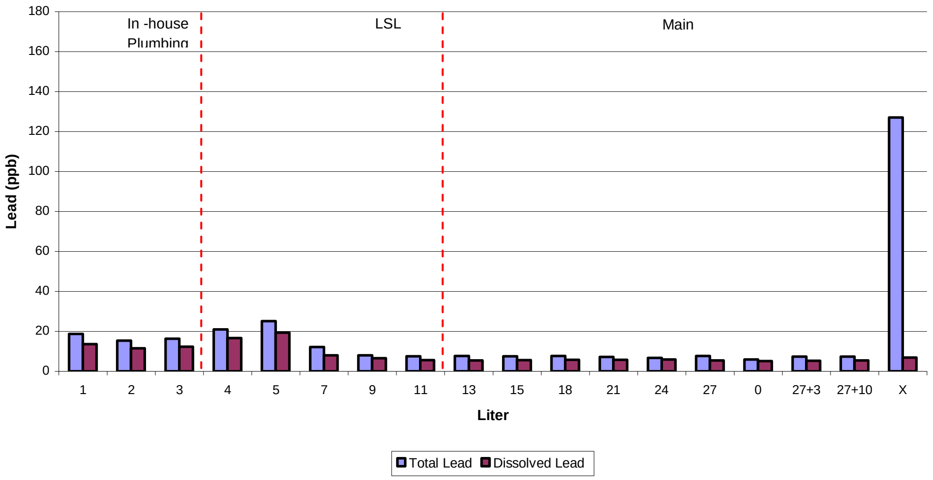

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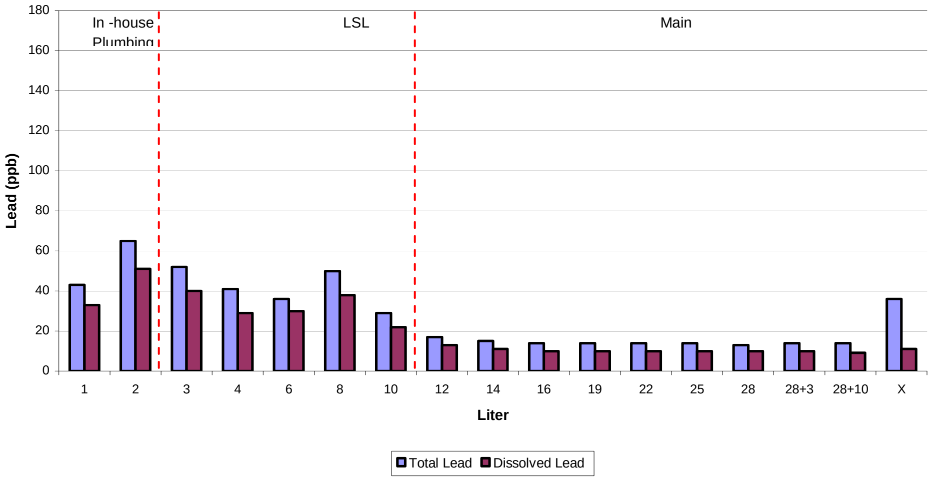

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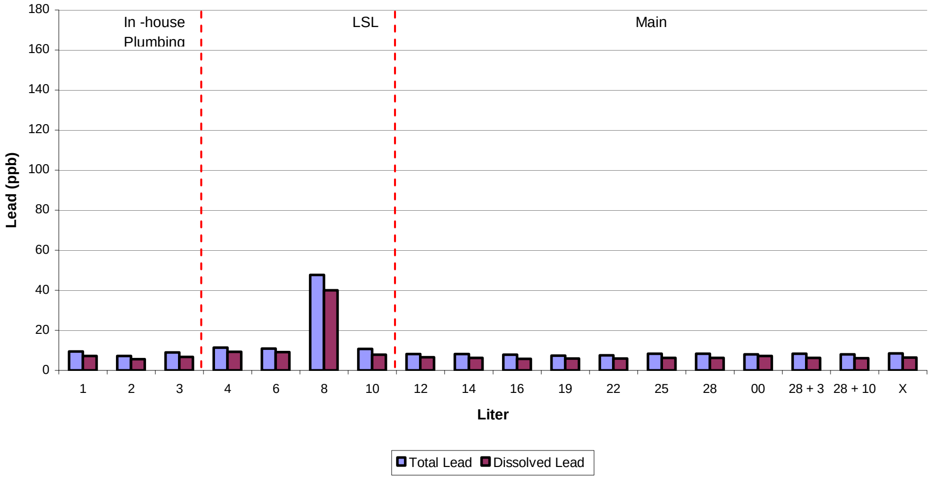

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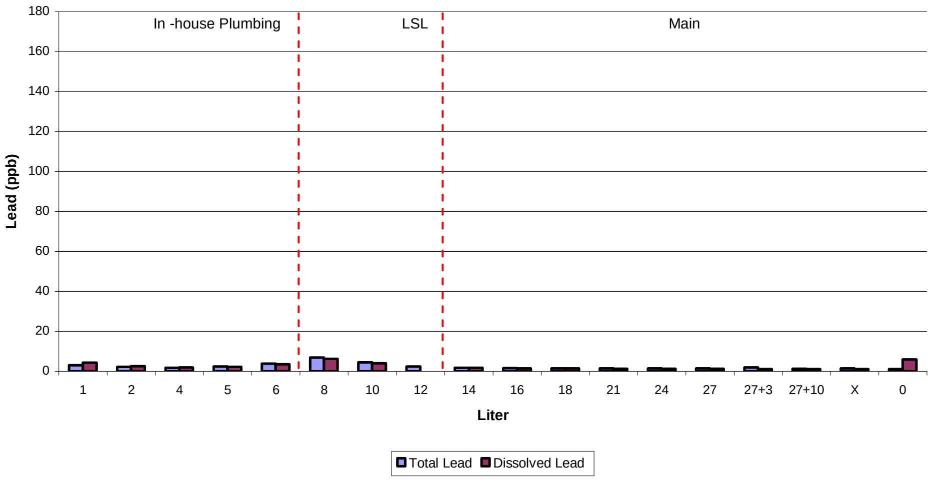

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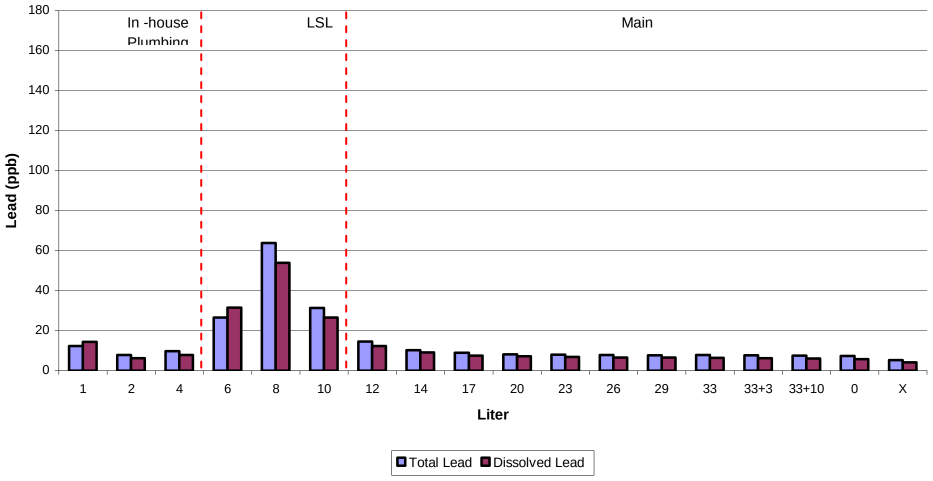

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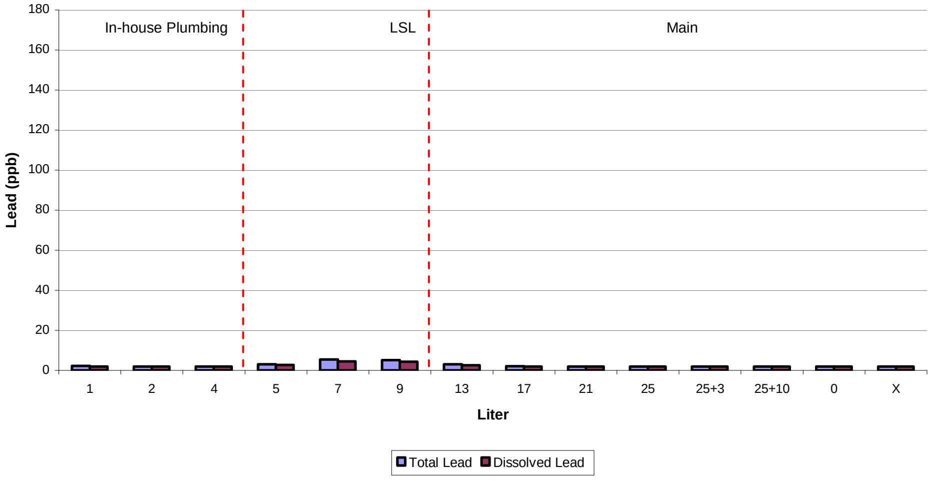

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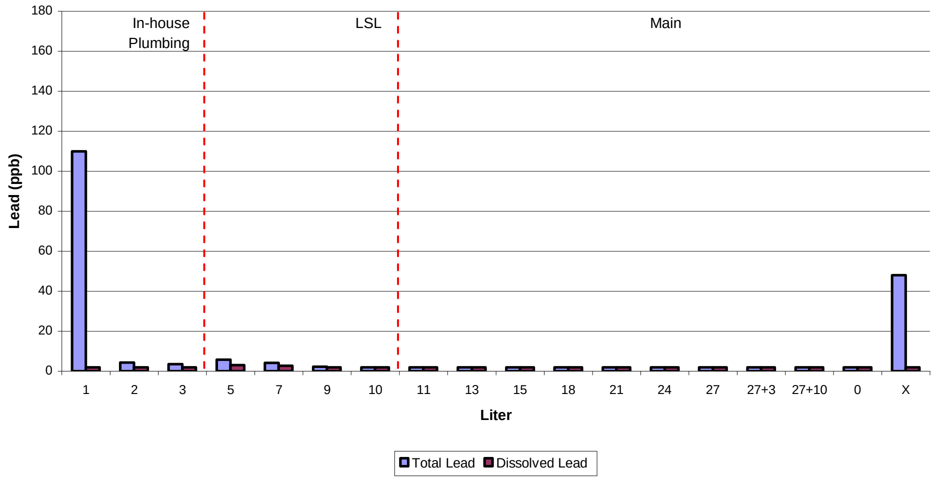

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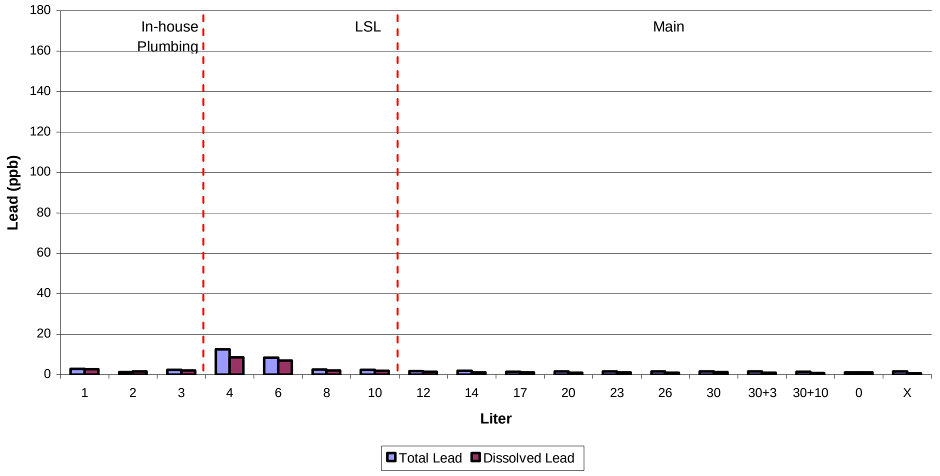

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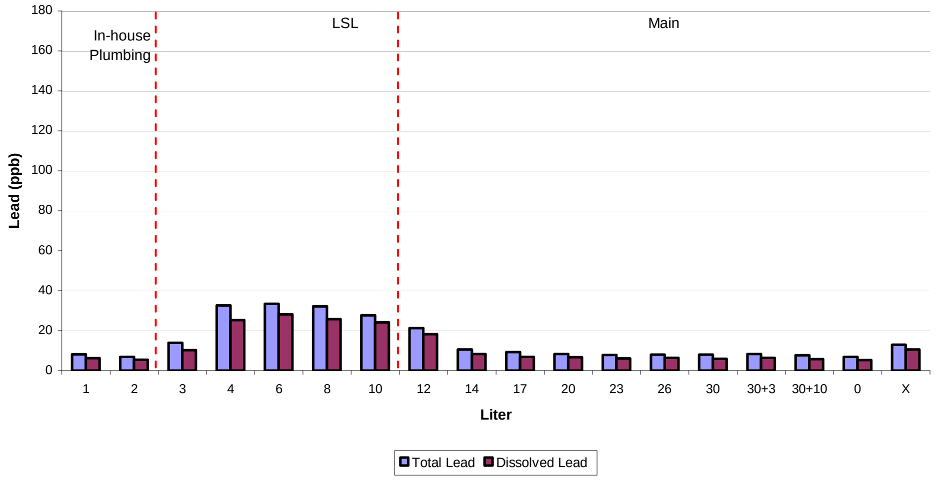

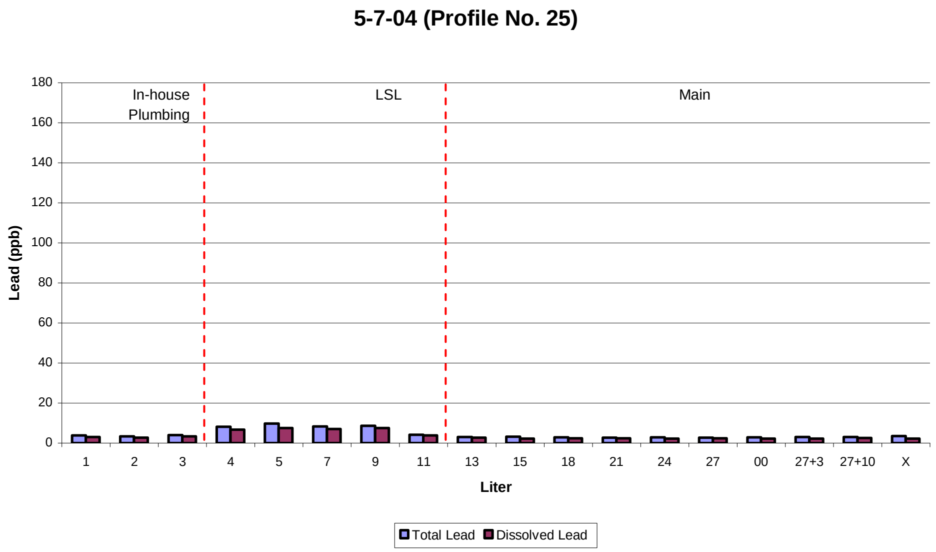
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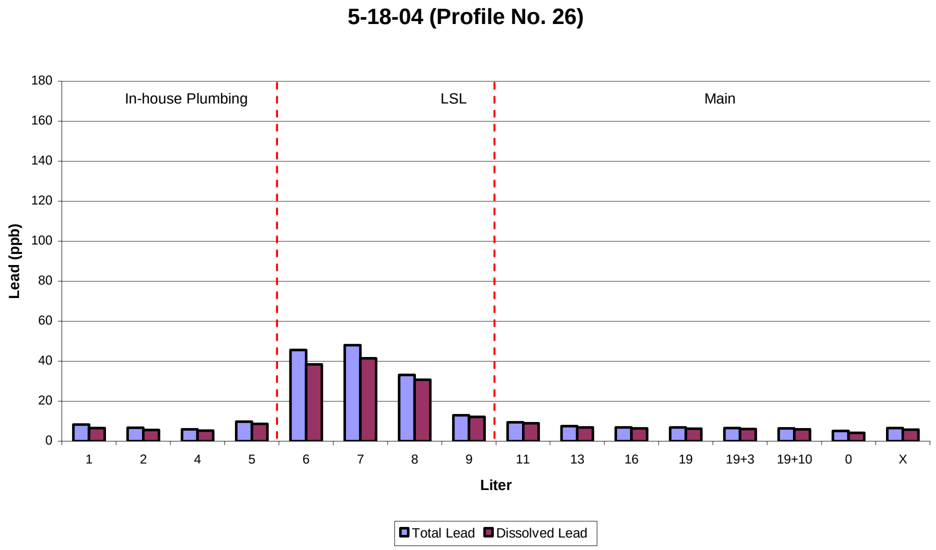
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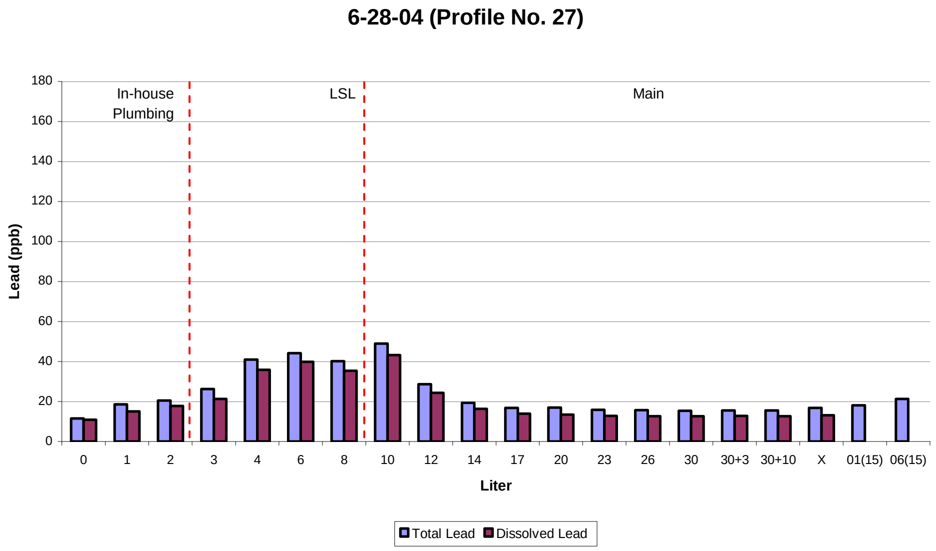
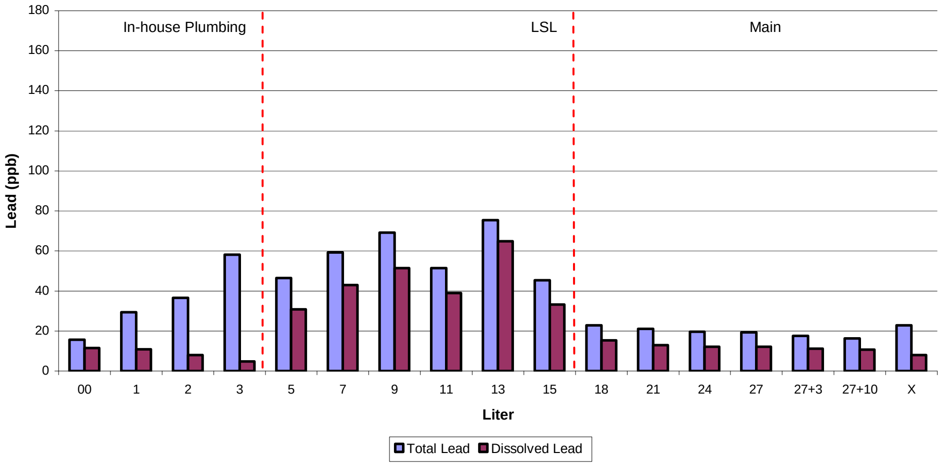

6-28-04 (Profile No. 27)

7-6-04 (Profile No. 28)



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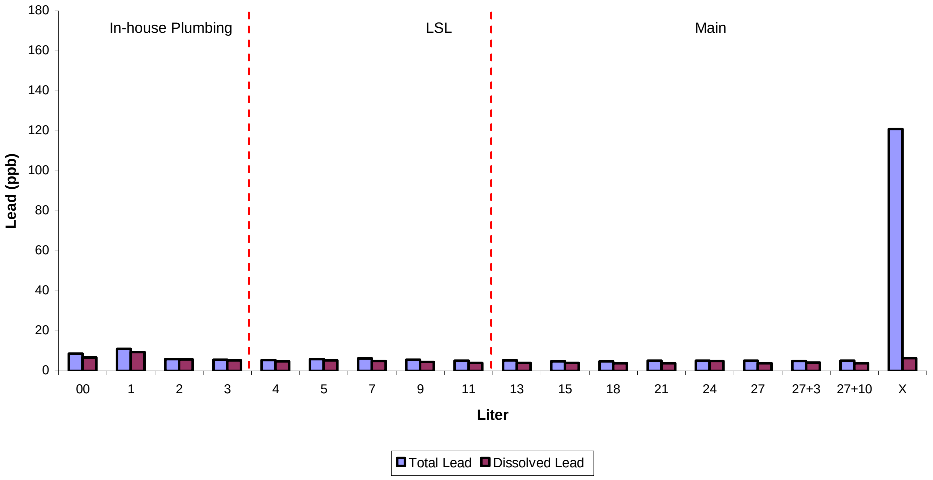

D.3 Total and Dissolved Lead Profiles from Samples Drawn After Initiation of Orthophosphate Treatment Program

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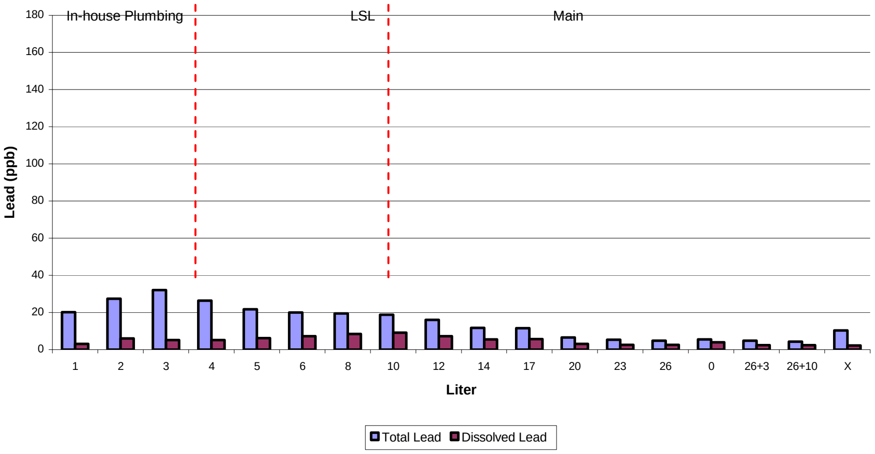
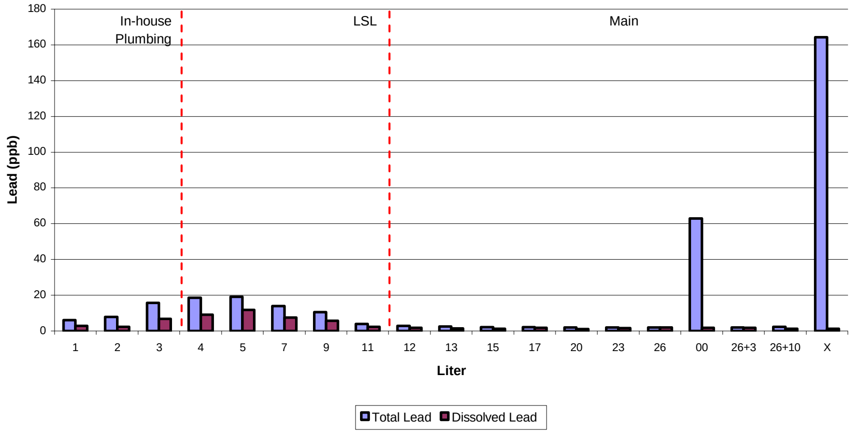


12-6-04 (Profile No. 31)



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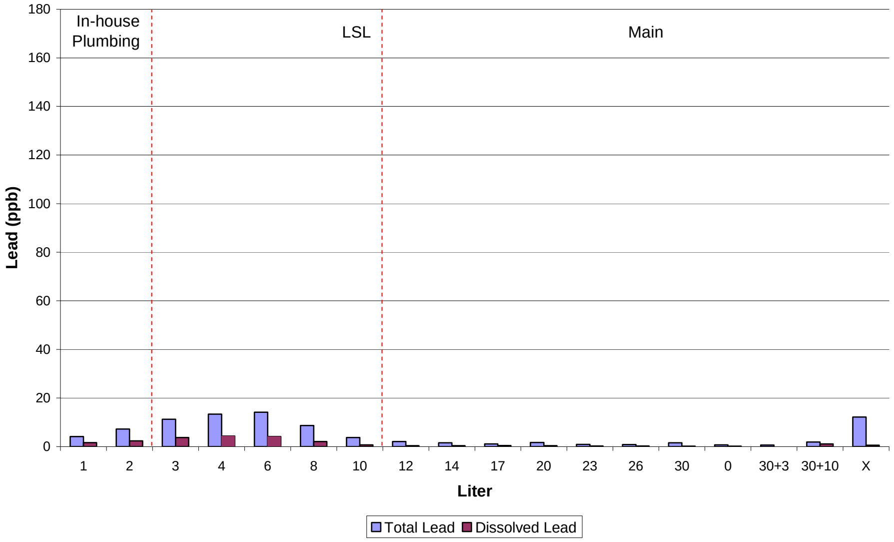

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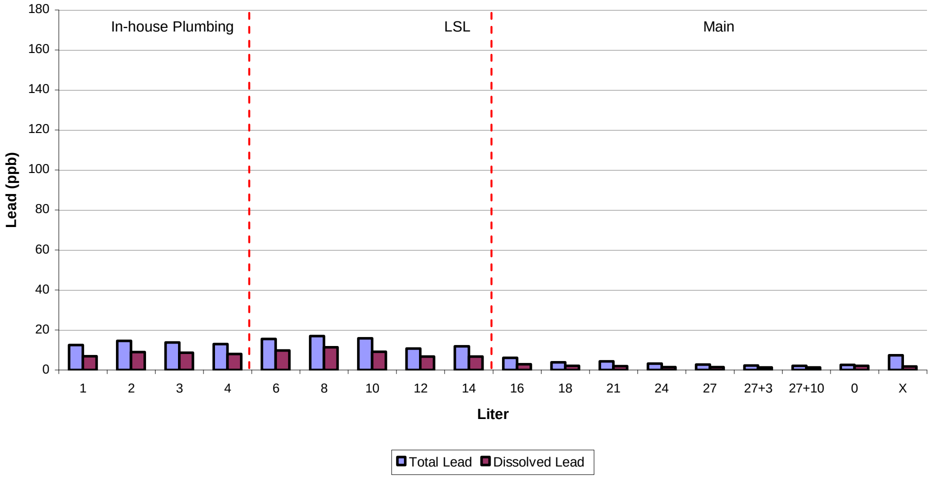

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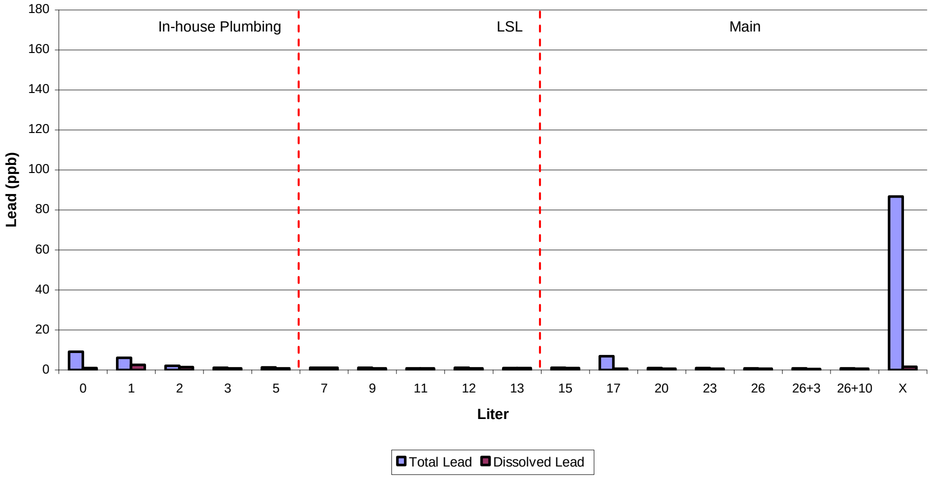
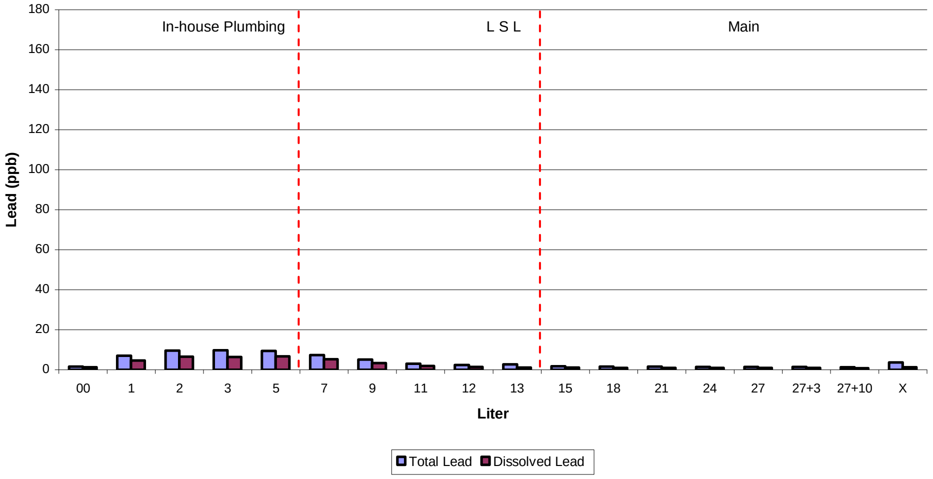


3-30-05 (Profile No. 35)



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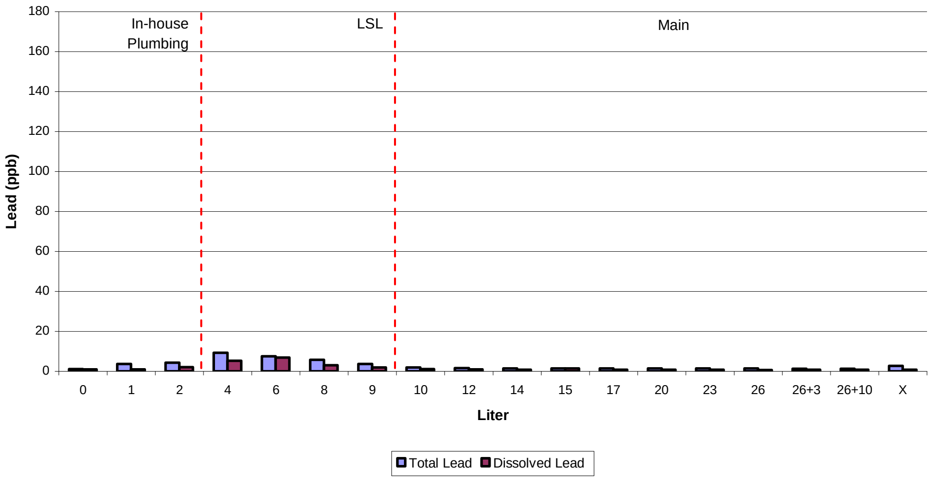

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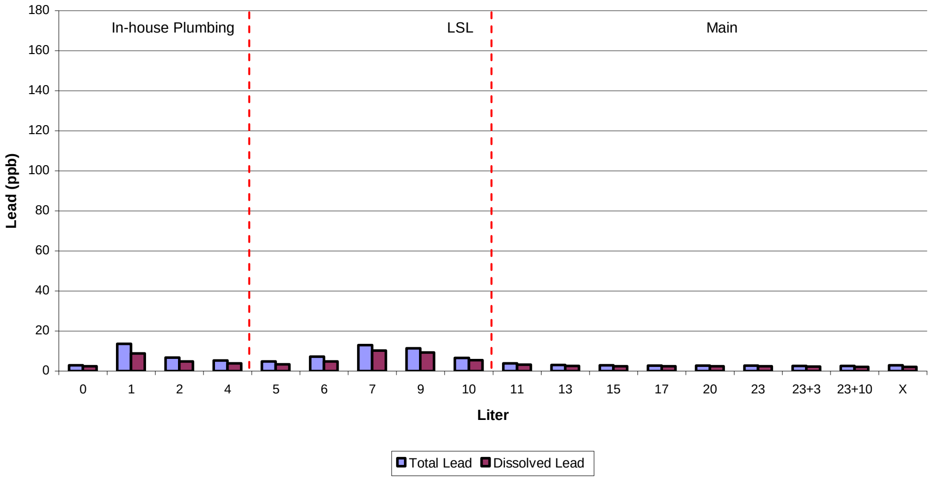

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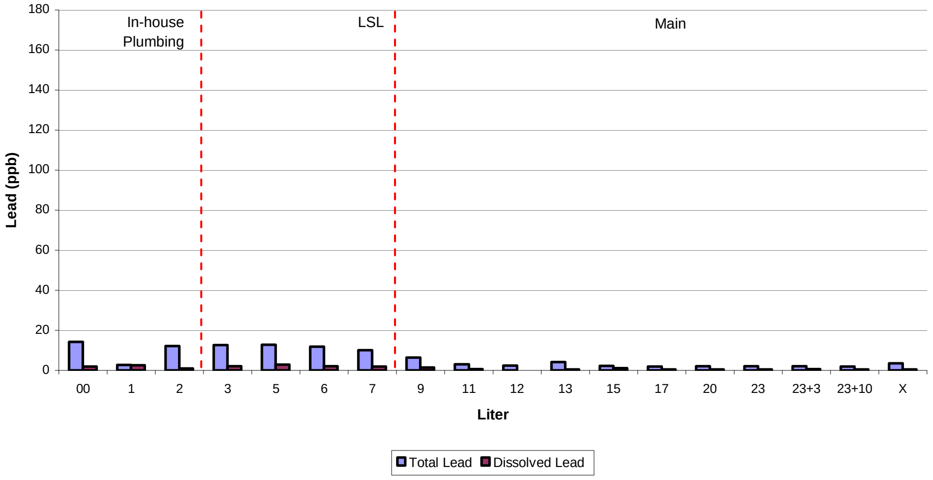

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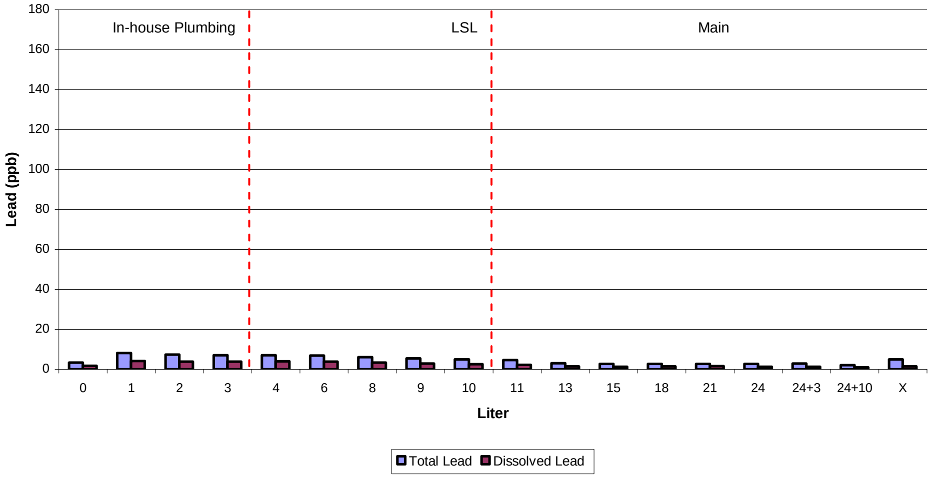

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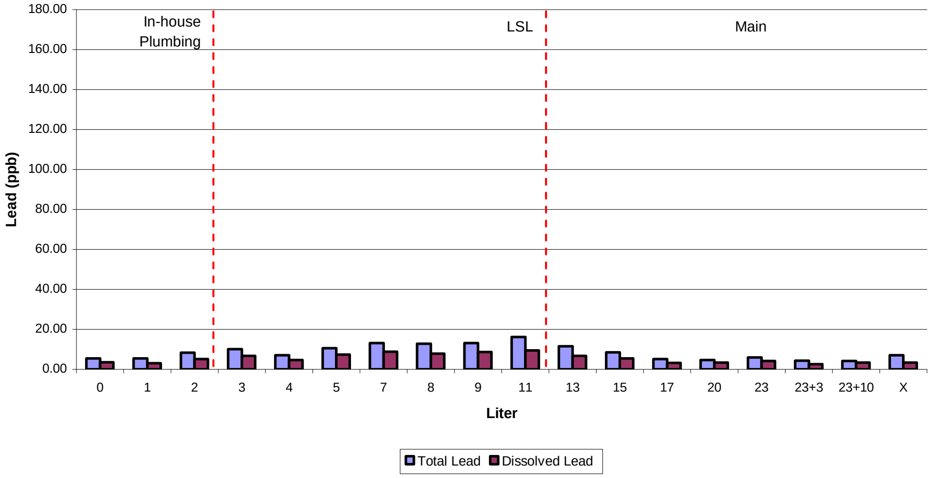

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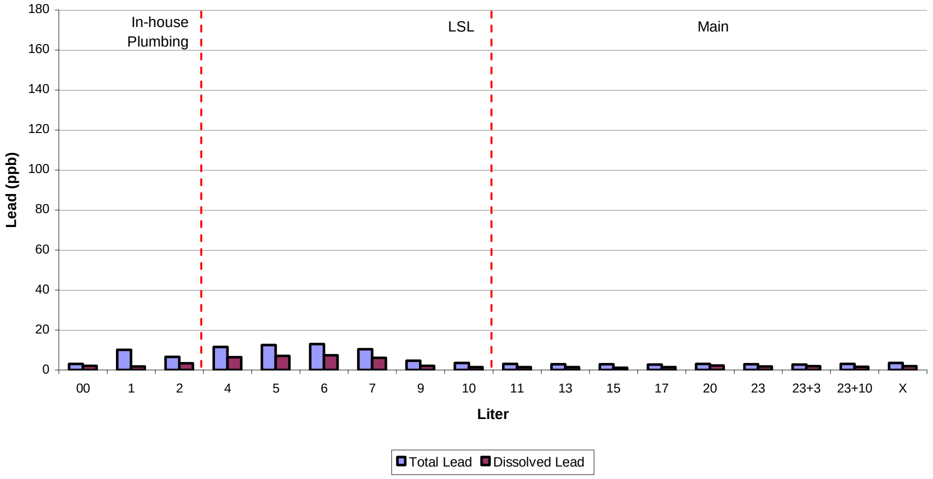

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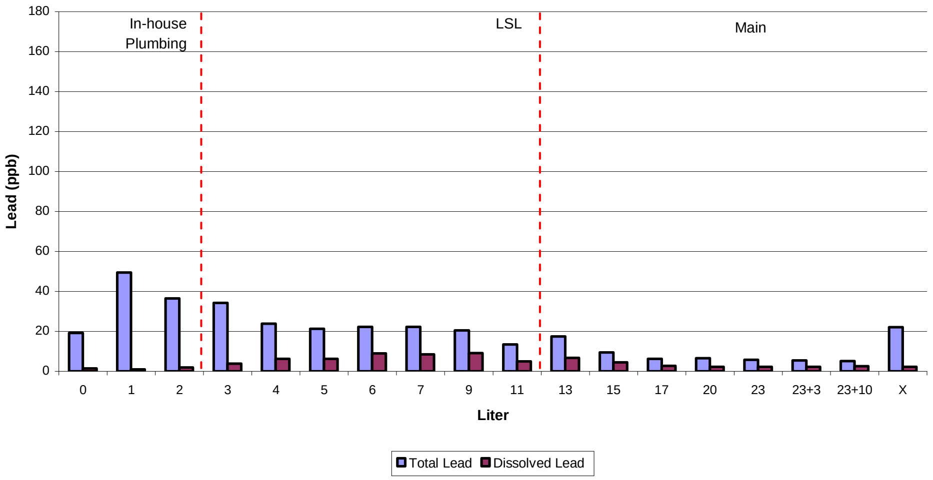

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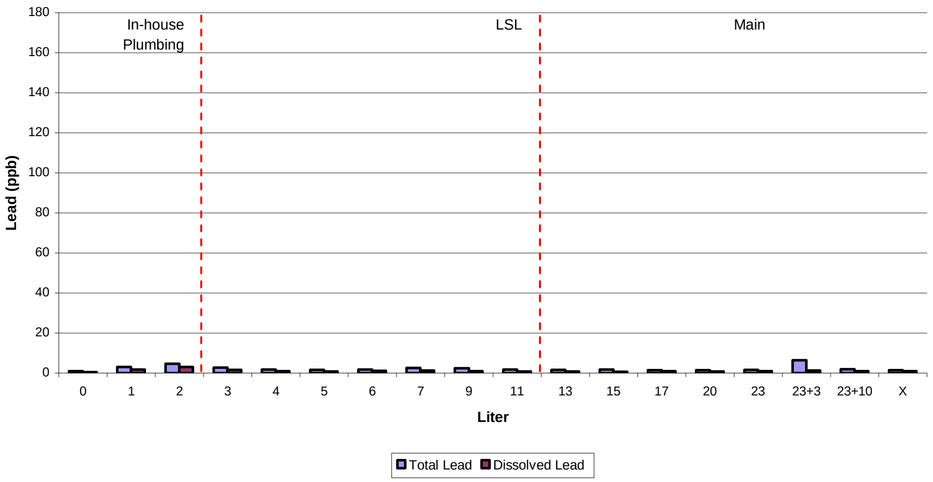

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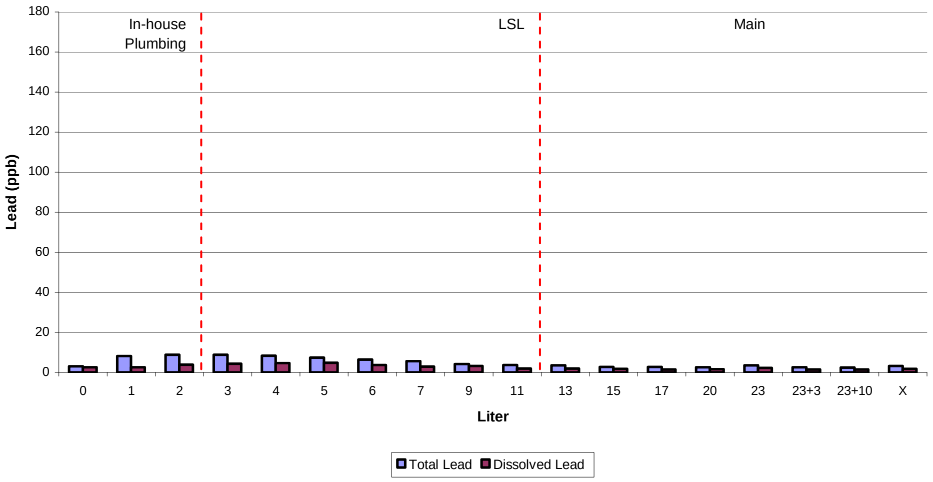

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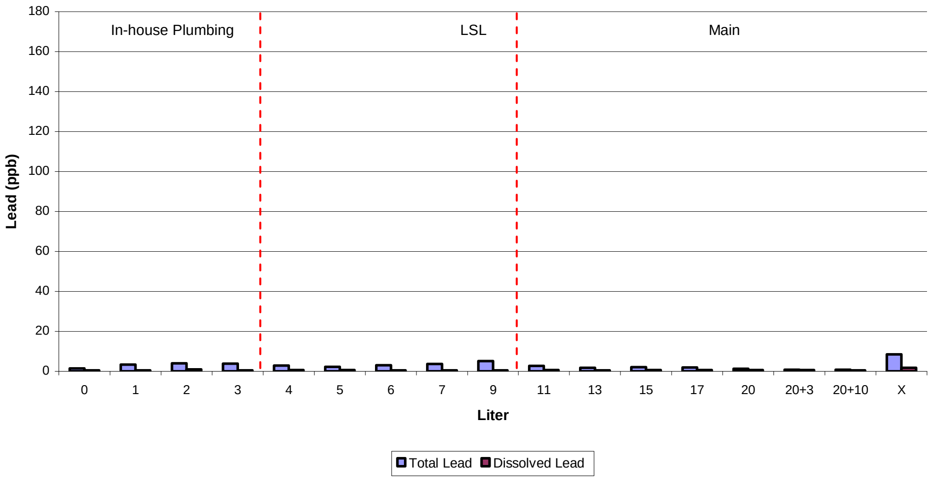

Appendix E Technical Memorandum from Dr. Anne Camper, July 30, 2004

TECHNICAL MEMORANDUM

TO: **The Cadmus Group**

FROM: **Anne K. Camper**

DATE: **July 30, 2004**

RE: **Evaluation of Washington, DC Distribution System; Orthophosphate Addition Effects on Microbial Water Quality**

In accordance with my agreement with The Cadmus Group, and based upon the information I have received from them and from telephone conversations with the Technical Expert Working Group, I have prepared this technical memo to address specific questions posed by Cadmus.

Questions included:

1. Considering WASA's distribution system infrastructure (e.g., extent and age of cast iron pipes) and water quality, do you believe that orthophosphate addition will help control biofilm growth? More specifically, how will the addition of orthophosphate affect TCR compliance? Do you have any other recommendations for controlling biofilm growth and improving TCR compliance?

2. What detrimental effects could there be in a distribution system such as WASA's from maintaining an orthophosphate residual of 3 mg/L?

3. Can the Aqueduct reduce the disinfectant residual concentration in the DC distribution system without adversely impacting TCR compliance?

4. WASA practices unidirectional flushing in their distribution system. They routinely flush the entire system approximately every two years. How important is unidirectional flushing for the DC distribution system? In your opinion, how often should WASA flush their entire system (e.g., once a year, once every two years, once every five years)?

Before these questions are addressed, some general comments are necessary. Each distribution system is unique. The nature and extent of biofilms in distribution systems is influenced by the interaction of many factors including pipe materials, water quality (including disinfectant and organic matter) etc. Therefore, extrapolating the performance of a corrosion inhibitor, disinfectant, or other treatment change on the response of biofilms from one system to another should be done with caution. It is also important to note that there can be a difference between the control of biofilms and the suspended cells that are measured during routine monitoring. The tendency is to assume that a reduction in HPC counts also means a reduction in biofilms. It is only possible to infer some connection between suspended cell counts and biofilm cell numbers in non-disinfected systems. Even then, detachment of biofilm cells may not be constant even under steady flow conditions. This is further complicated by flow reversals, surges in velocity, etc. If a disinfectant residual is present, the suspended cells may be reduced in number but the biofilm organisms are unaffected. When evaluating the impact of a treatment change on biofilm or suspended HPC and coliform counts, historical trends prior to the change must be taken into consideration. Separation of variables in full-scale systems is nearly impossible; a decrease in

HPC counts after the change may not be related to the new practice but to some other variable like decreasing water temperatures. This can be partially ascertained by evaluating historical data at that location.

QUESTION 1. DISTRIBUTION SYSTEM INFRASTRUCTURE AND ORTHOPHOSPHATE

Distribution system materials

A review of the provided information indicates that the majority of the WASA system is unlined iron or steel, with a large portion being cast iron (Section 6, Distribution Piping Improvements, CDM Report). In general, the literature and practice has shown that biofilms on iron surfaces are more problematic than those on other types of surfaces (LeChevallier et al. 1998, LeChevallier 1997, Delanoue et al. 1997, Neden et al. 1992, Niquette et al. 2000, Kerr et al. 1999). LeChevallier et al. (1996) showed that coliform occurrences correlated directly with the number of miles of unlined cast iron pipe in the distribution system. Another study showed that the biofilm densities on iron were significantly higher than those on plastic-based materials such as PVC with densities on cement intermediate to plastic-based materials and iron (Niquette et al. 2000). Neden et al. (1992) reported that cast iron pipes had the highest counts, while PVC was the lowest. Camper (1996) demonstrated in laboratory studies that mild steel had 10-fold higher HPC and coliforms than polycarbonate surfaces in reactors operated in an identical fashion. In another laboratory study, Kerr et al. (1999) found the highest counts and species diversity on cast iron when compared to medium-density polyethylene and uplasticized PVC. In another laboratory study where iron, PVC, cement and epoxy were compared, biofilm levels on iron were always higher than the other materials with the exception of when the systems were fed biologically treated water (Camper et al. 2003). It was also found that increases in DOC led to general increases in biofilm and effluent HPC, and this effect was most pronounced for reactors that contained iron. Parallel field testing results indicated that either iron had the highest regrowth, or the type of material had no influence on the number of bacteria present.

Involvement of organic matter

One of the difficulties in interpreting the importance of iron surfaces on regrowth is the interaction of iron oxides with natural organic matter. As will be explained below, these iron surfaces have an affinity for natural organic matter, but the potential for immobilized organic matter to act as a carbon and energy source for biofilm organisms has been largely ignored. The industry generally attempts to correlate fractions of the organic matter (AOC and BDOC) obtained from bulk water fractions with growth determined in suspended systems to what can be expected in the distribution system. However, in many distribution systems, AOC and/or BDOC levels have not been correlated with regrowth. There are several reasons for this inconsistency: (1) an inadequate number of AOC or BDOC measurements to truly represent the level of organic carbon available for growth, (2) a significant interaction of other factors (disinfectant, distribution system materials, etc) that govern microbial growth, and/or (3) the presence of organic carbon promoting biological growth not measured by these tests. In fact, Najm et al. (2000) report that utilities should not rely on AOC or BDOC levels alone to assess the potential for regrowth; other factors should be considered as well. The third possibility, that there are components of the organic material recalcitrant to degradation in the bulk fluid, is discussed here in the context of interaction with iron oxide surfaces and corrosion control.

Part of the recalcitrant components of total organic carbon in water is humic and fulvic acids. Until recently, there has been only one reference suggesting that biofilm bacteria are capable of using humic materials (Volk et al. 1997). In our laboratory it was demonstrated that soil derived humic substances fed at a level of 1.4 mg/L, resulted in a biofilm that was at least one log higher than the same water before the addition of humic substances (Burr et al. 2004). In earlier work, humic substances supported nearly the same number of biofilm and suspended cells in a simulated drinking water distribution system as more readily available carbon sources (amino acids and carbohydrates)at the same concentration of carbon (Butterfield et al. 2000b, Ellis et al. 2000). Across the reactor, nearly 80% of the humic substances were removed. This may be caused by the large amount of substrate bound to the biofilm (8.3 - 11 µg C/cm^2), which would lead to growth rates independent of the bulk fluid concentration. This adsorption may influence the ability for microorganisms to degrade humics. This phenomenon is most widely studied on iron oxides (Parfitt et al. 1977, Tipping 1981, Tipping et al. 1981, Davis 1982, Gu et al. 1996). Gu et al. (1995) showed that different fractions of NOM are adsorbed by iron oxide with different affinities and capacities.

Implementation of corrosion control on distribution system biofilms

As will be described in more detail below, implementation of corrosion control has been seen to decrease biofilm cell numbers and suspended cell counts in systems containing corroding iron when all other parameters are held constant. It is unknown if the effect relates to improvement of disinfectant efficacy by reducing the amount of available iron to react with the disinfectant, to the reduced availability of the adsorbed organic matter, or other causes. It is likely that there is a combination effect that is dependent on the type of organic matter, the surface, and the disinfectant.

To see if corrosion control may improve disinfectant efficacy, work has been done with reactors exposed to free chlorine or monochloramine with and without the presence of corrosion control chemicals (orthophosphate, polyphosphate, pH adjustment). In ductile iron annular reactors, there was a substantial demand for both disinfectants. Influent concentrations of 3.25 mg/L in both cases resulted in barely measurable residuals. When compared to the control reactor (no disinfectant), the chlorinated reactor had higher numbers of culturable cells in the biofilm. The counts from the monochloramine system were lower than that of the parallel control system, and lower than when chlorine was used. Overall, monochloramine appeared to be a slightly better disinfectant under these conditions and the addition of a corrosion control chemical improved biofilm control, especially in the chloraminated reactor, with orthophosphate being most effective (Abernathy and Camper, 1998a, b). These results support field observations that monochloramine may be more effective at controlling biofilms grown on corroding ferrous metal distribution system materials, and the combination of monochloramine and corrosion control for improving microbial water quality has been demonstrated (Schreppel et al. 1997). Since corroding surfaces are often considered to problems in full-scale distribution systems, the use of monochloramine as a secondary disinfectant may be indicated when the primary material in the network is unlined cast or ductile iron pipes, and the use of corrosion control schemes may also improve biofilm control. However, even this observation must be extrapolated with care. As shown by Batte et al. (2000), phosphate added to a reactor system containing non-corroding material (polycarbonate) seemed to protect the biofilms from both chlorine and monochloramine (both at an applied dose of 0.5 mg/L) when compared to systems with the disinfectants but lacking the phosphate.

Because of the suspected interaction of humic substances with iron oxides, a project was specifically designed to determine if the presence of iron oxides enhanced biofilm growth in the presence of humic substances with phosphate and pH adjustment for corrosion control (Butterfield et al. 2002a). For this work, the biofilms were grown in small columns containing glass beads, glass beads covered with a synthetically created iron oxide, or crushed corrosion products taken from a cast iron drinking water distribution pipe. The surfaces were initially exposed to humic substances (termed “loading”) with the exception of a control. After initial exposure, all but one column received influent humics at a concentration of ca. 3 mg/L. For glass beads, the humics addition was pH adjusted to 7.3, 8 or 9. For corrosion products, only pH 7.3 and 8 were used. For both corrosion products and glass beads, a set of columns at pH 7.3 received chlorine at an effluent residual of 0.15 - 0.2 mg/L, another was chlorinated plus phosphate added. A control with humics and phosphate at pH 7.3 was also run. The data for cell counts in the effluent and on the beads were subjected to a weighted hierarchical process called the simple multiattribute rating technique was used to determine which columns resulted in the best performance, which was selected to be the least number of bacteria in the biofilm and effluent. The addition of humic substances was a major factor in biofilm formation. The absence of added humics was the second most important factor following chlorine. The interaction between iron oxides and humics also was high for the corrosion products, suggesting that the interaction of humics with a reactive iron surface is favorable for biofilm formation. The corrosion products removed from the distribution system had a much higher adsorption affinity for the humics. They also retained sufficient humics during the initial loading that even if no other humics were added to the column influent, far more biofilm than the equivalent iron oxide bead system was supported. Of the corrosion control schemes tested, pH adjustment had little positive effect (in fact, the pH 9 system had higher counts than the column held at pH 7.3). Phosphate addition with chlorine was slightly more effective than chlorine alone when the corrosion products were used.

In a full-scale system (Southern California Water Company-Southwest District) with over half of the pipeline being unlined iron and steel, polyphosphate blend was added to a portion of the distribution system in a pilot scale test to determine if this would reduce disinfectant (free chlorine) demand by decreasing corrosion. The polyphosphate blend was utilized because the deposits formed should be softer than those produced by orthophosphate, thus making removal by flushing easier to accomplish. A secondary anticipated benefit was reduction in HPC. For approximately the first six months after phosphate addition, the HPC counts increased from 600 - 800 CFU/mL up to 1600 CFU/mL. The counts then gradually declined over a two year period to an average below 100 CFU/mL. During the first six months, the chlorine residual steadily increased and then remained constant. This study suggested that it may take three years to achieve an overall improvement in water quality after implementation of corrosion control and that flushing should be used to help remove any loosened deposits (Cohen et al. 2003).

A report issued by the American Water Works Association Research Foundation (Kirmeyer et al. 2000) provides information on changes in water quality from five extensively monitored systems and case studies from eight utilities that implemented corrosion control. Several of these utilities added orthophosphate, polyphosphate, or both with and without pH adjustment. Specifically, Detroit utilized orthophosphate at 3 mg/L phosphate, Philadelphia increased their phosphate dose, and Hartford, Connecticut gradually added blended phosphate to attain a level of 1 mg/L phosphate. For the case histories, it was found that Springfield MA, Portland ME, Cedar Rapids, IA and Charleston SC implemented phosphate addition. Evanston, IL added a phosphate/polyphosphate blend. A general conclusion was that phosphate corrosion control had minimal secondary impacts (red water, elevated microbial counts, etc.) provided that adequate residuals were maintained and the pH was held at 7.3 - 7.8. Systems most at risk for adverse effects included those with large amounts of unlined iron pipe, highly varying distribution water quality due to many changes in practice or unbuffered water with pH swings, and those systems that implemented large changes in water quality. This report specifically indicates that for phosphate, doses should be increased incrementally at values of approximately 0.2 - 0.5 mg/L as phosphate. They also recommend flushing to help control any negative impacts.

The data from the 4th High monitoring program (Table 1) are somewhat ambiguous on the effect of phosphate addition on HPC counts. At some locations there seems to be elevated counts while at others the numbers remain low. A comparison was made to data collected prior to phosphate addition at the 4-H 4 site in April and May; all of these counts are below 84 CFU/ml. Data from August of 2003 to present at this site have counts as high as 4400 (7/14/04) but the count the next day is only 33 CFU/ml. This illustrates the inherent variability in HPC counts. With the information provided, it can only be said that there does not appear to be a dramatic impact of phosphate addition on HPC counts in the 4th High system.

Based on the results listed above and other sources, it is probable that phosphate addition will have a beneficial effect on regrowth in the WASA system in the long term. Although there are some circumstances where phosphate addition could stimulate microbial growth (seen in the Scandinavian countries) the WASA water is likely to be carbon limited rather than phosphate limited. Better biofilm control could be from improved disinfectant efficacy or in modification of the surface chemistry so that the organisms are not as likely to grow. However, the effect may take some time to occur, and in the short term, there may be elevated counts. In the remainder of the distribution system that has not been flushed, increased bacterial counts are probable. This may be seen with coliforms as well; phosphate will be added at a time when there has been a general upward trend in coliform positives. In addition, late summer is associated with warm water conditions and is the season when violations are most likely to occur. There could be sporadic coliform releases from the pipe surfaces until the new surface equilibrium is reached. Unfortunately, the disinfectant concentration present is not likely to kill these organisms, especially if they are released in clumps or if they associated with particulate matter released from the pipe surface from the softening of the scales. Ideally, it would have been beneficial to have the entire system flushed before the addition of phosphate to minimize the potential for increased microbial counts.

Other recommendations for controlling biofilm growth and improving TCR compliance

For overall water quality improvement, including reducing disinfection by products, reducing microbial growth, and potentially improving taste and odor, reduction in natural organic matter is a high priority. There is a great deal of published literature and practical experience that has shown this approach to be beneficial in improving microbial water quality during distribution. As a case in point, the study on pipe material conducted in our laboratory (Camper et al. 2003) showed the same level of biofilm on iron, PVC, cement and epoxy when exposed to biologically treated water in the absence of disinfectant. When monochloramine or free chlorine were added to maintain a residual of 0.2 mg/L, bacterial levels on the iron surfaces became elevated and the suspended counts also increased; the disinfectants could not control the increased amounts of biofilm growth and detachment. However, the importance of the disinfectant in controlling bacterial growth, even when organic matter is reduced, is apparent in the literature. The results from an American Water Works Association Research Foundation funded field project (Najm et al. 2000) suggests that the suspended cell counts are more heavily influenced by chlorine residuals than the level of BDOC or AOC. Waters with very low concentrations of AOC/BDOC still required the presence of residual to keep bacterial numbers within acceptable levels. Along with the information presented earlier, it is apparent that there is an interaction between many water quality factors that contributes to microbial numbers in distribution systems, with the type and quantity of natural organic matter and disinfectants being key players.

Another recommendation is the removal/relining of the iron pipes. The reported interactions of natural organic matter, disinfectants, and iron pipes suggest that the iron surfaces are a major factor in regrowth.

QUESTION 2. WHAT DETRIMENTAL EFFECTS COULD THERE BE IN A DISTRIBUTION SYSTEM SUCH AS WASA'S FROM MAINTAINING AN ORTHOPHOSPHATE RESIDUAL OF 3 MG/L?

These comments are restricted to the potential impact on microbial growth/biofilms. There is no information available in the literature on the effect of dose of phosphate on regrowth, provided that phosphate is not the limiting nutrient for bacterial growth. As stated above, it is unlikely that the WASA water is phosphate limited (more likely organic carbon limited). The only potential effect will be the rate at which the surfaces are impacted by the corrosion inhibitor and the time required to reach equilibrium. There may be initial sloughing of the deposits, causing higher bacterial counts, followed by a gradual decline in numbers. The slope of this line may be impacted by the dose of phosphate, but there are no data to support this. Experience has shown, however, that the goal should be to reach equilibrium and not to change practices just because deleterious effects are seen initially; these may be short-term and overcome as the system adjusts to the new water quality (Kirmeyer et al. 2000).

QUESTION 3. CAN THE AQUEDUCT REDUCE THE DISINFECTANT RESIDUAL CONCENTRATION IN THE DC DISTRIBUTION SYSTEM WITHOUT ADVERSELY IMPACTING TCR COMPLIANCE?

If corrosion control has a positive impact on microbial counts with the HPC numbers declining with time and a downward trend in the detection of total coliforms, it is possible that the chloramine dose can be reduced. It would be best to determine if the corrosion control scheme was producing desirable results prior to reducing the disinfectant, however, to ensure that control can be maintained. In addition, it is important to ascertain that there are measurable residuals in the dead ends and low flow sections of the distribution system. Again, if corrosion control is adequate, it may be feasible to deliver a residual to these locations even if the concentration leaving the plant is decreased.

QUESTION 4. WASA PRACTICES UNIDIRECTIONAL FLUSHING IN THEIR DISTRIBUTION SYSTEM. THEY ROUTINELY FLUSH APPROXIMATELY EVERY TWO YEARS. HOW IMPORTANT IS UNIDIRECTIONAL FLUSHING FOR THE DC DISTRIBUTION SYSTEM? HOW OFTEN SHOULD THEY FLUSH?

Flushing the distribution system has several benefits. Good unidirectional flushing will remove loose deposits that contain organisms and materials that cause color, may scour the pipe surface, moves disinfectant residuals into areas that may have levels that are too low, decreases water age, helps control nitrification, and in the case of the corrosion inhibitor, will ensure that it reaches all points of the distribution system. In dead ends and low flow areas, flushing, looping, and bleed-off may ensure that the potential benefits from corrosion control access these problem sites. Flushing of the DC system, especially in light of the presence of a predominance of unlined iron pipes, is critical for maintaining water quality. This practice will have the most benefit in areas where flows are typically low enough that loose deposits accumulate. It would have been beneficial to have the DC system flushed prior to phosphate addition to minimize any adverse impacts on scale release, microbial counts, and color. In lieu of this, however, spot flushing should be used to help remediate sites if adverse effects are seen.

For microbial control, flushing can remove loose deposits that contain bacteria (Barbeau et al. 1999, Gauthier et al. 1997). Typical flushing velocities will do little to remove the tightly adherent deposits such as tubercles. These deposits also contain organisms that will be protected from shear, disinfection, and predation. There may be some effect on biofilm bacteria on the surfaces of the deposits, although the effects are probably limited. McMath et al. (1997) tested a system where biofilms had developed under low flow conditions and then incrementally increased the flow and collected the bacteria that were detached from the surface. Bacteria were released from the surface for over 48 hrs, which far exceeds the time a part of the distribution system is flushed. Donlan and Pipes (1988) showed a linear relationship between flow velocity and HPC density on coupons placed in a full scale system. It is possible, though, that this effect was due to greater transport of disinfectant to the surface rather than increase in shear at higher flow velocities. After flushing, the biofilm can and will regrow within a time scale much shorter than the flushing interval. Actual recovery times will depend on water quality, the amount of biofilm remaining after flushing, and the surface upon which the organisms are attached. In Zurich, Switzerland, the water is unchlorinated and the entire distribution system is flushed twice a year to keep microbial counts low (Klein and Forster 1998). Regardless, flushing has been used by many utilities to help improve microbial water quality, and it should be considered as part of the program in the DC system.

It is difficult to determine the frequency at which the flushing should take place. Some information suggests that flushing should initially take place frequently to remove loose deposits that have accumulated over the years (Friedman et al. 2003). Once the system is relatively clean, it may be possible to increase the time period between flushing. The interval may be determined by other water quality parameters, including color, ability to maintain a disinfectant residual, potential for nitrification, etc. Other important parameters are cost, ability to dechlorinate and discard the flushed water, water availability during drought conditions, personnel, etc.

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